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in fcc Metals with Application
to Specific Heat and Neutron Scattering**

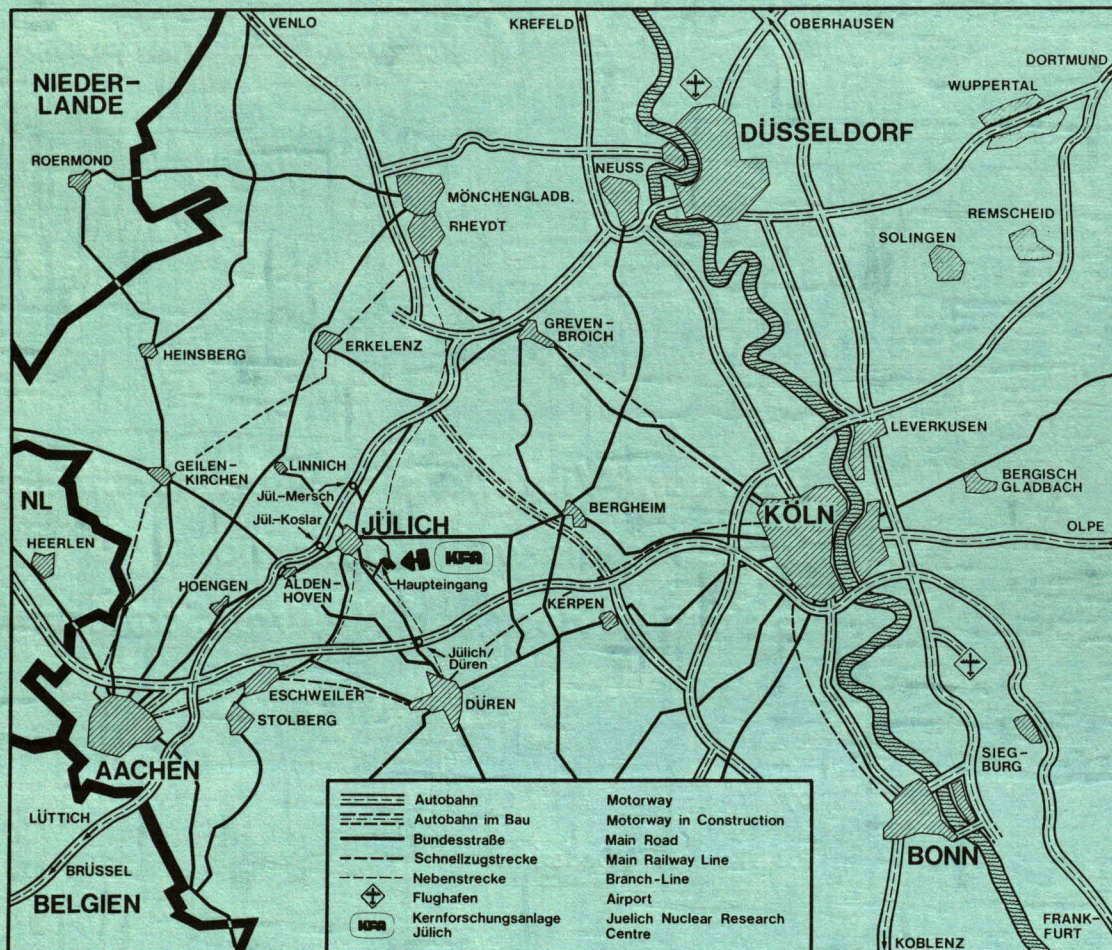
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Resonant Vibrations of Self-Interstitials in fcc Metals with Application to Specific Heat and Neutron Scattering

by

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Abstract:

Some aspects of resonant vibrations of self-interstitials in the 100-dumbbell configuration in fcc-metals are discussed by extending previous calculations of Zeller et al. and Schober et al. Employing a simple defect model with nearest-neighbour interaction the local frequency spectrum of the defect is calculated showing several localized modes and low-frequency resonant modes. The change in the total density of states due to the defects is expressed as the derivative of a generalized phase shift which is used to calculate the change in the lattice specific heat due to single interstitials. An appreciable increase of the specific heat is observed giving a peak at $9-10^0$ K in $\Delta C_v/C_v$ for Cu. Inelastic neutron scattering away from the one-phonon lines is proposed as a method to observe the resonant modes induced by self-interstitials. The model calculation in Cu shows that the well defined resonant modes due to dumbbell vibrations, especially the peak corresponding to resonant E_g -mode, have appreciable intensity and could presumably be detected in neutron scattering measurements. The effect of di-interstitials on the phonon dispersion in Al is also discussed.

1. Introduction

The physical understanding of point defects in metals is of central importance for many technological problems. Therefore the investigation of defects in metals has attracted considerable attention. Point defects can be classified as substitutional impurities, vacancies and interstitials. The present study concerns the vibrational properties of self-interstitials in fcc-metals.

The introduction of point defects in an otherwise pure host crystal can significantly change the vibrational properties of the crystal. New characteristic modes localized near the defects may appear whose frequencies can be estimated by $\omega^2 = f_E/M$, where f_E is the Einstein force constant of the defect and M is the defect mass. Two different kind of modes can occur: 1) Localized modes due to a light defect mass and/or due to defects strongly bound to the lattice. These modes have frequencies above the maximum frequency $\omega_{\max}$ of the ideal lattice. 2) Resonant modes, with frequency $\omega \ll \omega_{\max}$, due to a heavy defect mass and/or due to defects weakly bound to the lattice.

For self interstitials in fcc metals the distance between the interstitial and its neighbours is considerably smaller than the nearest neighbour distance in the ideal lattice. Thus there is a strong repulsion between the atoms in the defect region and consequently the force constants are appreciably larger than the ideal lattice nearest neighbour force constant

and one expects localized modes /1,2/. In a computer simulation of copper Scholz and Lehmann /3/ have found that the 100-dumbbell vibrates both with high-frequency localized modes as well as low-frequency resonant modes. The simultaneous occurrence of both kinds of modes for a single defect is quite unusual and cannot be understood by the Einstein formula $\omega^2 \approx f_E/M$. It can be explained, however, by the strongly compressed lattice around the interstitial /4/. These resonant modes are quite important in understanding the physical properties of the irradiated metals. They explain the large experimentally observed changes in the elastic constants /5/. They lead to drastic changes in phonon dispersion curves /6,7/, and in the low-temperature lattice specific heat /8,9/. They cause large thermal displacements of the interstitial atoms /8,9/ (see also Ref. 10 and sections 4-6). The present report is an extension of the work of Zeller and Dederichs /8,9/ and Schober et al. /7/. Especially we will evaluate the changes of the specific heat due to interstitials which have been recently measured by Monsau and Wollenberger in electron irradiated Cu crystals /30/. Following a suggestion of Schilling /47/ we further calculate the "diffuse" one-phonon scattering in the vicinity of the resonance frequency, for q-values away from the phonon-line. Here one expects an incoherent, i.e. dispersion free, intensity which as a function of frequency is Lorentzian around the resonance frequency.

The outline of this report is as follows: In section 2 we discuss the general theory for the interstitial defects,

the Green's function for the ideal lattice and the defect lattice is introduced. The connection between the Green's function and the local density of states is discussed.

In section 3 we study the vibrational properties of the 100-dumbbell in an fcc lattice with a simple nearest-neighbour model. The local frequency spectrum of the dumbbell is calculated which shows that the interstitial virtually vibrates only with high-frequency, localized modes and low-frequency resonant modes /8,9/. A new localized mode with A_{1g} symmetry, hitherto not reported, has been found just above the maximum frequency of the ideal lattice.

In section 4 we discuss the change in lattice specific heat due to defects. The change in the density of states, which enters the calculation of specific heat change, is expressed as derivative of a generalized phase shift which is determined by the quantities restricted to the defect space of the single defect. The calculated lattice specific heat in Cu with low concentration of single interstitials shows an anomalous increase with a peak in $\Delta C_V/C_V$ at 9-10°K.

In section 5 we discuss the additional "diffuse" inelastic one-phonon neutron scattering due to a low concentration of 100-dumbbells in Cu. Away from the main one-phonon line we find well defined peaks corresponding to the resonance modes E_g , A_{2u} and E_u . Especially the E_g peak has appreciable intensity and can hopefully be observed in future experimental measurements /48/.

In section 6 we have studied the effect of di-interstitials in fcc metals on the phonon dispersion curves. The calculated frequency shift of the transverse (100) phonon in Al shows a resonance behaviour at wavevector $\zeta \approx 0.1$ ($\nu = 0.88$ THz), a result corroborated from the local frequency spectrum of the di-interstitial. The calculation highlights the importance of di-interstitials and other small clusters in understanding the perturbed phonons in n-irradiated metals. The different resonance frequencies of the various small agglomerates are expected to smear out the sharp resonance structure obtained in the calculated results for single interstitials /7/.

2. General Theory of a Lattice with Interstitial Defects

The lattice dynamics of imperfect lattices has been discussed widely and several reviews on the subject are available (see e.g. /2, 11 - 14/). We felt it necessary to include some of the relevant material only to make this report self contained. We first discuss the lattice Green's function which is basic to the whole theory.

2.1 Perfect Lattice Green's Function

In the harmonic approximation the equation of motion of an atom in the direction i at site m (for a monoatomic lattice) is given by

$$M^m \ddot{s}_i^m(t) + \sum_{nj} \phi_{ij}^{mn} s_j^n(t) = 0 \quad (2.1)$$

where M^m is the mass of atom m and $s_i^m(t)$ is its displacement. The ϕ_{ij}^{mn} are the coupling parameters giving the ij component of the force constants between the atoms m and n . In the general case it is more convenient to work with the dynamical matrix

$$D_{ij}^{mn} = \frac{1}{\sqrt{M^m}} \phi_{ij}^{mn} \frac{1}{\sqrt{M^n}} \quad (2.2)$$

Assuming a harmonic vibration of frequency ω , the equation of motion (2.1), in terms of the dynamical matrix, is written as

$$\sum_{nj} \sqrt{M^m} [D_{ij}^{mn} - \omega^2 \delta_{ij} \delta_{mn}] \sqrt{M^n} s_j^n = 0 \quad (2.3)$$

or in matrix form

$$\underline{L}(\omega^2) \underline{s} = 0, \quad (2.4)$$

where

$$\underline{L}(\omega^2) = \underline{M}^{1/2} (\underline{D} - \omega^2 \underline{I}) \underline{M}^{1/2}. \quad (2.5)$$

The Green's function is defined as the inverse of the matrix $\underline{L}(\omega^2)$

$$G(\omega) = [\underline{L}(\omega^2)]^{-1}$$

or

$$G_{ij}^{mn}(\omega) = \frac{1}{\sqrt{M^m M^n}} \sum_{\alpha} \frac{\xi_i^m(\alpha) \xi_j^{n*}(\alpha)}{\omega_{\alpha}^2 - (\omega + i\epsilon)^2}, \quad (2.6)$$

where $\xi_i^m(\alpha)$ is an element of a unitary matrix which diagonalizes the dynamical matrix so that the equation (2.4) is transformed into an eigenvalue equation

$$(\underline{D} - \omega_{\alpha}^2) \underline{\xi}(\alpha) = 0. \quad (2.7)$$

Here $\xi(\alpha)$'s are the eigenvectors and ω_{α}^2 are the eigenvalues of the dynamical matrix $\underline{D}$. The infinitesimal positive quantity ϵ has been introduced in (2.6) to ensure causality, i.e., the so called retarded Green's functions are used. The eigenvectors $\xi(\alpha)$ satisfy the usual orthonormality and closure conditions:

$$\sum_{mi} \xi_i^{m*}(\alpha) \xi_i^n(\beta) = \delta_{\alpha\beta},$$

$$\sum_{\alpha} \xi_i^m(\alpha) \xi_j^n(\alpha) = \delta_{ij}^{mn}. \quad (2.8)$$

In the special case of an ideal lattice all masses are equal ($M^m = M^0$) and the coupling parameters have translational symmetry. Thus in the ideal lattice the eigenfunctions $\xi(\alpha)$'s are plane waves and can be labelled by a wavevector $\underline{k}$ and a polarization index σ

$$\xi_i^{\sigma m}(\underline{k}\sigma) = \frac{1}{\sqrt{N}} e_i(\underline{k}\sigma) e^{i\underline{k} \cdot \underline{R}^m}, \quad (2.9)$$

where $e_i(\underline{k}\sigma)$ is the eigenvector of the dynamical matrix

belonging to the normal mode ($\underline{k}\sigma$) and N is the number of atoms in the lattice. Thus the ideal lattice Green's function is given by

$$G_{ij}^{mn}(\omega) = \frac{1}{MN} \sum_{\underline{k}\sigma} \frac{e_i(\underline{k}\sigma) e_j(\underline{k}\sigma)}{\omega_{\underline{k}\sigma}^2 - (\omega + i\epsilon)^2} e^{i\underline{k}(\underline{R}^m - \underline{R}^n)}, \quad (2.10)$$

where $\omega_{\underline{k}\sigma}$ are the eigenfrequencies. In the ideal lattice - since ϕ is real and symmetric - the polarization vectors can be chosen as real so that

$$\xi^*(\underline{k}) = \xi(-\underline{k}) \quad \text{and} \quad \omega_{\underline{k}\sigma} = \omega_{-\underline{k}\sigma}.$$

The exponential in (2.10) can be replaced by $\cos \underline{k} \cdot \underline{R}^{m-n}$, therefore

$$G_{ij}^{mn}(\omega) = G_{ij}^{m-n}(\omega) = G_{ij}^{-(m-n)}(\omega) = G_{ji}^{m-n}(\omega). \quad (2.11)$$

Using the identity

$$\frac{1}{x - i\epsilon} = P \frac{1}{x} + i\pi \delta(x)$$

we write the real and imaginary part of the Green's function as

$$\text{Re } G_{ij}^{mn}(\omega) = \frac{1}{M} \sum_{\alpha} P \frac{\xi_i^m(\alpha) \xi_j^n(\alpha)}{\omega_{\alpha}^2 - \omega^2} = \text{Re } G_{ij}^{mn}(-\omega) \quad (2.12a)$$

$$\begin{aligned} \text{Im } G_{ij}^{mn}(\omega) &= \frac{\pi}{M} \text{Sgn } \omega \sum_{\alpha} \xi_i^m(\alpha) \xi_j^n(\alpha) \delta(\omega_{\alpha}^2 - \omega^2) \\ &= -\text{Im } G_{ij}^{mn}(-\omega). \end{aligned} \quad (2.12b)$$

Clearly

$$G(\omega) = G^*(-\omega). \quad (2.13)$$

The real and imaginary parts of the Green's functions are not independent of each other but related by the Kramers-Kronig relation

$$\operatorname{Re} G(\omega) = \frac{1}{\pi} \int_0^{\infty} d\omega'^2 \mathcal{P} \frac{1}{\omega'^2 - \omega^2} \operatorname{Im} G(\omega') . \quad (2.14)$$

2.2 Connection between density of states and Green's functions

The same site ideal lattice Green's function at site m is

$$G_{ii}^{mm}(\omega) = \frac{1}{M N} \sum_{\underline{k}\sigma} \frac{e_i(\underline{k}\sigma) e_j(\underline{k}\sigma)}{\omega_{\underline{k}\sigma}^2 - (\omega + i\epsilon)^2} . \quad (2.15)$$

Making use of the orthonormality condition for the polarization vectors we can write

$$\begin{aligned} \operatorname{Im} \sum_i G_{ii}^{mm}(\omega) &= \frac{\pi}{M N} \operatorname{Sgn} \omega \sum_{\underline{k}\sigma} \delta(\omega_{\underline{k}\sigma}^2 - \omega^2) \\ &= \frac{\pi}{M N} \frac{1}{2\omega} \sum_{\underline{k}\sigma} \delta(\omega_{\underline{k}\sigma} - \omega), \quad \omega > 0. \end{aligned} \quad (2.16)$$

Summing over all the lattice sites we get

$$\operatorname{Im} \sum_{mi} G_{ii}^{mm}(\omega) = \frac{\pi}{2M\omega} \sum_{\underline{k}\sigma} \delta(\omega_{\underline{k}\sigma} - \omega) = \frac{\pi}{2M\omega} \overset{0}{Z}(\omega), \quad (2.17)$$

where $\overset{0}{Z}(\omega) = \sum_{\underline{k}\sigma} \delta(\omega_{\underline{k}\sigma} - \omega)$ is the total density of states in the ideal lattice, i.e., the number of frequencies in the interval $(\omega, \omega + d\omega)$. Eqn. (2.17) shows that the total density of states can be expressed as the sum of the imaginary parts of the same site Green's functions over all the sites. This suggests the way to define in a non-ideal lattice the so called local density of states of an atom m in i -direction by

$$\begin{aligned} z_i^m(\omega) &= \frac{2\omega M^m}{\pi} \text{Im} G_{ii}^{mm}(\omega) \\ &= \sum_{\alpha} |\xi_i^m(\alpha)|^2 \delta(\omega_{\alpha} - \omega), \quad \omega > 0. \end{aligned} \quad (2.18)$$

We note that

$$\int_0^{\infty} d\omega z_i^m(\omega) = \sum_{\alpha} |\xi_i^m(\alpha)|^2 = 1, \quad (2.19)$$

i.e. the distribution $z_i^m(\omega)$ is normalized with respect to ω . $z_i^m(\omega)$ gives the number of frequencies in the interval $(\omega, \omega+d\omega)$ multiplied by the square of the amplitude of atom m in i -direction. $z_i^m(\omega)$ is the quantitative measure of the number of modes contributing to the vibrational behaviour of atom m . In a defect lattice $z_i^m(\omega)$ will in general be different for each atom and each direction.

Often the moments of the imaginary part of the mass-transformed Green's function $y(\omega) (= \sqrt{M} G(\omega) \sqrt{M})$ can provide already useful information regarding the frequency spectrum without calculating the Green's function explicitly,

$$\begin{aligned} \frac{1}{\pi} \int d\omega^2 (\omega^2)^n \text{Im} y(\omega) &= \int d\omega^2 (\omega^2)^n \delta(D - \omega^2) \\ &= (D)^n. \end{aligned} \quad (2.20)$$

Thus the zeroth moment ($n=0$) gives the normalization for $z_i^m(\omega)$ if we take the ii -matrix element of eqn. (2.20) while the second moment of $z_i^m(\omega)$ is

$$\langle \omega^2 \rangle = \int_0^{\infty} d\omega \omega^2 z_i^m(\omega) = D_{ii}^{mm} = \frac{\Phi_{ii}^{mm}}{M^m} \quad (2.21)$$

giving the Einstein frequency of atom m in i -direction.

The concept of a local density of states is quite useful in the context of defect lattice dynamics. We will see in section 3 that the local spectrum of a defect completely describes the vibrational behaviour of the defect atom. It is particularly useful for calculating those vibrational properties which do not depend on correlations of different atoms. For instance the thermal displacement squared of an atom is

$$\langle (S_i^m)^2 \rangle_T = \int_0^\infty d\omega \frac{Z_i^m(\omega)}{2M^m\omega} \hbar \coth(\hbar\omega/2kT) \quad (2.22)$$

The total spectrum of the lattice can be expressed as the sum of the local frequency spectra of all the N atoms of the lattice

$$Z(\omega) = \sum_{mi} Z_i^m(\omega) = \sum_{mi} \sum_{\alpha} |\xi_i^m(\alpha)|^2 \delta(\omega_{\alpha} - \omega). \quad (2.23)$$

Using the orthonormality of $\xi_i^m(\alpha)$ we get

$$Z(\omega) = \sum_{\alpha=1}^{3N} \delta(\omega_{\alpha} - \omega) \quad \text{with} \quad \int d\omega Z(\omega) = 3N. \quad (2.24)$$

It may be noted that all the thermodynamic properties of the crystal can be expressed in terms of the total spectrum $Z(\omega)$ and consequently in terms of the local frequency spectra of all the atoms (see section 4.1).

2.3 Green's Function for the Defect lattice

In matrix form the Green's function for the defect lattice may be given by (see eqn. 2.6)

$$(\phi - M\omega^2) G(\omega) = 1 \quad (2.25)$$

while that of the ideal lattice is given by

$$(\Phi - \overset{\circ}{M} \omega^2) \overset{\circ}{G}_1(\omega) = 1 \quad (2.26)$$

(all the quantities pertaining to the ideal lattice are denoted by an upper index 0, e.g., $\overset{\circ}{G}$, $\overset{\circ}{\phi}$ etc.) In general the coupling parameters ϕ and the mass M of the defect lattice differ from the quantities $\overset{\circ}{\phi}$ and $\overset{\circ}{M}$ in the ideal lattice. In the case of vacancies and interstitials also the total number of atoms are different.

For a substitutional defect, the coupling parameters around an impurity atom are changed in addition to the mass change at the impurity site. In general, the change in coupling parameters far away from the defect is negligibly small and only changes in the coupling parameters between the defect and its immediate neighbours are considered. Then the Green's function for the defect lattice is evaluated in terms of the ideal lattice Green's function and the "perturbation" which is strongly localized in space.

We write eqn (2.25), assuming only one impurity atom, as

$$(\overset{\circ}{\Phi} - \overset{\circ}{M} \omega^2 + V(\omega)) G_1(\omega) = 1 \quad (2.27a)$$

or

$$G_1(\omega) = \overset{\circ}{G}_1(\omega) - \overset{\circ}{G}_1(\omega) V(\omega) G_1(\omega) \quad (2.27b)$$

with

$$V(\omega) = \Phi - \overset{\circ}{\Phi} - (M - \overset{\circ}{M}) \omega^2 \quad (2.28)$$

and

$$\overset{\circ}{G}_1(\omega) = (\overset{\circ}{\Phi} - \overset{\circ}{M} \omega^2)^{-1}.$$

Eqn. (2.27) can be directly solved for $G(\omega)$ to give

$$G_1(\omega) = \frac{1}{1 + \overset{\circ}{G}_1 V} \overset{\circ}{G}_1 = \overset{\circ}{G}_1 \frac{1}{1 + V \overset{\circ}{G}_1} . \quad (2.29)$$

An equivalent expression for $G(\omega)$ can be obtained by inserting expression (2.29) into the right side of eqn. (2.27b)

$$G_1(\omega) = \overset{\circ}{G}_1 - \overset{\circ}{G}_1 t(\omega) \overset{\circ}{G}_1 \quad (2.30)$$

with

$$t(\omega) = V \frac{1}{1 + \overset{\circ}{G}_1 V} .$$

Thus the Green's function is given in terms of the ideal lattice Green's function and the t-matrix which is restricted to the defect space spanned by the defect and its immediate neighbours. In order to calculate $t(\omega)$ we have only to invert the finite matrix $(1 + \overset{\circ}{G}V)$ with dimension $3n$, if n is the number of atoms affected by the perturbation. The use of group theory by exploiting the point symmetry of the impurity can further reduce the problem.

An alternative formulation of the defect problem has been proposed by Krumhansl and Matthew /15-16/ which is particularly suitable for interstitials where additional degrees of freedom are introduced in the lattice. The method provides a direct description of the local vibrational properties of the defect - in the sense that the description has a simple Einstein-oscillator like structure.

We introduce projection operators on the different subspaces of the lattice. Thus we take a projector P_C pertaining to a central subspace C consisting of the defect and its immediate

neighbours (in most cases the defect alone), a projector P_R pertaining to the rest lattice R of all other atoms, so that

$$P_C = P_C^2, \quad P_R = P_R^2, \quad P_C + P_R = 1. \quad (2.31)$$

The subspace R can be further split up into a neighbour region N, consisting of all atoms which are either directly coupled to the central region or for which force constants are changed, and into an unperturbed subspace U of host atoms

$$P_R = P_N + P_U, \quad P_C + P_N + P_U = 1. \quad (2.32)$$

We use these projector operators to partition the coupling matrix as

$$\Phi = P_C \Phi P_C + P_C \Phi P_R + P_R \Phi P_C + P_R \Phi P_R. \quad (2.33)$$

or in matrix form

$$\Phi = \begin{pmatrix} \Phi_{CC} & \Phi_{CR} \\ \Phi_{RC} & \Phi_{RR} \end{pmatrix} = \left(\begin{array}{c|cc} \Phi_{CC} & \Phi_{CN} & 0 \\ \hline -\Phi_{NC} & \Phi_{NN} & \Phi_{NU} \\ 0 & \Phi_{UN} & \Phi_{UU} \end{array} \right). \quad (2.34)$$

Here Φ_{CC} is the Einstein coupling of the central region when the rest lattice is in the frozen state, Φ_{RR} is the coupling of the atoms in the rest lattice while the defect is fixed, and Φ_{CR} describes the coupling of the defect with the neighbours in the rest lattice. In the unperturbed region U the coupling constants are unchanged, i.e., $\Phi_{NU} = \Phi_{NU}$ and $\Phi_{UU} = \Phi_{UU}$.

Similar to the coupling matrix Φ we write the Green's function and mass matrices in the partitioned form

$$G = \begin{pmatrix} G_{CC} & G_{CR} \\ G_{RC} & G_{RR} \end{pmatrix}, \quad M = \begin{pmatrix} M_{CC} & 0 \\ 0 & M_{RR} \end{pmatrix}. \quad (2.35)$$

By inserting the partitioned form of the quantities in eqn. (2.25)

we get

$$(\Phi_{CC} - M_{CC} \omega^2) G_{CC} + \Phi_{CR} G_{RC} = 1$$

$$\Phi_{RC} G_{CC} + (\Phi_{RR} - M_{RR} \omega^2) G_{RC} = 0 \quad (2.36a)$$

$$\Phi_{RC} G_{CR} + (\Phi_{RR} - M_{RR} \omega^2) G_{RR} = 1$$

$$(\Phi_{CC} - M_{CC} \omega^2) G_{CR} + \Phi_{CR} G_{RR} = 0. \quad (2.36b)$$

Eqn. (2.36a) couples the Green's function $G_{CC}(\omega)$ of the defect, i.e. the displacement of the defect due to a unit force on the defect, with the Green's function $G_{RC}(\omega)$, i.e., the atomic displacements in the rest lattice due to a force on the defect. Similarly eqn. (2.36b) describes the coupling of the Green's function for the rest lattice $G_{RR}(\omega)$ with the Green's function $G_{CR}(\omega)$. From eqn. (2.36) the Green's functions G_{CC} , G_{RR} , G_{CR} and G_{RC} are easily determined. The result is

$$G_{CC} = (\Phi_{CC} - \Phi_{CR} \hat{G}_{RR} \Phi_{RC} - M_{CC} \omega^2)^{-1} \quad (2.37a)$$

$$G_{RR} = (\Phi_{RR} - \Phi_{RC} \hat{G}_{CC} \Phi_{CR} - M_{RR} \omega^2)^{-1} \quad (2.37b)$$

$$G_{RC} = -\hat{G}_{RR} \Phi_{RC} G_{CC} \quad (2.37c)$$

$$G_{CR} = -G_{CC} \Phi_{CR} \hat{G}_{RR} = G'_{RC} \quad (2.37d)$$

where G'_{RC} is transpose of G_{RC} . $\hat{G}_{RR} = (\Phi_{RR} - M_{RR} \omega^2)^{-1}$ describes the vibrations of the atoms in the rest lattice when the interstitial is fixed and $\hat{G}_{CC} = (\Phi_{CC} - M_{CC} \omega^2)^{-1}$ describes the Einstein vibrations of the interstitial. The Green's function $G_{CC}(\omega)$ determines the local vibrational properties of the interstitial

which is more easily elucidated if we put it in terms of the "effective force constant" /17/ $\phi_{CC}^{\text{eff}}(\omega)$:

$$G_{CC} = \frac{1}{\phi_{CC} - \phi_{CR} \hat{G}_{RR} \phi_{RC} - M_{CC} \omega^2} = \frac{1}{\phi_{CC}^{\text{eff}}(\omega) - M_{CC} \omega^2}. \quad (2.38)$$

Clearly the eqn. (2.38) has the form of the Einstein approximation for the interstitial region where ϕ_{CC}^{eff} is the effective coupling of the defect when it is embedded in the lattice. The correction $-\phi_{CR} \hat{G}_{RR} \phi_{RC}$ to the Einstein term ϕ_{CC} describes the effect of the dynamic relaxations of the atoms in the rest lattice. $G_{CC}(\omega)$ is easily determined once G_{RR} is known. For the present case of an interstitial the subspace R contains all the atoms of the ideal lattice and G_{RR} can easily be calculated in terms of the ideal lattice Green's function $\hat{G}$ by

$$\hat{G}_{RR} = \hat{G} - \hat{G} V_{RR} \hat{G}_{RR} = \hat{G} - \hat{G} \hat{t} \hat{G}, \quad (2.39)$$

with

$$\hat{t} = V_{RR} \frac{1}{1 + \hat{G} V_{RR}} \equiv t_{NN}, \quad V_{RR} = \phi_{RR} - \phi - (M_{RR} - M) \omega^2 \equiv V_{NN},$$

as the perturbation is confined to the neighbour subspace N. In the calculation of $\hat{t}$ one has to invert a matrix of dimension 3 times the number of perturbed atoms in subspace N.

The Green's function G_{RR} is especially useful for the interstitial problem since it gives the vibrations of the host lattice in the presence of the interstitial by eliminating the additional degrees of freedom due to its presence. The elimination of the interstitial coordinates leads to an effective coupling between the lattice atoms. Again the expression for G_{RR} (eqn. 2.37b) has the simple Einstein oscillator like structure. The term

$-\phi_{RC} \hat{G}_{CC} \phi_{CR}$ represents the interstitial reaction to the lattice system. Thus G_{RR} describes the collective motion of the lattice giving the perturbed phonons of the defect lattice. G_{RR} can be calculated by the standard Green's function method

$$G_{RR} = \frac{1}{\phi - M\omega^2 - \tilde{V}_{RR}} = \overset{\circ}{G}_1 - \overset{\circ}{G}_1 \tilde{V}_{RR} G_{RR}, \quad (2.40)$$

if we add to the perturbation V_{RR} the interstitial induced interaction between the host atoms

$$\tilde{V}_{RR} = V_{RR} - \phi_{RC} \hat{G}_{CC} \phi_{CR}. \quad (2.41)$$

In terms of the t-matrix G_{RR} is given by

$$G_{RR} = \overset{\circ}{G}_1 - \overset{\circ}{G}_1 \tilde{t} \overset{\circ}{G}_1 \quad (2.42)$$

with

$$\tilde{t} = \tilde{V}_{RR} \frac{1}{1 + \overset{\circ}{G}_1 \tilde{V}_{RR}}$$

Compared with the standard Green's function method, the advantage of the present method lies in the fact that the Green's function $G_{CC}(\omega)$ of the defect is described by an Einstein-type force constant $\phi_{CC}^{\text{eff}}(\omega)$ which gives the local vibrational properties of the defect. However the numerical effort is the same in both cases.

3. Vibration of 100-dumbbell in fcc-metals

The most stable structure of self-interstitials in fcc-metals seems to be the 100-split configuration (dumbbell). Recent diffuse X-ray scattering experiments of Ehrhart, Haubold and Schilling show the 100-dumbbell to be the stable interstitial configuration in Al and Cu /18-20/; elastic relaxation measurements in Al /21/, magnetic relaxation measurements in Ni /22/, and elastic constant measurements in Cu and Al /23,24/ also confirm this structure. Numerous computer calculations /10,25/ also lead to the same configuration. The 100-dumbbell configuration is shown in fig. 1.

3.1 Defect model

For an understanding of the resonant vibrations of the dumbbell the coupling constants for a central potential $V(r)$ will be considered. For two atoms at distance R one obtains a longitudinal force constant $f_{\parallel} = V''(R)$ for displacements parallel to R ("spiral spring") and a transversal force constant $f_{\perp} = V'(R)/R$ for displacements perpendicular to R ("leaf" or "bending spring"). For the ideal lattice the nearest neighbour force constant, $f_{\parallel} = f_{\parallel}^0$ is the most dominant force constant, e.g., in fcc-crystals $f_{\parallel}$ is usually a factor 10 larger than all other force constants - and $f_{\perp}$ can be neglected in the first approximation. However, in the compressed region of the interstitial both the force constants become much more larger and $f_{\perp}$ can not be neglected. From computer simulation /10/ typical values for the force constants between the two dumbbell atoms are $f_{\parallel} \approx 7f_{\parallel}^0$ and $f_{\perp} \approx -0.6 f_{\parallel}^0$ and between one of the dumbbell atoms and its nearest neighbours are $f_{\parallel} \approx 4 f_{\parallel}^0$

and $f_{\perp} \approx -0.3 f_{\parallel}^0$. Thus as a result of the strong interaction the longitudinal force constant $f_{\parallel}$ is very large while due to the repulsion of atoms $f_{\perp}$ is always negative and becomes comparable to $f_{\parallel}^0$ which represents the restoring forces of the ideal lattice. Such a negative bending spring can be visualized as being produced by a compressed spiral spring which is unstable against the displacement perpendicular to the spring axis.

To discuss the vibrational behaviour of the interstitial we consider the following model with nearest neighbour interactions (fig. 1). The defect is described by a vacancy at position (0,0,0) and two interstitials at (0,0, $\pm d$). The coupling between the two dumbbell atoms is represented by a spiral spring $f_{\parallel}$ and a leaf spring $f_{\perp}$ while $F_{\parallel}$ and $F_{\perp}$ represent the interaction of a dumbbell atom with its four nearest neighbours. The vacancy is described by zero coupling constants to its neighbours. All other coupling constants are the same as in the ideal lattice and longer ranged force constant changes are neglected.

The coupling parameters for the defect model described can be calculated using the tetragonal symmetry of the 100-dumbbell /9/

$$\Phi^{(00d,00-d)} = - \begin{pmatrix} f_{\perp} & 0 & 0 \\ 0 & f_{\perp} & 0 \\ 0 & 0 & f_{\parallel} \end{pmatrix}$$

$$\Phi^{(110,000)} = - \frac{1}{2} \begin{pmatrix} f^0 & f^0 & 0 \\ f^0 & f^0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$$\begin{aligned} \phi^{(011,00d)} &= -\frac{1}{1+(1-d)^2} \begin{pmatrix} F_{\perp} + F_{\perp}(1-d)^2 & 0 & 0 \\ 0 & F_{\parallel} + F_{\perp}(1-d)^2 & (F_{\parallel} - F_{\perp})(1-d) \\ 0 & (F_{\parallel} - F_{\perp})(1-d) & F_{\parallel}(1-d)^2 + F_{\perp} \end{pmatrix} \\ \phi^{(110,000)} &= 0 \end{aligned} \quad (3.1)$$

Due to the transversal springs this model is not rotationally invariant. But more complex models with additional transversal springs between the nearest neighbours to restore the rotational invariance yield similar results /8-9/. Thus in the following calculations we use this simple model without rotational invariance.

3.2 Local Spectra and Resonant- and Localized Modes

The resonant vibrations of the defect can be best described by the Green's function $G_{ii}^{dd}(\omega)$ which is the dynamic response of the defect, i.e. its displacement in the i-direction due to a unit force with frequency ω acting on it in the i-direction. The imaginary part of the defect Green's function gives the local frequency spectrum of the defect (Eqn.(2.18))

$$Z_i^d(\omega) = \frac{2M\omega}{\pi} \text{Im} G_{ii}^{mm}(\omega) \quad (3.2)$$

i.e. the frequencies with which the defect vibrates in the i-direction. For the calculation of the defect Green's function with the help of equations (2.38) and (2.39) we have to invert 39×39 matrices as 13 atoms, i.e., the vacancy and 12 neighbours of the vacancy and the interstitials are involved in the change of force constants. The site symmetry (point group D_{4h}) of the defect can be utilized to decompose the total representations into

irreducible representations /26/:

$$3 A_{1g} + 2 A_{2g} + 2 B_{1g} + 3 B_{2g} + 4 E_g + A_{1u} + 4 A_{2u} + 2 B_{1u} + 2 B_{2u} + 6 E_u \quad (3.3)$$

Out of these the displacements of the dumbbell atoms involve only in four different representations (A_{1g} , E_g , A_{2u} , E_u). The dumbbell atoms move parallel to their axis in the A-type modes and perpendicular to it in E-type modes. Only the even modes (A_{1g} , E_g) stress the springs $f_{\parallel}$ or $f_{\perp}$ between the dumbbell atoms. As a result the "breathing mode" A_{1g} leads to localized modes where relatively weak leaf springs are not important; whereas the three other modes give rise to resonant or localized vibrations depending on whether the motion of the neighbouring atoms is in phase or out of phase with the dumbbell atoms. The four force constants $f_{\parallel}$, $f_{\perp}$, $F_{\parallel}$ and $F_{\perp}$ are fitted to computer simulation results by means of the two sum rules for $Z_i^d(\omega)$ (see eqn. (2.20))

$$\langle \omega^2 \rangle_i^d = \int_0^{\infty} d\omega \omega^2 Z_i^d(\omega) = \phi_{ii}^{dd} / M, \quad (3.4)$$

$$\langle \frac{1}{\omega^2} \rangle_i^d = \int_0^{\infty} d\omega \frac{1}{\omega^2} Z_i^d(\omega) = M G_{ii}^{dd}(0). \quad (3.5)$$

The first term $M \langle \omega^2 \rangle$ gives the Einstein force constant ϕ_{ii}^{dd} , which can be calculated directly from the relaxed configuration and the known interaction potential $V(R)$. Since the spectrum $Z_i^d(\omega)$ is weighted by ω^2 , ϕ_{ii}^{dd} virtually determines the high frequencies of the localized modes. The second term $\frac{1}{M} \langle \frac{1}{\omega^2} \rangle$ is the static response $G_{ii}^{dd}(\omega=0)$ of the defect. Thus $\langle \frac{1}{\omega^2} \rangle$ virtually determines the low frequency resonant modes.

The local spectrum of a dumbbell atom in Cu has been calculated with the specific choice of the four force constants

$$f_{||} = 8.14 f_{||}^0, \quad F_{||} = 5.55 f_{||}^0 \quad (3.6)$$

$$f_{\perp} = -0.66 f_{||}^0, \quad F_{\perp} = -0.30 f_{||}^0 \quad (3.7)$$

which are obtained in computer simulation by Zeller /27/ using a Morse potential. In the calculation the distance between the dumbbell atoms is chosen as $2d = 0.5a$ (a =lattice constant) in order to get angles similar to that in the real structure. For the calculation of the perfect lattice Green's function for Cu a modified Gilat-Raubenheimer method /28/ has been used. To obtain the perfect lattice phonons we use a sixth neighbour axially symmetric model /29/ derived from Born-von Karman fits to the measured phonons in neutron scattering experiments. The calculated local frequency spectrum is plotted in fig. 2. Group theory has not been used to decompose the Green's function and perturbation matrices. We obtain three different resonant modes (E_g, A_{2u}, E_u) and five different localized modes ($A_{1g}, A_{2u}, E_g, E_u, A_{1g}$). The frequencies of the resonant modes are

$$\omega_{\text{res}}^{E_g} = 1.06, \quad \omega_{\text{res}}^{A_{2u}} = 1.60, \quad \omega_{\text{res}}^{E_u} = 2.28 \quad (3.7)$$

and that of the localized modes are

$$\begin{aligned} \omega_{loc}^{A_{1g}} &= 7.42, \quad \omega_{loc}^{A_{2u}} = 9.16, \quad \omega_{loc}^{E_g} = 10.02, \\ \omega_{loc}^{E_u} &= 10.21, \quad \omega_{loc}^{A_{1g}} = 12.26. \end{aligned} \quad (3.8)$$

All the frequencies in eqns. (3.7) and (3.8) are given in THz. The motion of the dumbbell atoms are indicated by arrows in fig. 2. Our results are essentially identical with the earlier results of Zeller /9/ and Dederichs et al. /10/. As a slight modification we obtain a second localized mode with A_{1g} symmetry having a frequency $\omega_{loc}=7.42$ just above the band edge $\omega_{max} = 7.31$ of the ideal lattice. These deviations are due to some slightly different values for the coupling parameters of the defect and of the ideal lattice.

4. Lattice Specific Heat

4.1 Frequency spectrum and Thermodynamic functions

In the harmonic approximation the thermodynamic functions are additive functions of the normal mode frequencies and as a result, they can be expressed as averages over the frequency spectrum. For example the internal energy of the crystal is given by

$$E = \sum_{\alpha} \epsilon(\omega_{\alpha}, T) = \int d\omega Z(\omega) \epsilon(\omega, T), \quad (4.1)$$

where

$$\epsilon(\omega, T) = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1} \quad (4.2)$$

is the energy of a single oscillator of frequency ω , k is Boltzmann constant, T is the absolute temperature and $Z(\omega)$ the total frequency spectrum of the crystal given by

$$Z(\omega) = \sum_{\alpha=1}^{3N} \delta(\omega - \omega_{\alpha}) = 2\omega T_r \delta(\omega^2 - D) \quad (4.3)$$

with

$$D = \frac{1}{\sqrt{M}} \Phi \frac{1}{\sqrt{M}}$$

The second equation follows since ω_{α}^2 are the eigenvalues of the dynamical matrix D . In eqn. (4.3) the trace can also be performed in the real space representation. Then the total spectrum $Z(\omega)$ can be expressed in terms of the local spectra $Z_i^m(\omega)$ for each atom m and direction i as discussed in section 2.2.

$$Z(\omega) = 2\omega \sum_{mi} \langle mi | \delta(\omega^2 - D) | mi \rangle = \sum_{mi} Z_i^m(\omega) \quad (4.4)$$

with

$$Z_i^m(\omega) = \frac{2\omega}{\pi} I_m y_{ii}^{mm}(\omega) = \frac{2\omega M^m}{\pi} I_m G_{ii}^{mm}(\omega)$$

and

$$y(\omega) = \{ D - (\omega + i\epsilon)^2 \}^{-1}.$$

For a disordered crystal the thermodynamic properties are therefore determined by the configurational averaged Green's functions

$$\langle y_{ij}^{mn}(\omega) \rangle = \langle \sqrt{M^m} G_{ij}^{mn}(\omega) \sqrt{M^n} \rangle \quad (4.5)$$

For a low concentration c of point defects we need only to consider changes in $E(V, T)$ linear in c :

$$E(V, T) = \overset{0}{E}(V, T) + N_d e(V, T), \quad (4.6)$$

where $e(V, T)$ is the formation energy and $N_d = cN$ is the total number of defects. Thus for the temperature dependence of these quantities we need the change $\Delta Z(\omega)$ of the total spectrum linear in c . From the exact equation

$$Z(\omega) = \frac{2\omega}{\pi} \text{Tr} I_m y(\omega) = \frac{2\omega}{\pi} \text{Tr} I_m \{ y^0(\omega) - y^0(\omega) T(\omega) y^0(\omega) \} \quad (4.7)$$

we obtain the change in the total spectrum as

$$\Delta Z(\omega) = N_d \Delta Z(\omega) = -N_d \frac{2\omega}{\pi} I_m \text{Tr} \{ y^0(\omega) t(\omega) y^0(\omega) \} \quad (4.8)$$

where the total T-matrix is approximated by the sum of the

individual t-matrices. Thus the vibrational contribution to the formation energy e is given by

$$e(T) = \int d\omega \Delta Z(\omega) \xi(\omega, T). \quad (4.9)$$

where $\Delta Z(\omega)$ is the change of the spectrum $Z(\omega)$ due to a single defect.

4.2 Change in Density of States $\Delta Z(\omega)$

The calculation of changes in thermodynamic quantities due to defects can be carried out if the change in the density of states is known. For a low concentration of defects the change $\Delta Z(\omega)$ of the total spectrum is equal to the number of defects N_α times the change $\Delta Z(\omega)$ due to a single defect (eqn. 4.8)) which itself is given by

$$\begin{aligned} \Delta Z(\omega) &= \sum_{\alpha} \{ \delta(\omega - \omega_{\alpha}^1) - \delta(\omega - \omega_{\alpha}^0) \} \\ &= \frac{2\omega}{\pi} \text{Tr} \text{Im} \{ y^1(\omega) - y^0(\omega) \} \\ &= - \frac{2\omega}{\pi} \text{Tr} \text{Im} \{ y^0(\omega) t(\omega) y^0(\omega) \}, \end{aligned} \quad (4.10)$$

where ω_{α}^1 and ω_{α}^0 are the frequencies of a crystal with a single defect and of the ideal lattice, respectively and $y^1(\omega)$ and $y^0(\omega)$ are the corresponding Green's functions. Due to the infinite range of the Green's function $y_{ij}^{mn}(\omega)$ eqn. (4.10) is not suitable for actual calculations. However we can use the following relation

$$y_{ij}^0(\omega) y_{ij}^0(\omega) = \frac{\partial}{\partial \omega^2} y_{ij}^0(\omega) \quad (4.11)$$

to get $\Delta Z(\omega)$ as

$$\begin{aligned}\Delta Z(\omega) &= -\frac{1}{\pi} \text{Im} \text{Tr} \, t(\omega) \frac{\partial y^0(\omega)}{\partial \omega} \\ &= -\frac{1}{\pi} \text{Im} \sum_{mn} t_{ij}^{mn}(\omega) \frac{\partial y_{ij}^{mn}(\omega)}{\partial \omega} .\end{aligned}\quad (4.12)$$

Here, due to the finite range of the t-matrix the summation is restricted to the few sites in the perturbation region. Another expression for $\Delta Z(\omega)$ can be obtained if we note the following expression for t-matrix

$$t(\omega) = \Delta D \frac{1}{1 + y^0(\omega) \Delta D} , \quad (4.13)$$

where ΔD is the change in the dynamical matrix D . Inserting this in (4.12) one obtains

$$\Delta Z(\omega) = -\frac{1}{\pi} \text{Im} \text{Tr} \frac{d}{d\omega} \ln(1 + y^0(\omega) \Delta D) \quad (4.14)$$

$$= -\frac{1}{\pi} \text{Im} \frac{d}{d\omega} \ln \{ \text{Det} | 1 + y^0(\omega) \Delta D | \} , \quad (4.15)$$

where in writing (4.15) $\text{Tr} \ln \dots = \ln \text{Det} \dots$ has been used.

Eqn. (4.15) is interesting in as much as one need not calculate the t-matrix by inverting the matrix $1 + y^0(\omega) \Delta D$.

Yet another expression, quite analogous and more useful for actual calculations, can be obtained in terms of the Green's function $G^0(\omega)$. Starting from eqn. (4.10), we have

$$\Delta Z(\omega) = -\frac{1}{\pi} \frac{\partial}{\partial \omega} \text{Tr} \text{Im} \{ \ln(D - (\omega + i\epsilon)^2) - \ln(D^0 - (\omega + i\epsilon)^2) \} \quad (4.16)$$

since $y(\omega) = \{ D - (\omega + i\epsilon)^2 \}^{-1}$.

Now the first term can be expressed as

$$\begin{aligned} \text{Tr} \ln (D - (\omega + i\epsilon)^2) &= \ln \text{Det} (D - (\omega + i\epsilon)^2) \\ &= \ln \left\{ \text{Det} \frac{1}{M} \cdot \text{Det} (\Phi - M(\omega + i\epsilon)^2) \right\}. \end{aligned} \quad (4.17)$$

Due to the derivative $\frac{d}{d\omega}$, the mass determinant drops out and eqn. (4.16) reduces to

$$\begin{aligned} \Delta Z(\omega) &= -\frac{1}{\pi} \frac{\partial}{\partial \omega} \text{Tr} \text{Im} \left\{ \ln(\Phi - M(\omega + i\epsilon)^2) - \ln(\Phi^0 - \hat{M}(\omega + i\epsilon)^2) \right\} \\ &= -\frac{1}{\pi} \frac{\partial}{\partial \omega} \text{Tr} \text{Im} \ln \left\{ \hat{G}_1(\omega) (\Phi - M(\omega + i\epsilon)^2) \right\} \\ &= -\frac{1}{\pi} \frac{\partial}{\partial \omega} \text{Tr} \text{Im} \ln \left\{ 1 + \hat{G}_1(\omega) V(\omega) \right\} \end{aligned} \quad (4.18)$$

$$= -\frac{1}{\pi} \text{Tr} \text{Im} \left\{ \frac{1}{1 + \hat{G}_1(\omega) V(\omega)} \frac{\partial}{\partial \omega} (\hat{G}_1(\omega) V(\omega)) \right\}. \quad (4.19)$$

Whereas the eqns. (4.15), (4.17) in terms of D and $\emptyset$ are quite analogous, eqn. (4.19) differs from the analogous eqn. (4.12), as in (4.19) $V(\omega)$ also has to be differentiated. The foregoing results can be further simplified by using the site symmetry of the defect.

Like the local spectrum $Z_1^m(\omega)$ the changed frequency spectrum $\Delta Z(\omega)$ obeys some simple sum rules. If the defect does not introduce additional degrees of freedom into the lattice (substitutional impurity) we have

$$\int d\omega \Delta Z(\omega) = 0. \quad (4.20)$$

Thus the positive and negative contributions cancel each other. The second moment is given by

$$\begin{aligned} \langle \omega^2 \rangle &= \int d\omega \omega^2 \Delta Z(\omega) = \sum_{mi} \Delta D_{ii}^{mm} \\ &= \sum_{mi} \left\{ \frac{\Phi_{ii}^{mm}}{M^m} - \frac{\Phi_{ii}^{mm}}{\bar{M}^m} \right\} \end{aligned} \quad (4.21)$$

Thus $\langle \omega^2 \rangle$ gives the difference between all Einstein frequencies in the defect and ideal crystal lattice. For the case of vacancies and interstitials the sum rule (4.20) is not valid. Instead for an interstitial we have

$$\int d\omega \Delta Z(\omega) = \int d\omega \left\{ \sum_{\alpha} \delta(\omega - \omega_{\alpha}) - \sum_{\alpha'} \delta(\omega - \omega_{\alpha}') \right\} = 3, \quad (4.22)$$

since the interstitial introduces three extra degrees of freedom into the lattice. Likewise for a vacancy we have -3. In these cases the matrices Φ , $\bar{\Phi}$ and G , $\bar{G}$ are of different dimensions. Starting again from eqn. (4.18) we have

$$\begin{aligned} \Delta Z(\omega) &= -\frac{1}{\pi} \frac{\partial}{\partial \omega} \text{Im} \left\{ \text{Tr} \ln (\Phi - M(\omega + i\epsilon)^2) \right. \\ &\quad \left. - \text{Tr} \ln (\bar{\Phi} - \bar{M}(\omega + i\epsilon)^2) \right\} \\ &= -\frac{1}{\pi} \frac{\partial}{\partial \omega} \text{Im} \ln \frac{\text{Det} |\Phi - M(\omega + i\epsilon)^2|}{\text{Det} |\bar{\Phi} - \bar{M}(\omega + i\epsilon)^2|} \end{aligned} \quad (4.23)$$

For an interstitial $(\Phi - M\omega^2)$ has the structure (see sec. 2.3)

$$\Phi - M\omega^2 = \begin{Bmatrix} \Phi_{CC} - M\omega^2 & \Phi_{CR} \\ \Phi_{RC} & \Phi_{RR} - \bar{M}\omega^2 \end{Bmatrix} \quad (4.24)$$

The matrix $(\overset{\circ}{\Phi} - \overset{\circ}{M}\omega^2)$ can be enlarged by adding a unit matrix in the interstitial subspace so that the $\text{Det}(\overset{\circ}{\Phi} - \overset{\circ}{M}\omega^2)$ remains unchanged:

$$\overset{\circ}{\Phi} - \overset{\circ}{M}\omega^2 = \begin{pmatrix} 1 & 0 \\ 0 & \overset{\circ}{\Phi} - \overset{\circ}{M}\omega^2 \end{pmatrix}, \quad \overset{\circ}{G} = \frac{1}{\overset{\circ}{\Phi} - \overset{\circ}{M}\omega^2} = \begin{pmatrix} 1 & 0 \\ 0 & \frac{1}{\overset{\circ}{\Phi} - \overset{\circ}{M}\omega^2} \end{pmatrix} \quad (4.25)$$

Using expressions (4.24), (4.25) in eqn. (4.23) for $\Delta Z(\omega)$ we get

$$\Delta Z(\omega) = -\frac{1}{\pi} \frac{\partial}{\partial \omega} \text{Im} \ln \text{Det} | \overset{\circ}{G}(\omega)(\Phi - M\omega^2) | \quad (4.26)$$

where $\overset{\circ}{G}(\omega)(\Phi - M\omega^2)$ has the structure

$$\overset{\circ}{G}(\omega)(\Phi - M\omega^2) = \left\{ \begin{array}{cc} \Phi_{CC} - M\omega^2 & \Phi_{CR} \\ \frac{1}{\overset{\circ}{\Phi}_{RR} - \overset{\circ}{M}\omega^2} \Phi_{RC} & 1 + \frac{1}{\overset{\circ}{\Phi}_{RR} - \overset{\circ}{M}\omega^2} V_{RR} \end{array} \right\} \quad (4.27)$$

with $V_{RR} = \Phi_{RR} - \overset{\circ}{\Phi}_{RR}$.

The frequencies of the normal modes which are perturbed by the defect are solutions of the equation

$$\tilde{D}(\omega) = 0, \quad (4.28)$$

where $\tilde{D}(\omega) = \text{Det} | \overset{\circ}{G}(\omega)(\Phi - M\omega^2) |$.

For frequencies $\omega > \omega_{\max}$ we have localized modes which give rise to δ -function contribution to the total spectrum. Due to normalization of $\Delta Z(\omega)$, in case of substitutional impurity, a corresponding amount has to be missing in the band mode region $(0, \omega_{\max})$. If for some frequency inside the band mode region the equation

$$\text{Re } \tilde{D}(\omega) = 0 \quad (4.29)$$

has a solution then $\Delta Z(\omega)$ has a resonant character near this frequency ω_r :

$$\begin{aligned} \Delta Z(\omega) &= \frac{2\omega}{\pi} \frac{\gamma \omega}{(\omega^2 - \omega_r^2)^2 + \gamma^2 \omega^2} \\ &\simeq \delta(\omega - \omega_r) \quad \text{if } \gamma \ll \omega_r, \end{aligned} \quad (4.30)$$

i.e. the Lorentzian can be replaced by a δ -function in case of sharp resonances (low damping).

It should be mentioned that sharp singularities are observed /14/ in $\Delta Z(\omega)$ at the critical frequencies of the host lattice and that the low c -expansion is not valid at the critical points. However, for the calculation of the thermodynamic functions such an expansion is still valid, since due to the integration over ω the singularities are no longer important.

4.3 Phase Shift

If we introduce a generalized "phase shift" (π times the integrated density of states) by

$$\theta(\omega) = \tan^{-1} \left(\frac{-\text{Im } \tilde{D}(\omega)}{\text{Re } \tilde{D}(\omega)} \right) \quad (4.31)$$

the expression for the change in density of states $\Delta Z(\omega)$ (eqn. (4.26)) becomes

$$\Delta Z(\omega) = \frac{1}{\pi} \frac{d\theta(\omega)}{d\omega} \quad (4.32)$$

It should be pointed out that the determinant $\tilde{D}(\omega)$ is restricted to the perturbation region spanned by the defect and atoms

directly affected by the perturbation and can be calculated by the standard Green's function technique just as eqn. (4.19).

The contribution of localized and resonant modes to the change in the density of states $\Delta Z(\omega)$ can be easily understood if we consider the nature of the generalized phase shift $\theta(\omega)$. As is clear from eqn. (4.31) that $\theta(\omega)$ is a continuous function of ω except for jump discontinuities at isolated frequencies where $\text{Re}\tilde{D}(\omega) = 0$ and $\text{Im}\tilde{D}(\omega) = 0$, i.e., for $\omega > \omega_{\text{max}}$. Evidently such jumps occur at the frequencies of the localized modes. It is not hard to see that a jump discontinuity at a frequency ω_ℓ in the integrated density of states leads to a δ -function singularity in the derived function $\Delta Z(\omega)$, i.e., the change in density of states $\Delta Z(\omega)$ has a δ -function peak at each ω_ℓ . Near resonance frequencies, where $\text{Re}\tilde{D}(\omega)$ becomes zero and $\text{Im}\tilde{D}(\omega)$ is small, $\theta(\omega)$ shows a similar sharp increase which is however smeared out over the width of the resonance. The derivative $\Delta Z(\omega)$ then shows a Lorentzian behaviour (eqn. 4.30).

The calculated phase shift for the 100-dumbbell in Cu with the model described in the section 3.1 is presented in fig. 3. Figure 3 shows sharp increases at frequencies corresponding to E_g , A_{2u} and E_u resonant modes. While for E_g and E_u (doubly degenerate modes) the jump is $\sim 2\pi$, for A_{2u} it is $\sim \pi$. Thus the gain to the phase shift due to the resonant modes is $\sim 5\pi$ but a sharp depletion is observed near ω_{max} so that the phase shift at the band edge is $\sim -6\pi$. This is due to the near resonances (antiresonance) near the band edge. Above ω_{max} we get upward jumps due to the localized modes. Apart from the localized modes discussed in the section 3.3 two additional

localized modes at frequencies 8.16 and 8.21 THz are obtained where eqn. (4.28) is satisfied. These modes are due to vibrations of the neighbours of the dumbbell while the dumbbell itself remains at rest. Again the double degenerate modes E_g and E_u lead to jumps of 2π whereas the other single degenerate modes give jumps of π . In total all the localized mode contribute 9π to $\theta(\omega)$ so that $\theta(\infty) = 3\pi$ in agreement with the sumrule (4.22) for a single interstitial.

4.4 Change in specific heat

The lattice specific heat at constant volume can be calculated from the internal energy:

$$C_v(T) = \left(\frac{\partial E}{\partial T} \right)_v \quad (4.33)$$

$$\begin{aligned} &= \int_0^\infty d\omega Z(\omega) \frac{\partial \epsilon(\omega, T)}{\partial T}, \quad \epsilon(\omega, T) = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1} \\ &= k \int_0^\infty d\omega Z(\omega) \left(\frac{\hbar\omega}{kT} \right)^2 e^{\frac{\hbar\omega}{kT}} (e^{\frac{\hbar\omega}{kT}} - 1)^{-2} \\ &= k \int_0^\infty d\omega Z(\omega) \left(\frac{\hbar\omega}{2kT} \right)^2 \text{Cosech}^2 \left(\frac{\hbar\omega}{2kT} \right). \end{aligned} \quad (4.34)$$

The change in the specific heat due to defects is

$$\Delta C_v(T) = N_d k \int_0^\infty d\omega \Delta Z(\omega) \left(\frac{\hbar\omega}{2kT} \right)^2 \text{Cosech}^2 \left(\frac{\hbar\omega}{2kT} \right). \quad (4.35)$$

Substituting $\Delta Z(\omega)$ from eqn. (4.32), the change in specific heat in terms of the phase shift is

$$\Delta C_v(T) = \frac{N_d k}{\pi} \int_0^\infty d\omega \frac{d\theta(\omega)}{d\omega} \left(\frac{\hbar\omega}{2kT} \right)^2 \text{Cosech}^2 \left(\frac{\hbar\omega}{2kT} \right). \quad (4.36)$$

Integrating eqn. (4.36) once by parts we get

$$\Delta C_v(T) = -\frac{2N_d k}{\pi} \int_0^{\infty} d\omega \theta(\omega) \operatorname{Cosec} h^2\left(\frac{\hbar\omega}{2kT}\right) \cdot \left(1 - \left(\frac{\hbar\omega}{2kT}\right) \operatorname{Cot} h\left(\frac{\hbar\omega}{2kT}\right)\right) \quad (4.37)$$

It should be noted that the relevant dynamics of the imperfect crystal is contained in the function $\theta(\omega)$ and the integration in (4.37) is straightforward once $\theta(\omega)$ is known.

The calculated values of $\theta(\omega)$ (see fig. 3) have been used to calculate the change in lattice specific heat of Cu due to a low concentration c of statistically distributed 100-dumbbells (single interstitials). The relative change $\Delta C_v(T)/c C_v(T)$ as a function of temperature is presented in fig. 4. A peak at $9-10^\circ \text{ K}$ is observed. At this temperature an enhancement factor of 68.5 is seen so that for a concentration $c = 10^{-4}$ of interstitials the relative increase in the specific heat is expected to be 0.7 %. Such an anomalous increase in specific heat is due to the low-frequency resonant modes E_g , A_{2u} and E_u which directly involve the motion of the dumbbell atoms. The contributions of the high frequency localized mode is negligible. Considering only the contributions of the three dumbbell resonances (E_g , A_{2u} , E_u) Zeller and Dederichs /8/ have predicted a 1 % increase in the specific heat for the same concentration. Recently Wollenberger and Monsau /30/ were able to measure the change of the specific heat of Cu after electron irradiation at 4.2 K and observed a temperature anomaly with a peak at about 12 K being in qualitative agreement with our calculations. A similar anomalous increase of the lattice specific heat due to resonance modes is well known for heavy substitutional point defects in metals /31,32/.

5. Resonant Scattering of Neutrons by Self-interstitials

5.1 Theory of Neutron Scattering

The theory of neutron scattering from perfect as well as from defect lattice has been discussed by many authors (see e.g. /12,14/). The differential cross section for the scattering of neutrons per unit solid angle per unit outgoing energy in the first Born approximation is given by

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{K_f}{K_i} \sum_{i,f} p_i(T) |\langle f | \sum_n a_n e^{i\mathbf{K} \cdot \mathbf{r}_n} | i \rangle|^2 \cdot \delta\left(\omega + \frac{E_i - E_f}{\hbar}\right), \quad (5.1)$$

where $\underline{K}_i$ and $\underline{K}_f = \underline{K}_i - \underline{K}$ are the initial and final wavevectors of the neutron, respectively and

$$\hbar \omega = E_i - E_f = \frac{\hbar^2}{2m} (\underline{K}_i^2 - \underline{K}_f^2) \quad (5.2)$$

is the energy transferred from the neutron to the crystal (energy loss), m being the mass of the neutron. The initial and final states of the crystal with energies E_i and E_f are denoted by $|i\rangle$ and $|f\rangle$ respectively, and $p_i(T)$ is the statistical weight of the state $|i\rangle$. Here $\underline{r}^n = \underline{R}^n + \underline{s}^n$ is the instantaneous position of the atom n and a_n is the scattering length of nucleus n . The differential cross section can also be written as a Fourier integral over time dependent correlation functions (Van Hove /33/)

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{K_f}{K_i} \sum_{mn} e^{-i\mathbf{K}(\underline{R}^m - \underline{R}^n)} a_m a_n S^{mn}(\underline{K}, \omega) \quad (5.3)$$

with

$$S^{mn}(\underline{k}, \omega) = \int \frac{dt}{2\pi} e^{i\omega t} \left\langle e^{-i\underline{k} \cdot \underline{s}^m(t)} e^{i\underline{k} \cdot \underline{s}^n(0)} \right\rangle_T.$$

In the harmonic approximation the correlation functions S^{mn} can be further simplified due to the following identity /12/

$$\left\langle e^{-i\underline{k} \cdot \underline{s}^m(t)} e^{i\underline{k} \cdot \underline{s}^n(0)} \right\rangle_T = e^{-\frac{1}{2} \langle (\underline{k} \cdot \underline{s}^m)^2 \rangle_T} e^{-\frac{1}{2} \langle (\underline{k} \cdot \underline{s}^n)^2 \rangle_T} \cdot e^{\langle (\underline{k} \cdot \underline{s}^m(t)) (\underline{k} \cdot \underline{s}^n(0)) \rangle_T} \quad (5.4)$$

Expanding (5.4) in terms of the time dependent correlations $\langle \underline{k} \cdot \underline{s}^m(t) \underline{k} \cdot \underline{s}^n(0) \rangle_T$ the first term describes the zero-phonon or elastic scattering

$$\left(\frac{d^2\sigma}{d\Omega d\omega} \right)_{\text{elastic}} = \left| \sum_m a_m e^{-M_K^m} e^{i\underline{k} \cdot \underline{R}^m} \right|^2 \delta(\omega), \quad (5.5)$$

where M^m is the Debye-Waller factor of atom m . All other terms involve one or more phonon excitations and represent the in-elastic scattering processes. The next term, i.e. the one-phonon scattering, in which we will be interested in the following, is given by

$$\left(\frac{d^2\sigma}{d\Omega d\omega} \right)_{\text{one-phonon}} = \frac{K_f}{K_i} \sum_{mn} e^{-i\underline{k} \cdot (\underline{R}^m - \underline{R}^n)} a_m a_n \cdot e^{-M_K^m} e^{-M_K^n} \int_{-\infty}^{\infty} \frac{dt}{2\pi} e^{i\omega t} \langle \underline{k} \cdot \underline{s}^m(t) \underline{k} \cdot \underline{s}^n(0) \rangle_T. \quad (5.6)$$

The integral in (5.6) can be expressed in terms of the Green's function $G(\omega)$ /14/

$$\int_{-\infty}^{\infty} dt e^{i\omega t} \langle s_i^m(t) s_j^n(0) \rangle = 2\hbar (n(\omega) + 1) \text{Im} G_{ij}^{mn}(\omega), \quad (5.7)$$

where $n(\omega) = (e^{\hbar\omega/KT} - 1)^{-1}$. Using this the one phonon scattering is expressed as (further onwards the suffix "one-phonon" is

dropped)

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{k_f}{k_i} \frac{\hbar}{\pi} \frac{1}{1 - e^{\hbar\omega/kT}} \sum_{\substack{mn \\ i,j}} e^{-i\mathbf{K}(\mathbf{R}_i^m - \mathbf{R}_j^n)} \cdot a_m e^{-M_k^m} a_n e^{-M_k^n} k_i k_j \text{Im} G_{ij}^{mn}(\omega). \quad (5.8)$$

In the case of spin- or isotopic incoherence one has to average the scattering intensity over different spin states or isotope distribution on various sites which are assumed to be independent.

$$\begin{aligned} \overline{a_m a_n} &= \overline{a_m^2} \delta_{mn} + \overline{a_m} \overline{a_n} (1 - \delta_{mn}) \\ &= \overline{a_m} \overline{a_n} + (\overline{a_m^2} - \overline{a_m}^2) \delta_{mn}. \end{aligned} \quad (5.9)$$

Thus we have a "coherent scattering" given by (5.8) with a 's replaced by coherent scattering lengths $\overline{a}_m$ which corresponds to the interference of the waves scattered by different nuclei involving in this eqn. and a "incoherent scattering" determined by $(\overline{a_m^2} - \overline{a_m}^2)$ without any interference term where each nucleus scatters independently:

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{k_f}{k_i} \sum_m (\overline{a_m^2} - \overline{a_m}^2) S^{mm}(\mathbf{K}, \omega). \quad (5.10)$$

For the perfect crystal the coherent one phonon scattering eqn. (5.8), contains the Fourier transform of the Green's function $\text{Im} G_{ij}^{0mn}$, which can be obtained from eqn. (2.10)

$$\begin{aligned} \sum_{mn} e^{-i\mathbf{K}(\mathbf{R}_i^m - \mathbf{R}_j^n)} \text{Im} G_{ij}^{0mn}(\omega) &= \frac{\pi}{M} \text{sgn } \omega \sum_{\sigma} e_i(\mathbf{K}\sigma) e_j(\mathbf{K}\sigma) \delta(\omega_{\mathbf{K}\sigma}^2 - \omega^2) \\ &= \frac{\pi}{M} \sum_{\sigma} e_i(\mathbf{K}\sigma) e_j(\mathbf{K}\sigma) \frac{1}{2\omega_{\mathbf{K}\sigma}} \{ \delta(\omega_{\mathbf{K}\sigma} - \omega) - \delta(\omega + \omega_{\mathbf{K}\sigma}) \}. \end{aligned} \quad (5.11)$$

Thus for the perfect crystal the coherent scattering cross section is

$$\left(\frac{d^2\sigma}{d\Omega d\omega} \right)^{\text{coh}} = \frac{k_f}{k_i} \frac{\hbar}{2M} N \bar{a}^2 e^{-2M_K} \sum_{\sigma} \frac{(\underline{k} \cdot \underline{e}(\underline{k}_{\sigma}))^2}{\omega_{\underline{k}_{\sigma}}} \cdot \left\{ (n(\omega_{\underline{k}_{\sigma}}) + 1) \delta(\omega - \omega_{\underline{k}_{\sigma}}) + n(\omega_{\underline{k}_{\sigma}}) \delta(\omega + \omega_{\underline{k}_{\sigma}}) \right\} \quad (5.12)$$

where all the scattering length a_m are replaced by the coherent scattering length $\bar{a}$ of the crystal and similarly all Debye-Waller factors e^{-M^m} are equal. The first term $\sim \delta(\omega - \omega_{\underline{k}_{\sigma}})$ describes the energy-loss processes of the neutron with excitation of one phonon with energy $\hbar\omega_{\underline{k}_{\sigma}}$ while the second term represents the energy gain processes with absorption of one phonon. It may be observed that the coherent scattering $\sim \delta(\omega^2 - \omega_{\underline{k}_{\sigma}}^2)$ is peaked at frequencies $\omega_{\underline{k}_{\sigma}}$ and can be used to determine the dispersion law of the crystal vibrations.

The incoherent one-phonon scattering is essentially given by the spectrum of the ideal lattice

$$I_m \hat{G}_{ij}^{mm}(\omega) = \frac{\pi}{2\omega M} Z(|\omega|) \delta_{ij} \quad \text{for cubic crystals.}$$

Thus we obtain

$$\left(\frac{d^2\sigma}{d\Omega d\omega} \right)^{\text{incoh}} = \frac{k_f}{k_i} \frac{\hbar}{2M} N (\bar{a}^2 - \bar{a}^2) e^{-2M_K} \frac{k^2}{\omega} \cdot \frac{1}{1 - e^{-\hbar\omega/kT}} Z(|\omega|), \quad (5.13)$$

where $Z(|\omega|) = \frac{1}{3N} \sum_{\underline{k}_{\sigma}} \delta(\omega - \omega_{\underline{k}_{\sigma}})$ is the normalized frequency spectrum of the crystal. Thus through the incoherent scattering the frequency spectrum can be directly determined.

It may be noted that the incoherent scattering is structureless as function of $\underline{k}$ and the multiphonon contributions to the coherent scattering have no strong selection rule like one phonon processes. Thus the peaks corresponding to one-phonon coherent scattering are easily distinguished against the other components and the incoherent scattering which provide more or less a structureless background.

If we ignore the incoherent scattering due to spin and/or isotopic incoherence the one-phonon scattering from the defect lattice will be given by the configuration average of the eqn. (5.8)

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{k_f}{k_i} \frac{\hbar}{\pi} \frac{1}{1 - e^{-\hbar\omega/kT}} \sum_{\substack{m,n \\ i,j}} e^{-i\underline{k}(\underline{R}^m - \underline{R}^n)} \quad (5.14)$$

$$\cdot \langle a_m e^{-M_k^m} k_i \text{Im} G_{ij}^{mn}(\omega) k_j a_n e^{-M_k^n} \rangle,$$

because now the quantities within the sign $\langle \rangle$ are fluctuating and the average has to be taken over all possible configurations of the defects. Since the thermal displacements are usually small, $e^{-M_k} \approx 1$ is a good approximation for the Debye-Waller factor. Further we assume all scattering lengths to be equal $a_m = \bar{a}$. Then the cross section is directly given by the average Green's function $\langle G(\omega) \rangle$:

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{k_f}{k_i} \frac{\hbar}{\pi} \frac{\bar{a}^2}{1 - e^{-\hbar\omega/kT}} \sum_{\substack{m,n \\ i,j}} e^{-i\underline{k}(\underline{R}^m - \underline{R}^n)} \quad (5.15)$$

$$k_i \text{Im} \langle G_{ij}^{mn}(\omega) \rangle k_j.$$

Due to the presence of defects the phonons of the crystal are perturbed and the coherent peaks are given by the poles of the average Green's function $\langle G(\omega) \rangle$. If for a particular dynamical

structure of the defect , i.e., the defect mass and the changed force constants there is a resonance mode, the frequencies and life times of phonons with frequencies near that of the resonant mode are considerably affected. Such resonant perturbation of phonons has been widely investigated experimentally as well as the theoretically in dilute alloys /34-41/ as also in crystals with interstitials /6,7,42-45/ (see also sec. 6). However also for $\underline{k}$ values away from the phonon-line $\omega = \omega_0(\underline{k})$ an appreciable intensity due to resonant modes should appear if the frequency ω nearly coincides with the resonance frequency. Schilling /47/ has recently suggested to study this "diffuse" one-phonon scattering due to the resonance modes of self-interstitials. One expects an incoherent, i.e. dispersion free, intensity which is proportional to the concentration of defects and as a function of frequency Lorentzian around the resonance frequency. We have therefore performed model calculations to study this "diffuse" one-phonon scattering due to 100-dumbbells. In the next section we will discuss the effects on the phonon-line itself.

5.2 "Diffuse" One-Phonon-Scattering due to Self-interstitials

For the case of interstitials the Green's function for the defect lattice may be expressed as

$$G = G_{RR} + G_{RC} + G_{CR} + G_{CC} \quad (5.16)$$

The scattering cross section due to first term is given by

$$\left. \frac{d^2\sigma}{d\Omega d\omega} \right)^{\text{coh}} = \frac{k_f}{k_i} \frac{k}{\pi} \frac{\bar{a}^2}{1 - e^{-\hbar\omega/kT}} \sum_{\substack{m,n \\ i,j}} e^{-i\underline{k}(\underline{R}^m - \underline{R}^n)} \frac{k_i \text{Im} \langle G_{ij}^{mn}(\omega) \rangle k_j}{k_i \text{Im} \langle G_{ij}^{mn}(\omega) \rangle k_j} \quad (5.17)$$

where $\bar{a}$ is the coherent scattering length of the host lattice. This part of the scattering is purely coherent. We recall that the $G_{RR}(\omega)$ represents the perturbed phonon field of the rest lattice (host space) in the presence of the interstitial where the defect coordinates have been formally eliminated. Both the damping and shift in the normal mode frequencies of the lattice will result. This aspect will be dealt with in the next section, for the moment we are interested in the additional scattering due to interstitial only. To this end we write the Green's function G_{RR} as (eqn. (2.42))

$$G_{RR} = \overset{\circ}{G} - \overset{\circ}{G} \tilde{T} \overset{\circ}{G} , \quad (5.18)$$

where $\tilde{T}$ is the total T-matrix of the host system. By averaging (5.18) we see that $\langle G_{RR} \rangle$ is determined by the average T-matrix, since $\overset{\circ}{G}$ is independent of the defect distribution

$$\langle G_{RR} \rangle = \overset{\circ}{G} - \overset{\circ}{G} \langle \tilde{T} \rangle \overset{\circ}{G} . \quad (5.19)$$

For a low concentration of defects when the defects are assumed to be non-interacting, the total T-matrix is approximated by sum of the individual t-matrices ($T = \sum_{\alpha} t_{\alpha}$) the average of the T-matrix can be written as

$$\langle \tilde{T} \rangle = c \sum_{\mu} \tilde{t}^{\mu} , \quad (5.20)$$

where c is the atomic concentration of defects and where sum over μ goes over all the N lattice positions which can be occupied by a defect. Thus

$$\begin{aligned}
 \langle G_{RR}^{mn}(\omega) \rangle &= \bar{G}_{ij}^{mn}(\omega) - c \sum_{\substack{m'n', \mu \\ i'j'}} \bar{G}_{ii'}^{mm'}(\omega) \tilde{t}_{i'j'}^{m'-\mu, n'-\mu} \bar{G}_{jj'}^{n'n}(\omega) \\
 &= \bar{G}_{ij}^{mn}(\omega) - cN \sum_{\substack{m'n' \\ i'j'}} \bar{G}_{ii'}^{mm'}(\omega) \tilde{t}_{i'j'}^{m'n'} \bar{G}_{jj'}^{n'n}(\omega) \\
 &= \bar{G}_{ij}^{mn}(\omega) - N_d (\bar{G} \tilde{t} \bar{G})_{ij}^{mn}, \quad (5.21)
 \end{aligned}$$

The averages of the Green's functions G_{CR} , G_{RC} and G_{CC} can be similarly evaluated, the result in the dilute limit is

$$\langle G \rangle = \bar{G} + N_d (-\bar{G} \tilde{t} \bar{G} + G_{RC} + G_{CR} + G_{CC}), \quad (5.22)$$

where $\tilde{t}$, G_{RC} etc. refer to the single defect. Eqn. (5.22) allows the separation of additional scattering due to defects which is given by

$$\begin{aligned}
 \left(\frac{d^2 \sigma}{d\Omega d\omega} \right)^1 &= \frac{k_f}{k_i} \frac{\hbar}{\pi} \frac{\bar{a}^2 N_d}{1 - e^{-\hbar\omega/kT}} \sum_{\substack{m'n' \\ i'j'}} e^{-i\mathbf{k}(\mathbf{R}^m - \mathbf{R}^n)} \\
 &\cdot \text{Im} (-\bar{G} \tilde{t} \bar{G} + G_{RC} + G_{CR} + G_{CC}) K_i K_j. \quad (5.23)
 \end{aligned}$$

Carrying out the Fourier transform we obtain

$$\begin{aligned}
 \left(\frac{d^2 \sigma}{d\Omega d\omega} \right)^1 &= \frac{k_f}{k_i} \frac{\hbar}{\pi} \frac{N_d \bar{a}^2}{1 - e^{-\hbar\omega/kT}} \sum_{\sigma\sigma'} (\mathbf{k} \cdot \underline{\mathbf{e}}(\mathbf{k}\sigma)) (\mathbf{k} \cdot \underline{\mathbf{e}}(\mathbf{k}\sigma')) \\
 &\cdot \text{Im} \left[- \frac{1}{M(\omega_{\mathbf{k}\sigma}^2 - (\omega + i\epsilon)^2)} \tilde{t}^{\sigma\sigma'}(\mathbf{k}, \omega) \frac{1}{M(\omega_{\mathbf{k}\sigma'}^2 - (\omega + i\epsilon)^2)} \right. \\
 &- \frac{1}{M(\omega_{\mathbf{k}\sigma}^2 - (\omega + i\epsilon)^2)} \tilde{G}_{RC}^{\sigma\sigma'}(\mathbf{k}, \omega) - \frac{1}{M(\omega_{\mathbf{k}\sigma'}^2 - (\omega + i\epsilon)^2)} \tilde{G}_{CR}^{\sigma\sigma'}(\mathbf{k}, \omega) \\
 &\left. + \tilde{G}_{CC}^{\sigma\sigma'}(\mathbf{k}, \omega) \right], \quad (5.24)
 \end{aligned}$$

where

$$\begin{aligned}\tilde{t}^{\sigma\sigma'}(\underline{k}, \omega) &= \sum_{\substack{mn \\ ij}} e_i(\underline{k}\sigma) e^{-i\underline{k}\underline{R}^m} \tilde{t}_{ij}^{mn}(\omega) e^{i\underline{k}\underline{R}^n} e_j(\underline{k}\sigma') \\ \tilde{G}_{RC}^{\sigma\sigma'}(\underline{k}, \omega) &= \sum_{\substack{mn \\ ij}} e_i(\underline{k}\sigma) e^{-i\underline{k}\underline{R}^m} \{\phi_{RC} G_{CC} - \hat{t}^0 \phi_{RC} G_{CC}\}_{ij}^{mn} e^{i\underline{k}\underline{R}^n} e_j(\underline{k}\sigma') \\ \tilde{G}_{CR}^{\sigma\sigma'}(\underline{k}, \omega) &= \sum_{\substack{mn \\ ij}} e_i(\underline{k}\sigma) e^{-i\underline{k}\underline{R}^m} \{G_{CC} \phi_{CR} - G_{CC} \phi_{CR} \hat{t}^0\}_{ij}^{mn} e^{i\underline{k}\underline{R}^n} e_j(\underline{k}\sigma') \\ \tilde{G}_{CC}^{\sigma\sigma'}(\underline{k}, \omega) &= \sum_{\substack{mn \\ ij}} e_i(\underline{k}\sigma) e^{-i\underline{k}\underline{R}^m} G_{CCij}^{mn}(\omega) e^{i\underline{k}\underline{R}^n} e_j(\underline{k}\sigma') \quad (5.25)\end{aligned}$$

Here eqns. (2.37), (2.39) for G_{RC} , G_{CR} and G_{RR} have been used.

For high symmetry directions (100), (110) and (111) and away from the phonon line ($\omega \neq \omega_{\underline{k}\sigma}$) the additional scattering can thus be written as

$$\begin{aligned}\left(\frac{d^2\sigma}{d\omega d\omega}\right)^1 &= \frac{k_f}{k_i} \frac{\hbar}{\pi} \frac{\bar{a}^2}{1 - e^{-\hbar\omega/kT}} N_d \sum |\underline{k} \cdot \underline{e}(\underline{k}\sigma)|^2 \\ &\quad \cdot \left[-\frac{1}{M^2 (\omega_{\underline{k}\sigma}^2 - \omega^2)^2} \text{Im} \tilde{t}^{\sigma}(\underline{k}, \omega) \right. \\ &\quad \left. - \frac{1}{M (\omega_{\underline{k}\sigma}^2 - \omega^2)} \text{Im} (\tilde{G}_{RC}^{\sigma}(\underline{k}, \omega) + \tilde{G}_{CR}^{\sigma}(\underline{k}, \omega)) \right. \\ &\quad \left. + \text{Im} \tilde{G}_{CC}^{\sigma}(\underline{k}, \omega) \right]. \quad (5.26)\end{aligned}$$

The first term containing $\text{Im} \tilde{t}^{\sigma}(\underline{k}, \omega)$ gives the contribution of the host lattice system and is evidently the additional scattering due to the interstitial reaction to the host system. The last term represents the contribution of the interstitial atoms while the second term (mixed terms) results from the coupling of the interstitial atoms and lattice system. It is noted that the first term in eqn. (5.26) diverges for $\omega^2 = \omega_{\underline{k}\sigma}^2$. Thus the present theory is only valid away from the one-phonon line, i.e., if $|\omega^2 - \omega_{\underline{k}\sigma}^2| \gg \tilde{\omega}_{\sigma}^2(\underline{k}, \omega)$. Near the one-phonon line one has to sum up the "most

diverging" terms leading to a low-concentration approximation for the self energy which is discussed in section 6.1.

5.3 Model Calculation for 100-Dumbbell

We have calculated the additional scattering of neutrons due to 100-dumbbells in Cu with the defect model described in section 3. With this model the calculation has been performed for the three major symmetry directions using expression (5.26) considering only the energy gain processes for neutron. At first the temperature factor has been ignored and then it has been calculated at 25° K. The neutron scattering intensity to be plotted (figs. 5-18) corresponds to the quantity within bracket in (5.26) and is in units of 10^{-24} . To obtain the intensity in units of the atomic scattering cross section one has to multiply the plotted intensity by a factor $\frac{h}{4\pi^3 M} |\underline{K} \cdot \underline{e}(\underline{K}\sigma)|^2$.

(a) (K,0,0)

We present the neutron scattering intensity as function of frequency for the longitudinal mode $\underline{K} = (0.4, 0, 0) - \underline{e} = (100)$ in fig. 5 and for the transverse modes $(0.4, 0, 0) - (010)$ and $(0.8, 0, 0) - (010)$ in fig. 6 and 7 where the temperature factor $\{n(\omega) = (e^{h\omega/kT} - 1)^{-1}\}$ has not been included. In the case of transverse polarization (figs. 6,7) we observe well defined peaks at frequencies which correspond to the familiar E_u , A_{2u} and E_u resonant modes as obtained in the local spectrum of the dumbbell whereas in the case of longitudinal polarization (fig. 5) we get only two peaks corresponding to A_{2u} and E_u resonant modes. This shows that the librational mode E_g does not couple to the

longitudinal polarization while all the three modes E_u , A_{2u} and E_u couple to the transverse polarizations. It is seen that the intensity in the case of the longitudinal mode is very small as compared with the transverse case. Further figs. 6 - 7 show that the intensity of the E_g -peak is high compared to the A_{2u} and E_u modes. This shows that the E_g mode couples much more strongly than the others which is not hard to see in view of the fact that the A_{2u} and E_u modes correspond to translational motions of the dumbbell.

In figs. 8, 9, the intensity at 25° K is presented for $(0,4,0,0) - (010)$ and $(0.8,0,0) - (010)$. It may be seen that the intensity of the peaks is considerably reduced due to the thermal factor $n(\omega)$, for instance, the peak intensity corresponding to the E_g mode is reduced by a factor of $\sqrt{\frac{1}{6}}$. Naturally this reduction in intensity is more severe in the case of A_2 and E_u so that at 25° K only the E_g peak remains while the peak corresponding to A_{2u} remains in the form of a hump in fig. 9 and the peak due to E_u mode is almost absent.

(b) $(K,K,0)$

For this direction the intensity only for the transverse polarizations is presented as the intensity for the longitudinal polarization is comparatively small. The neutron scattering intensity is depicted for the (-110) polarization with $\underline{K} = (0.5, 0.5, 0)$ in fig. 10 while for the (001) polarization it is plotted in figs. 11, 12 for $\underline{K} = (0.4, 0.4, 0)$ and $(0.8, 0.8, 0)$, respectively. Again the temperature factor has been ignored. It is observed that the E_g mode does not couple with the (-110) polarization (fig. 10) while all the three modes couple with the

(001) polarization. The intensity at 25° K is presented in figs. 13, 14 for (001) polarization with $\underline{K} = (0.4, 0.4, 0)$ and $\underline{K} = (0.8, 0.8, 0)$, respectively. The peak due to E_g mode remains while the peak due to A_{2u} has negligible intensity and the E_u mode is practically absent.

(c) (K,K,K)

Again ignoring the temperature factor $n(\omega)$ the scattering intensity for the longitudinal polarization with $K = 0.5$ is given in fig. 15 while for the transverse case with $K = 0.5$, $\underline{e} = (-110)$ it is plotted in fig. 16, while only E_g mode is present in the case of longitudinal polarization, all the three modes couple the transverse modes. Contrary to (K00) and (KK0) in (KKK) the peak corresponding to the A_{2u} mode has more intensity than the E_g -peak (fig. 16). In fig. 17 we plot the intensity at 25° K for $K = 0.5$, $\underline{e} = (-110)$. The intensity of the A_{2u} mode is comparable to the E_g -peak in this case.

To see the K-dependence of the intensity we plot the intensity of the E_g -mode for the transverse polarization in all the three directions. Fig. 18, shows the K-dependence of the E_g -peak intensity of (K00)-(010), (KK0)-(001) and (KKK)-(-110), respectively. In order to see the relative contribution of different terms in expression (5.26), table I shows the total scattering, the contributions due to the lattice system, due to mixed terms and due to the interstitial space for different K-values in the case of (K00)-(010). It is observed that the peak intensity increases at small K-values but at higher K-values the variation is slow (fig. 18). From the table I we see

that the contributions from the host space and the mixed terms decrease with increasing K while the contribution from the interstitial space increases so that near the boundary of the Brillouin zone almost all the intensity comes from the interstitial space. That the contribution of the interstitial space is maximum at the boundary of BZ is evident if we notice that for E_g -mode $G^{\underline{d}\underline{d}}(\omega) = -G^{\underline{d}\bar{\underline{d}}}(\omega)$ and at the boundary in (K00) direction $\cos(\underline{K} \cdot (\underline{d} - \bar{\underline{d}})) = -1$ (dumbbell axis in x-direction) so that the contribution from the impurity term is $4G^{\underline{d}\underline{d}}(\omega)$ i.e. maximum. We hope that this "diffuse" one-phonon scattering due to interstitials can be experimentally observed /48/.

6. Effect of Di-interstitials on Phonon Dispersion Curve

The effect of dumbbell interstitials on the phonon dispersion curves of Cu and Al have been studied by Wood and Mostoller /6/ and Schober, Tewary and Dederichs /7/, respectively. These authors have predicted a resonant perturbation of (100) transverse phonons in these metals. However very detailed neutron scattering experiments of two groups are not conclusive: Nicklow et. al. /42,43/ have studied phonon dispersion in Cu after (n, γ) irradiation. They find a resonant like shift of the (100) T phonon line centered at $\underline{k} = \frac{2\pi}{a}(0.1,0,0)$. However in addition to the shift they see a strong structure in the phonon line, especially a shoulder at higher frequencies which also remains after annealing up to room temperatures. The origine of this peak, presumably due to intersitital type dislocation loops, is not understood. Nevertheless the measured shift of the phonon line, especially its annealing behaviour, shows the features as expected for a resonance mode. Böning et. al. /44,45/ has measured the dispersion in Al after neutron irradiation. Contary to the results in Cu, no resonance behaviour is found. Also here the interpretation of the measurements is not clear. One possible (and in our opinion the most likely) explanation results from the different irradiation conditions: After neutron irradiation, one expects in Al only a rather small percentage of single interstitials and large admixtures of small aggregates (di-interstitials, tri-interstitials, etc.). While all such multiple interstitials show a similar softening of the elastic constants /46/, they should have quite different resonant modes and frequencies so that the strong frequency dependence of the shift in resonant frequency could be wiped out for a mixture

of multiple interstitials. To illustrate this point we have therefore calculated the effects of di-interstitials on the phonon dispersion.

As pointed out in the last section the phonons in the defect crystal are given by poles of the Fourier transform of the average Green's function $\langle G(\omega) \rangle$. For the calculation of the average Green's function it is convenient to introduce an effective change $\Sigma(\omega)$ of the coupling matrix of the ideal lattice,

$$\langle G(\omega) \rangle = \frac{1}{\delta + \Sigma(\omega) - M\omega^2} = \overset{\circ}{G}(\omega) - \overset{\circ}{G}(\omega) \Sigma(\omega) \langle G(\omega) \rangle. \quad (6.1)$$

Averaging restores the translational invariance of the crystal and consequently $\langle G(\omega) \rangle$ or $\Sigma(\omega)$ has all the symmetries of the lattice. Thus the eigenfunctions of $\delta + \Sigma$ may be taken to be plane waves and the problem for the defect crystal is reduced to that of an ideal lattice. The remaining problem is the determination of the so called "self energy" $\Sigma(\omega)$.

The average Green's function $\langle G \rangle$ may be also given by (see eqn. (2.30))

$$\langle G(\omega) \rangle = \overset{\circ}{G}(\omega) - \overset{\circ}{G}(\omega) \langle T(\omega) \rangle \overset{\circ}{G}(\omega). \quad (6.2)$$

Comparing (6.1) and (6.2) we get

$$\langle T \rangle \overset{\circ}{G} = \Sigma \langle G \rangle = \Sigma (\overset{\circ}{G} - \overset{\circ}{G} \langle T \rangle \overset{\circ}{G}). \quad (6.3)$$

Solving for Σ we obtain

$$\Sigma(\omega) = \langle T(\omega) \rangle \frac{1}{1 - \overset{0}{G}(\omega) \langle T(\omega) \rangle} \quad (6.4)$$

The self energy is frequency dependent and complex giving rise to damping. Similar to $\overset{0}{\phi}$, $\Sigma(\omega)$ has the periodicity of the lattice and is a symmetrical matrix

$$\sum_{ij}^{mn} = \sum_{ij}^{m-n} = \sum_{ji}^{nm} \quad (6.5)$$

Thus the Fourier transform $\langle G(\omega) \rangle$ exists

$$\langle G \rangle(\underline{k}, \omega) = [\overset{0}{\phi}(\underline{k}) + \Sigma(\underline{k}, \omega) - \overset{0}{M}\omega^2]^{-1} \quad (6.6)$$

For high symmetry directions (100), (110) and (111) the polarization vectors $\underline{e}$ are determined by symmetry alone being independent of $|\underline{k}|$ and ω and the same as in the ideal lattice. That is

$$\langle G \rangle(\underline{k}, \omega) = \sum_{\sigma} |\underline{e}(\underline{k}\sigma)|^2 \langle G \rangle^{\sigma}(\underline{k}, \omega) \quad (6.7)$$

with

$$\langle G \rangle^{\sigma}(\underline{k}, \omega) = [\overset{0}{M} \omega_{\underline{k}\sigma}^2 + \Sigma^{\sigma}(\underline{k}, \omega) - \overset{0}{M}\omega^2]^{-1}.$$

In order to obtain an approximation for Σ in the dilute limit of small concentrations we use the approximation (5.30) for $\langle T \rangle$ in (6.3)

$$\begin{aligned} \Sigma &= c \sum_{\mu} t^{\mu} \frac{1}{1 - \overset{0}{G} c \sum_{\mu} t^{\mu}} \\ &= c \sum_{\mu} t^{\mu} + c^2 \{ \quad \} + \dots \\ &\cong c \sum_{\mu} t^{\mu} = N_d \langle t \rangle \quad \text{with} \quad \langle t \rangle = \frac{1}{N} \sum_{\mu=1}^N t^{\mu}. \end{aligned} \quad (6.8)$$

For the Fourier component $\Sigma^{\sigma}(\underline{k}, \omega)$ of the self energy we have in the dilute limit

$$\begin{aligned}
 \Sigma^{\sigma}(\underline{k}, \omega) &= c \sum_{mij} e^{-i\underline{k}(\underline{R}^m - \underline{R}^n)} \sum_{\mu} e_i(\underline{k}\sigma) t_{ij}^{m-\mu, n-\mu} e_j(\underline{k}\sigma) \\
 &= c \sum_{mn} e^{-i\underline{k}\underline{R}^m} e_i(\underline{k}\sigma) t_{ij}^{mn} e_j(\underline{k}\sigma) e^{i\underline{k}\underline{R}^n} \\
 &= c t^{\sigma}(\underline{k}, \omega) .
 \end{aligned} \tag{6.9}$$

The coherent one phonon cross section in terms of $\langle G \rangle^{\sigma}(\underline{k}, \omega)$ is

$$\begin{aligned}
 \frac{d^2\sigma}{d\Omega d\omega} &= \frac{k_f}{k_i} \frac{\hbar}{\pi} \frac{\bar{a}^2 N}{1 - e^{-\hbar\omega/kT}} \sum_{\sigma} |\underline{k} \cdot \underline{e}(\underline{k}\sigma)|^2 \text{Im} \langle G \rangle^{\sigma}(\underline{k}, \omega) \\
 &= \frac{k_f}{k_i} \frac{\hbar}{\pi} \frac{N \bar{a}^2}{1 - e^{-\hbar\omega/kT}} \sum_{\sigma} |\underline{k} \cdot \underline{e}(\underline{k}\sigma)|^2 \\
 &\quad - \Sigma_2^{\sigma}(\underline{k}, \omega)
 \end{aligned} \tag{6.10}$$

where

$$\Sigma = \Sigma_1 + i \Sigma_2 .$$

For the ideal lattice we get only intensity at $\omega^2 = \omega_{\underline{k}\sigma}^2$, in the defect crystal also the major intensity is expected near these ideal phonon lines and we put

$$\Sigma^{\sigma}(\underline{k}, \omega) = \Sigma^{\sigma}(\underline{k}, \omega_{\underline{k}\sigma}^0) . \tag{6.12}$$

Thus the ideal phonons given by

$$\sim \delta(\omega_{\underline{k}\sigma}^2 - \omega^2) \quad \text{or} \quad \omega = \omega_{\underline{k}\sigma}^0$$

are replaced by Lorentzian lines

$$\frac{-\Sigma_2^{\sigma}(\underline{k}, \omega)}{(\bar{M} \omega_{\underline{k}\sigma}^2 + \Sigma_1^{\sigma}(\underline{k}, \omega_{\underline{k}\sigma}^0) - \bar{M} \omega^2)^2 + (\Sigma_2^{\sigma}(\underline{k}, \omega_{\underline{k}\sigma}^0))^2} \tag{6.13}$$

Evidently for a low concentration of defects the shift in the phonon frequencies is given by

$$\dot{M}(\omega^2 - \omega_{\underline{k}\sigma}^2) = \sum_1^{\sigma} \quad \text{or} \quad \Delta\omega_{\underline{k}\sigma} = \frac{C}{2\dot{M}\omega_{\underline{k}\sigma}^2} t_1^{\sigma}(\underline{k}, \omega_{\underline{k}\sigma}) \quad (6.14)$$

and phonon width by

$$\gamma_{\underline{k}\sigma} = -\frac{1}{2\dot{M}\omega_{\underline{k}\sigma}^2} \sum_2^{\sigma} = -\frac{C}{2\dot{M}\omega_{\underline{k}\sigma}^2} t_2^{\sigma}(\underline{k}, \omega_{\underline{k}\sigma}) \quad (6.15)$$

6.2 Model for Di-interstitials in Al

The most stable di-interstitial in fcc consists of two parallel (100) dumbbells on nearest neighbour sites /46/. A nearest neighbour model for the interstitial-host interaction is considered. The defect is described by two vacancies at (0,0,0) and (1,1,0) and four interstitial atoms at (0,0,d), (1,1,d) (0,0,-d) and (1,1,-d). The defect space consists of the four interstitial atoms whereas the host space N consists of 20 atoms, i.e., two vacancies and their nearest neighbour lattice atoms.

The coupling parameters are given by a spiral spring $f_{\parallel}^1$ and a leaf spring $f_{\perp}^1$ between the dumbbell atoms of the same dumbbell, by spiral and leaf springs $f_{\parallel}^2$ and $f_{\perp}^2$ between the nearest dumbbell atoms of different dumbbells and by springs $f_{\parallel}^3$ and $f_{\perp}^3$ between a dumbbell atom and its nearest neighbours. The vacancies are described by zero coupling to their neighbours. We use the following force constants obtained in computer simulation by Zeller /27/ for a Morse potential.

$$\begin{aligned}
 f_{\parallel}^1 &= 7.0681 f_{\parallel}^0 & f_{\perp}^1 &= -0.8751 f_{\parallel}^0 \\
 f_{\parallel}^2 &= 1.2809 f_{\parallel}^0 & f_{\perp}^2 &= -0.0982 f_{\parallel}^0 \\
 f_{\parallel}^3 &= 4.8577 f_{\parallel}^0 & f_{\perp}^3 &= -0.0763 f_{\parallel}^0
 \end{aligned} \tag{6.16}$$

To restore the rotational invariance of the lattice additional leaf springs equal to $-0.24859 f_{\parallel}^0$ between certain neighbours has been introduced. Like the single interstitial the distance between the dumbbell atoms is set as $2d = 0.5 a$. The ideal force constants for Al were taken from Nicklow et al /49/. The ideal lattice Green's functions are calculated with the modified Gilat-Raubenheimer method.

6.3 Shift in transverse (100) phonon

For a statistical distribution of the three dumbbell directions the frequency shift for the transverse (100) phonons is calculated using expression (6.14) where $t^{\sigma}(\underline{k}, \omega)$ is replaced by $\tilde{t}^{\sigma}(\underline{k}, \omega)$ referring to the t-matrix $\tilde{t}$ of eq. (2.42) for the interstitial case which itself is averaged over the dumbbell directions i.e.

$$\tilde{t}^{\sigma}(\underline{k}, \omega) = \frac{1}{3} \sum_i \tilde{t}_i^{\sigma}(\underline{k}, \omega) \tag{6.17}$$

The calculated result with a concentration $c = 8.10 \times 10^{-4}$ is presented in fig. 19 along with the shift caused by single dumbbells calculated earlier by Schober et al /7/. The experimental result from Böning et al /44/ is also presented along with the calculated results taking a ratio of 3 to 1 between single and di-interstitials (fig. 19 c). The calculated result for the di-interstitial gives a sharp resonance near $\zeta = 0.1$

compared to the single interstitial resonance at $\tau = 0.16$. The calculated local frequency spectrum (not shown here) of the di-interstitial shows a sharp resonance peak at $\nu = 0.86$ THz. This resonance has B_{2g} symmetry and is thought to be a composition of the E_u and A_{2u} modes of the single dumbbell /46/. Fig. 3c should demonstrate what effects can occur for a mixture of small interstitial agglomerates as e.g. present after neutron-irradiation. Each agglomerate will show slightly different resonance frequencies which are presumably somewhat higher for the larger agglomerates. Due to the averaging over the different agglomerates the resulting frequency shift $\Delta\omega(\underline{K})$ may well be rather structureless as has been found experimentally /44,45/. While our present calculations for the single and di-interstitial do certainly not prove that this is the case, they nevertheless demonstrate that such an interpretation of the experimental results cannot be excluded.

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Table I:

Peak intensity in E_g mode for (K00) - (010) mode

K	Intensity			
	Total	Lattice term	Mixed terms	Impurity term
0.2	7.030	2.140	4.69	0.206
0.3	3.893	0.367	3.185	0.341
0.4	3.313	0.149	2.653	0.511
0.5	3.026	0.083	2.244	0.699
0.6	2.779	0.055	1.837	0.887
0.7	2.501	0.040	1.404	1.057
0.8	2.164	0.031	0.941	1.192
0.9	1.760	0.028	0.454	1.278
1.0	1.289	0.026	-0.045	1.308

Figure Caption

- Fig. 1: 100-dumbbell configuration in fcc
- Fig. 2: Local density of states of 100-dumbbell
(--- = spectrum of ideal lattice)
- Fig. 3: Generalized phase shift $\theta(\omega)$ (π times integrated density of states)
- Fig. 4: Temperature dependence of relative change $\Delta C_V(T)/c C_V(T)$ of the specific heat due to a concentration c of 100-dumbbells
- Fig. 5: Scattering intensity for $\underline{K} = (0,4,0,0)$, $\underline{e} = (100)$ without temperature factor. ($\underline{K}$ is in units of $2\pi/a$)
- Fig. 6: Scattering intensity for $\underline{K} = (0,4,0,0)$, $\underline{e} = (0,1,0)$; without temperature factor. ($\underline{K}$ is in units of $2\pi/a$)
- Fig. 7: Scattering intensity for $\underline{K} = (0.8,0,0)$, $\underline{e} = (0,1,0)$; without temperature factor. ($\underline{K}$ is in units of $2\pi/a$)
- Fig. 8: Scattering intensity for $\underline{K} = (0,4,0,0)$, $\underline{e} = (0,1,0)$; at 25° K. ($\underline{K}$ is in units of $2\pi/a$)
- Fig. 9: Scattering intensity for $\underline{K} = (0,8,0,0)$, $\underline{e} = (0,1,0)$; at 25° K. ($\underline{K}$ is in units of $2\pi/a$)
- Fig.10: Scattering intensity for $\underline{K} = (0.5,0.5,0)$, $\underline{e} = (-1,1,0)$; without temperature factor. ($\underline{K}$ is in units of $2\pi/a$)
- Fig.11: Scattering intensity for $\underline{K} = (0.4,0.4,0)$, $\underline{e} = (0,0,1)$; without temperature factor. ($\underline{K}$ is in units of $2\pi/a$)

Fig. 12: Scattering intensity for $\underline{K} = (0.8, 0.8, 0)$, $\underline{e} = (0, 0, 1)$; without temperature factor. ($\underline{K}$ is in units of $2\pi/a$)

Fig. 13: Scattering intensity for $\underline{K} = (0.4, 0.4, 0)$, $\underline{e} = (0, 0, 1)$; at 25° K. ($\underline{K}$ is in units of $2\pi/a$)

Fig. 14: Scattering intensity for $\underline{K} = (0.8, 0.8, 0)$, $\underline{e} = (0, 0, 1)$; at 25° K. ($\underline{K}$ is in units of $2\pi/a$)

Fig. 15: Scattering intensity for $\underline{K} = (0.5, 0.5, 0.5)$, $\underline{e} = (1, 1, 1)$; without temperature factor. ($\underline{K}$ is in units of $2\pi/a$)

Fig. 16: Scattering intensity for $\underline{K} = (0.5, 0.5, 0.5)$, $\underline{e} = (-1, 1, 0)$; without temperature factor. ($\underline{K}$ is in units of $2\pi/a$)

Fig. 17: Scattering intensity for $\underline{K} = (0.5, 0.5, 0.5)$, $\underline{e} = (-1, 1, 0)$; at 25° K. ($\underline{K}$ is in units of $2\pi/a$)

Fig. 18: Peak intensity in the E_g -mode for
 (a) $(K, 0, 0)$; $\underline{e} = (0, 1, 0)$
 (b) $(K, K, 0)$; $\underline{e} = (0, 0, 1)$
 (c) (K, K, K) ; $\underline{e} = (-1, 1, 0)$

Fig. 19: Shift of the (100) transverse phonon
 (a) due to single-interstitial
 (b) due to di-interstitials
 (c) due to a mixture of 75 % single intersititals
 and 25 % di-interstitials
 along with the experimental results /44,45/
 $\underline{K} = \frac{2\pi}{a}(\zeta, 0, 0)$

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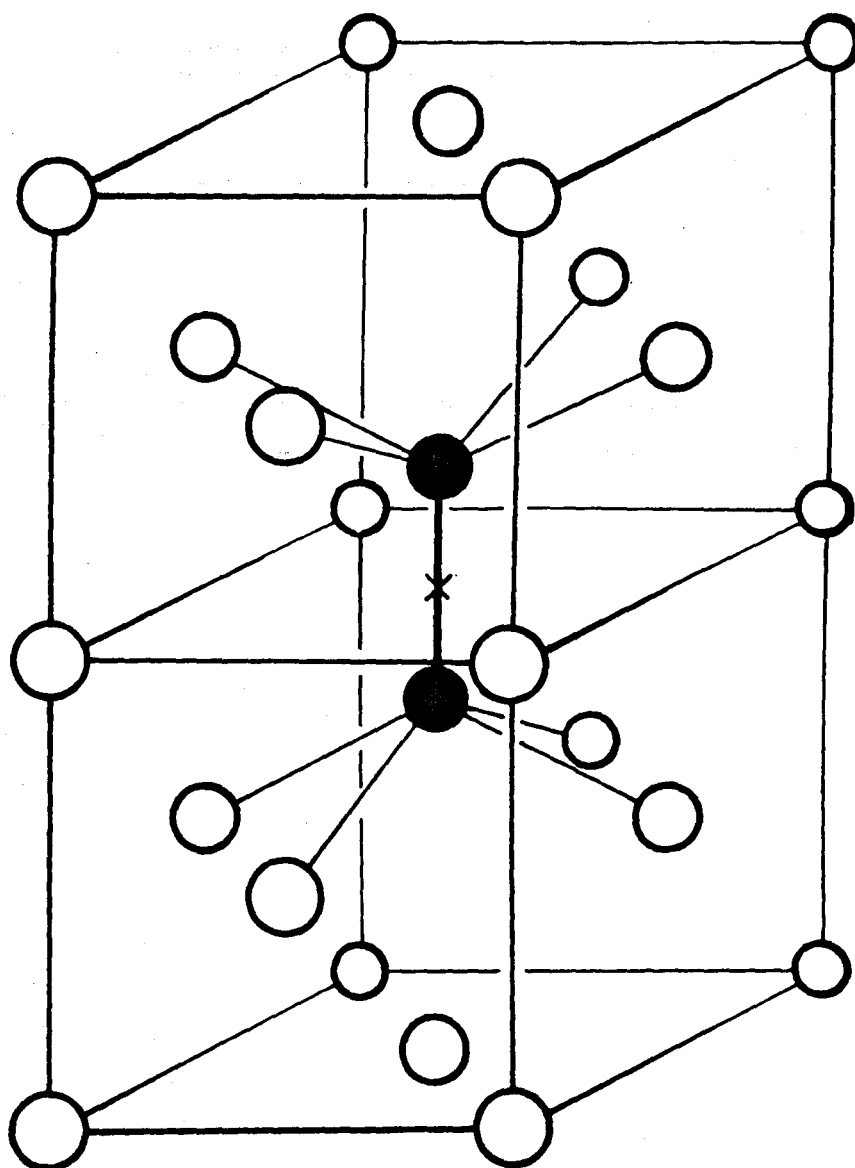


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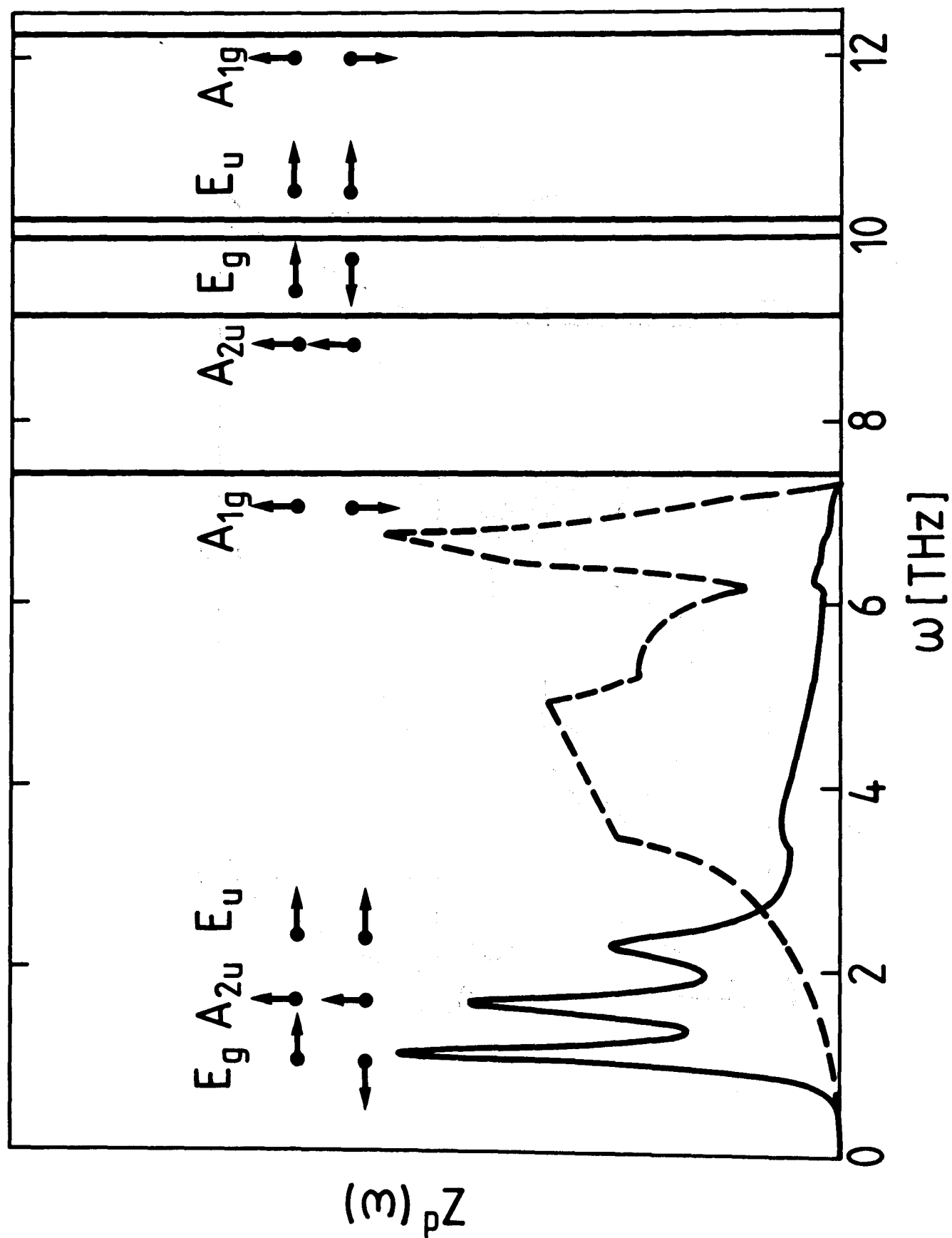


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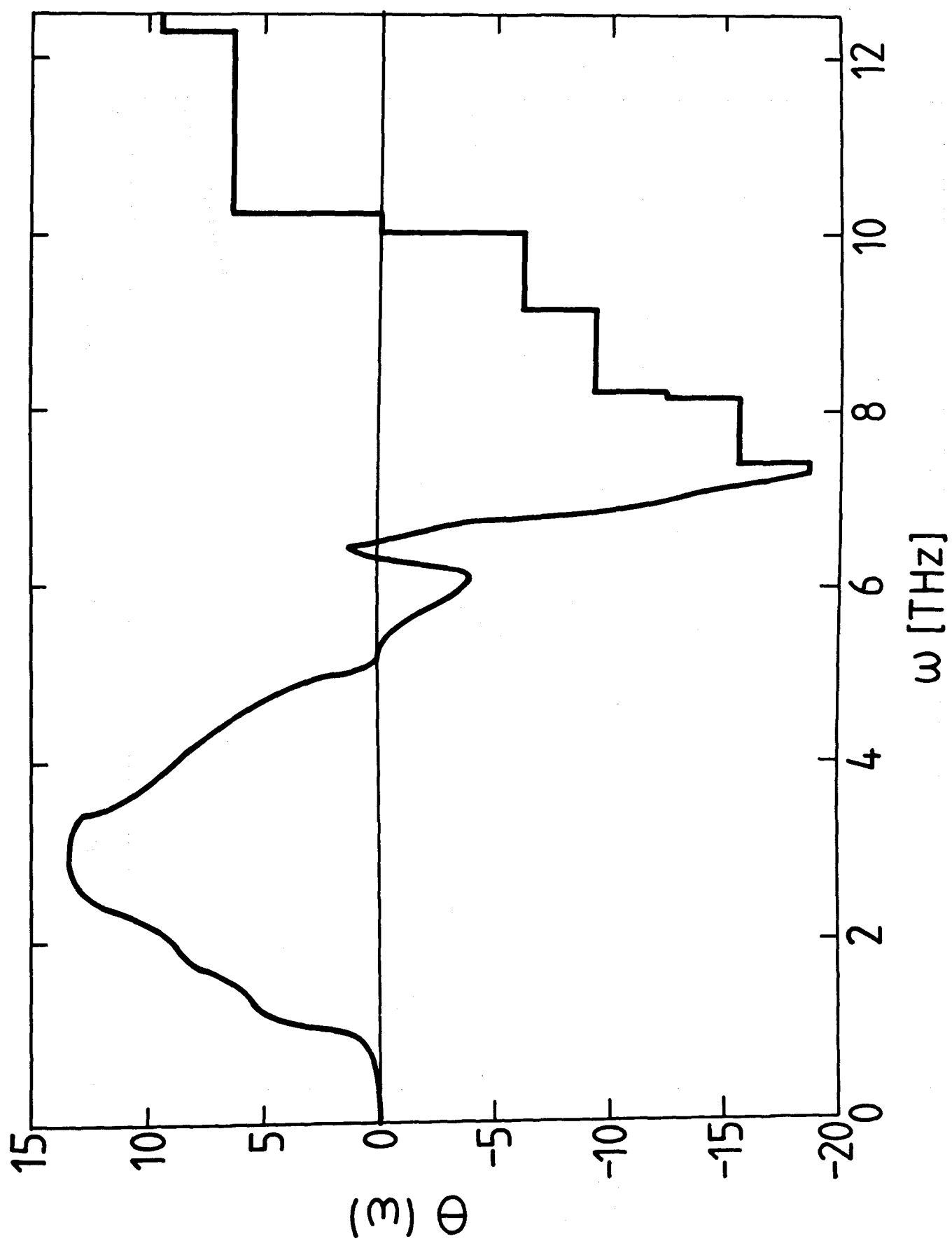


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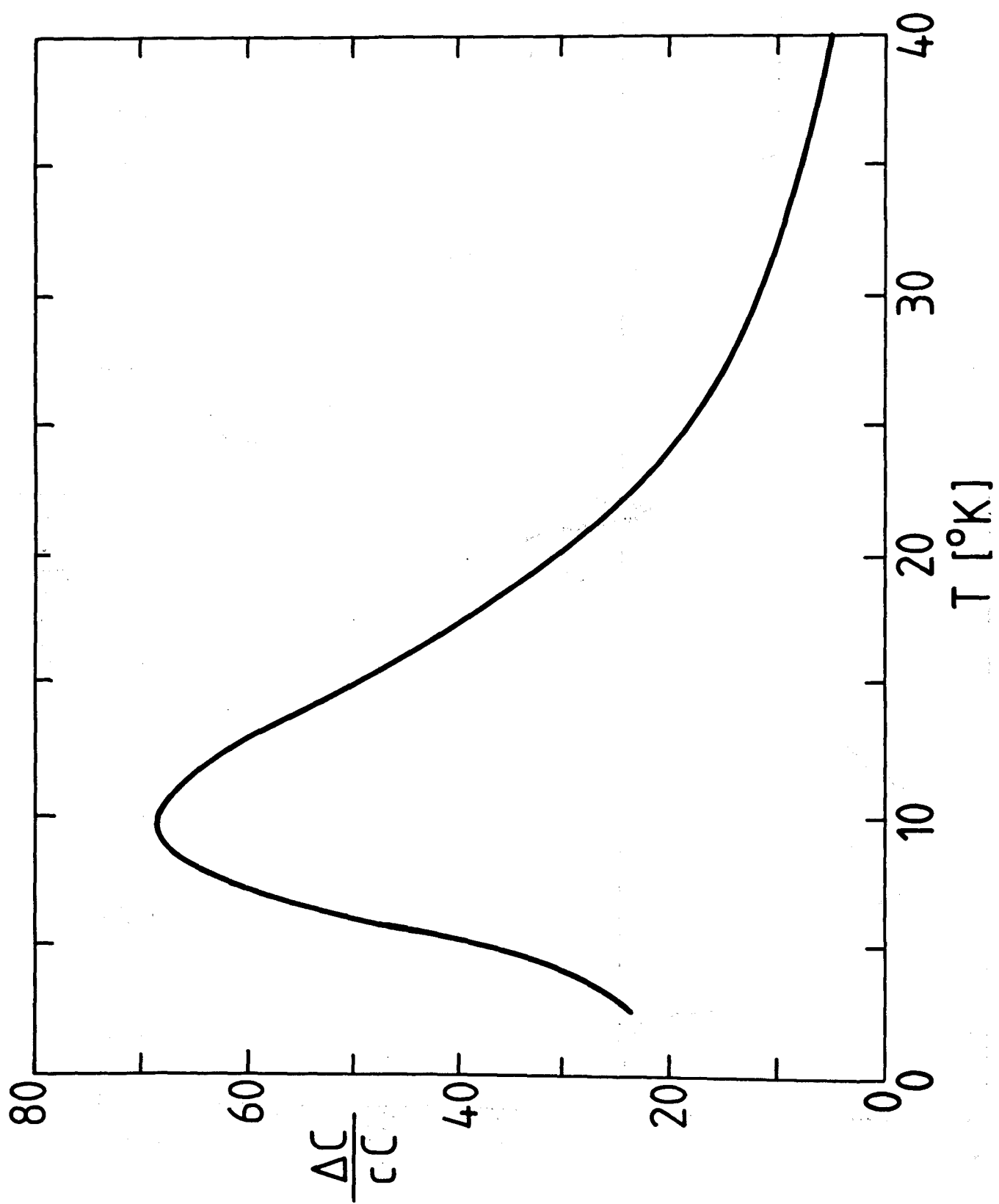


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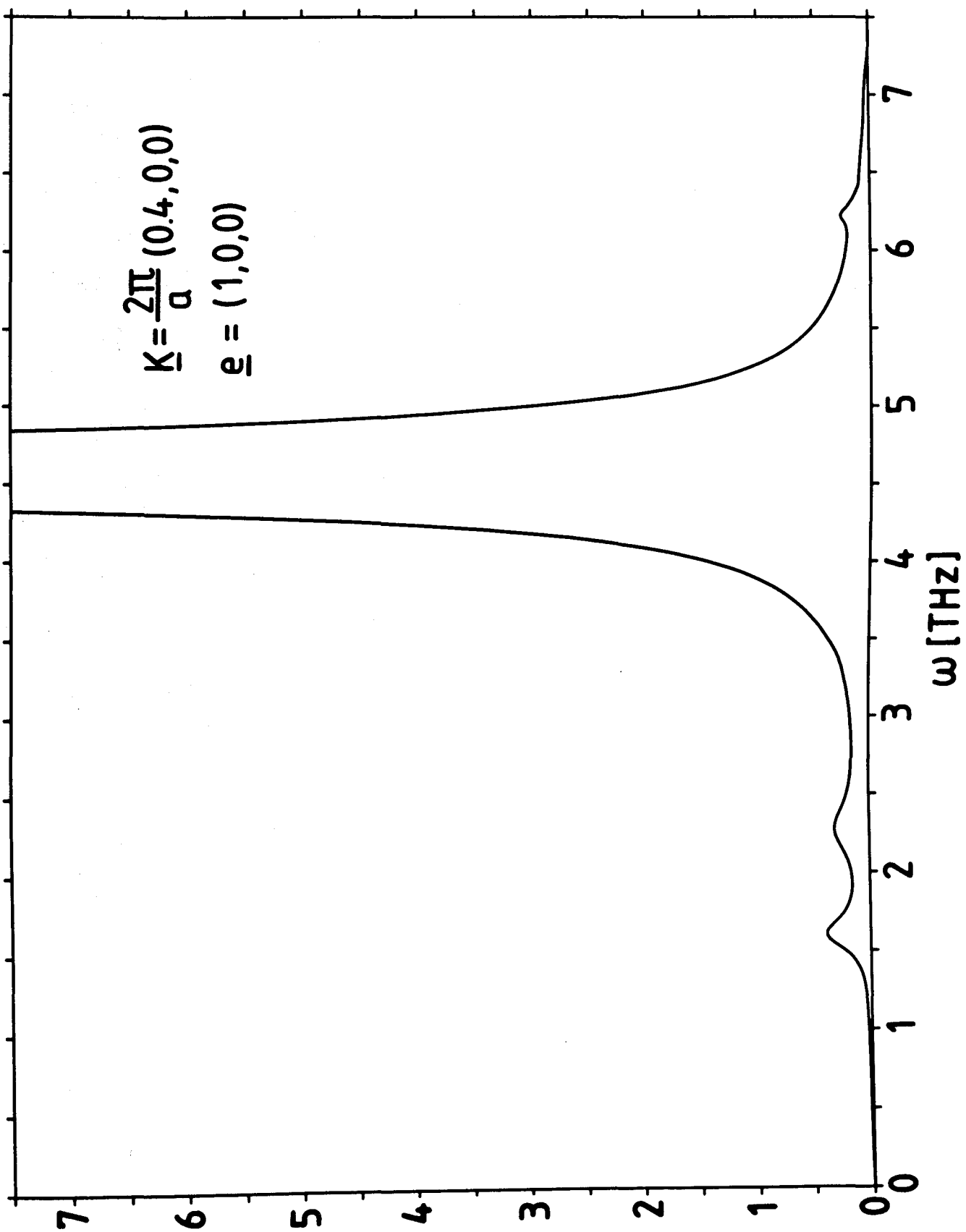


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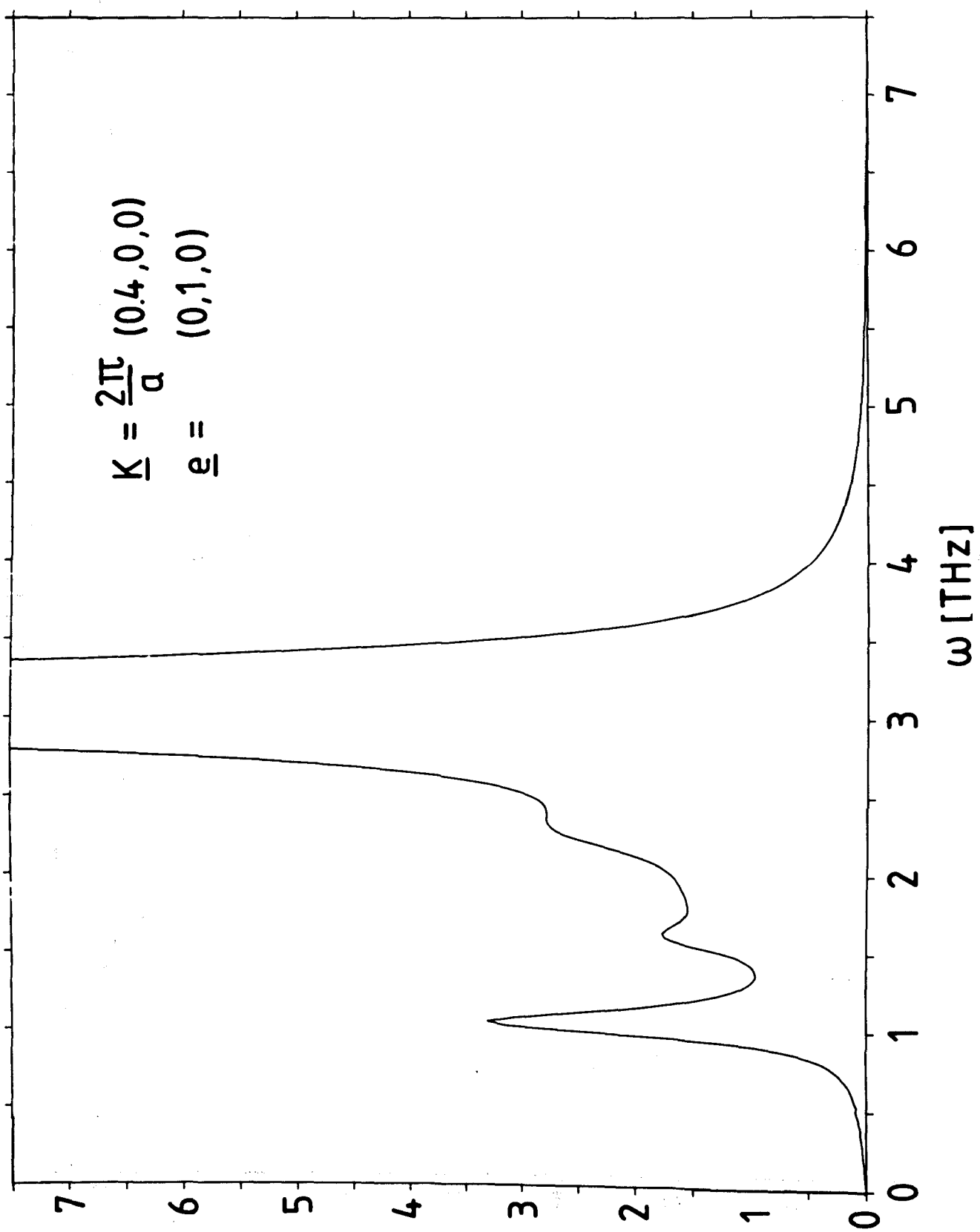


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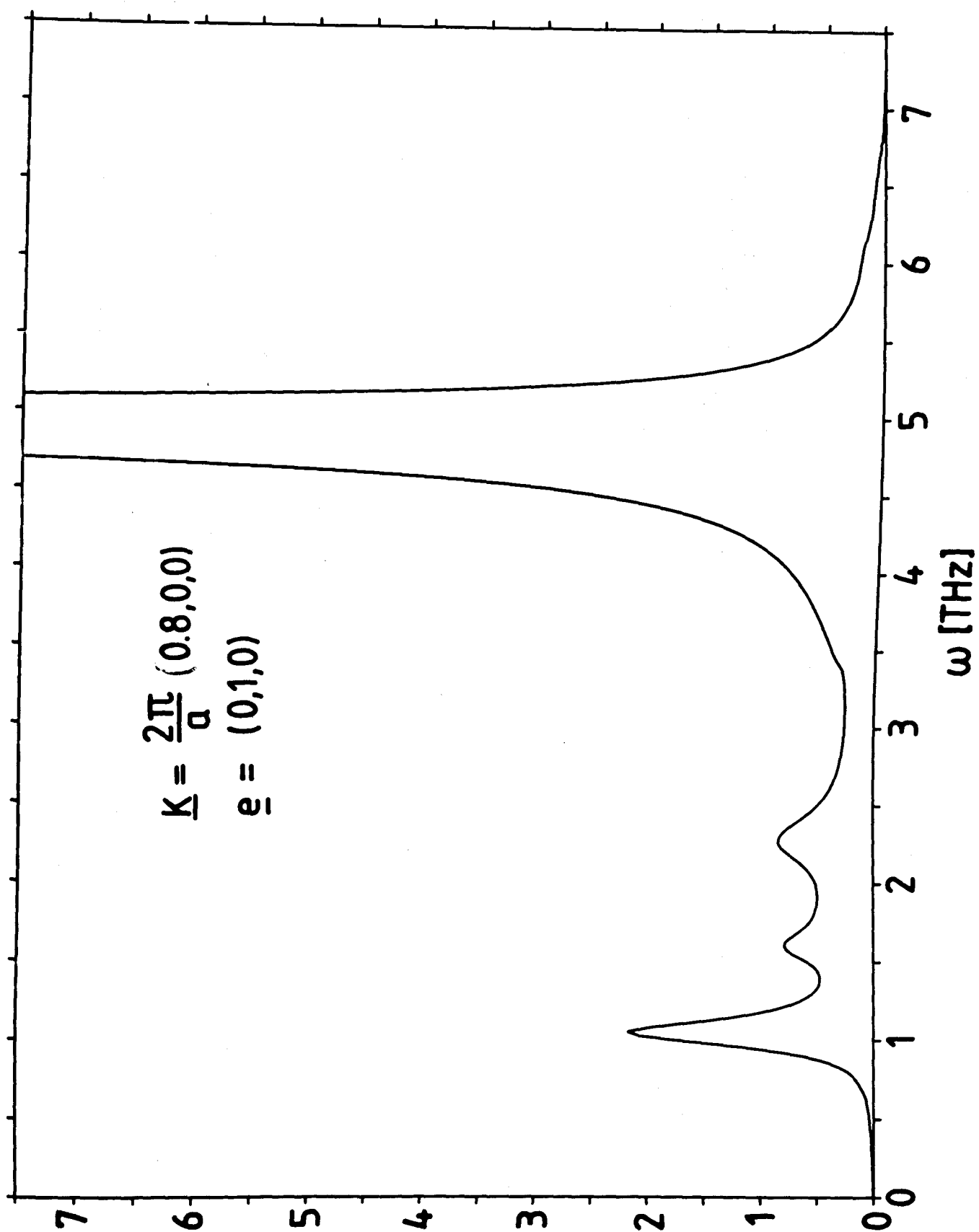


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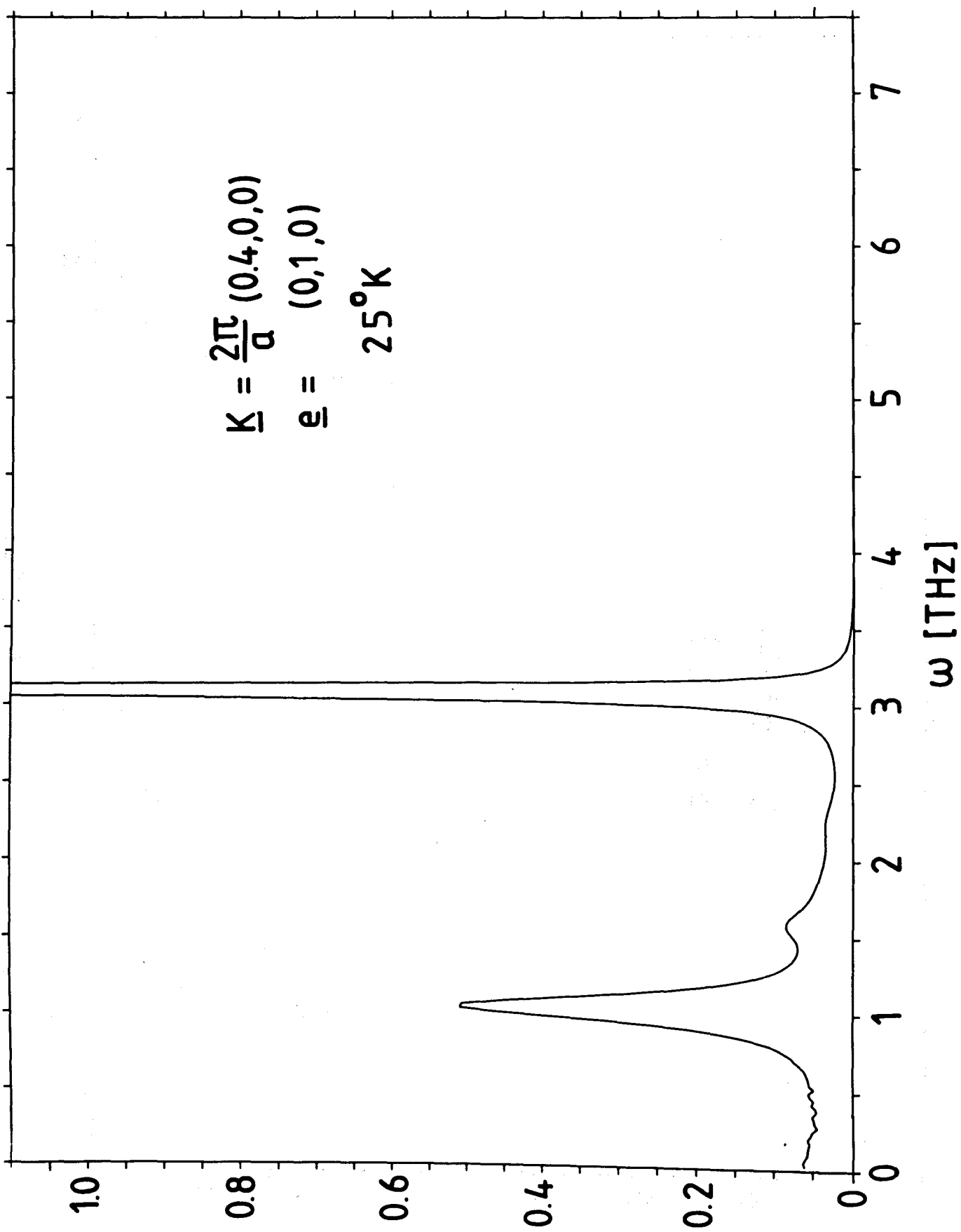


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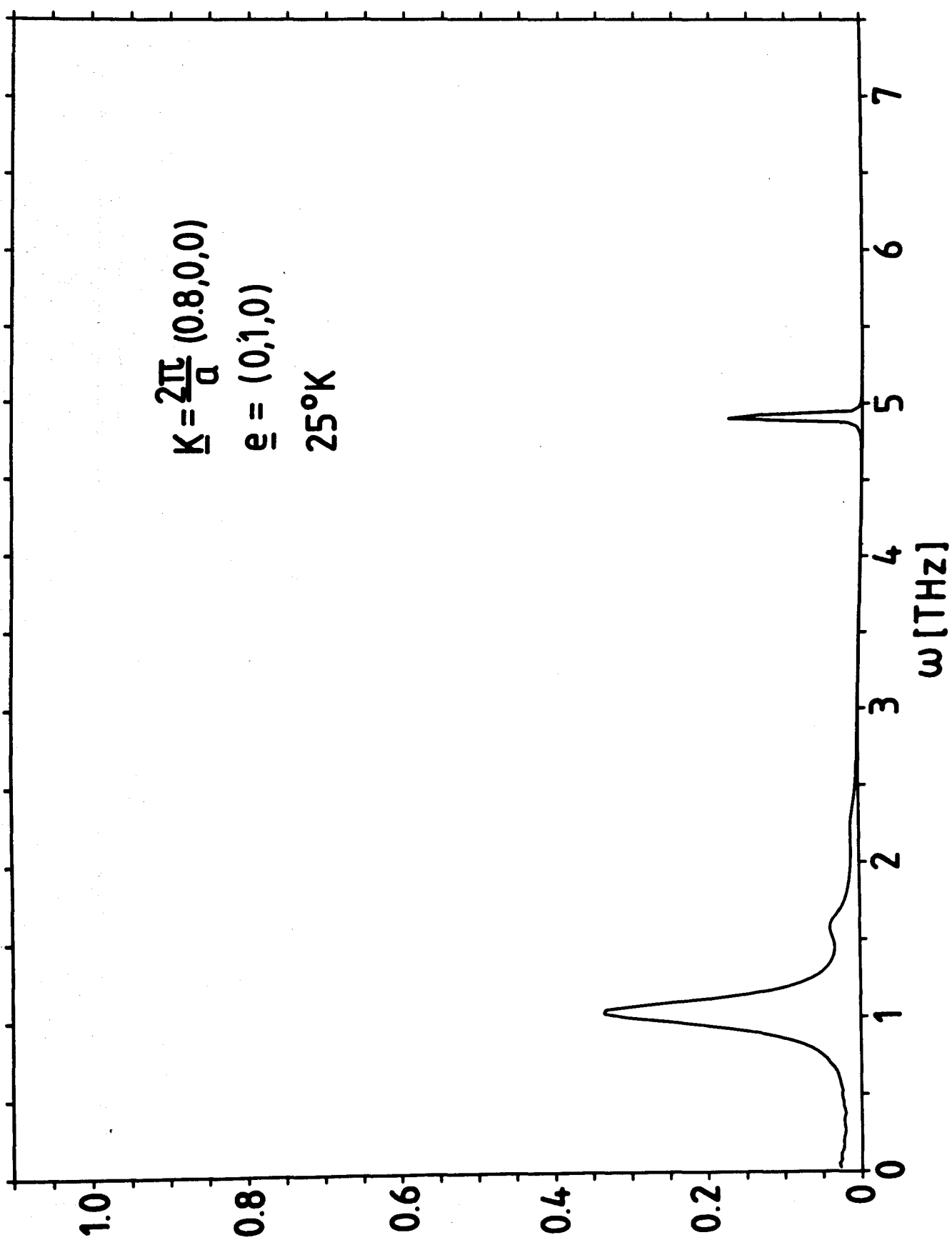


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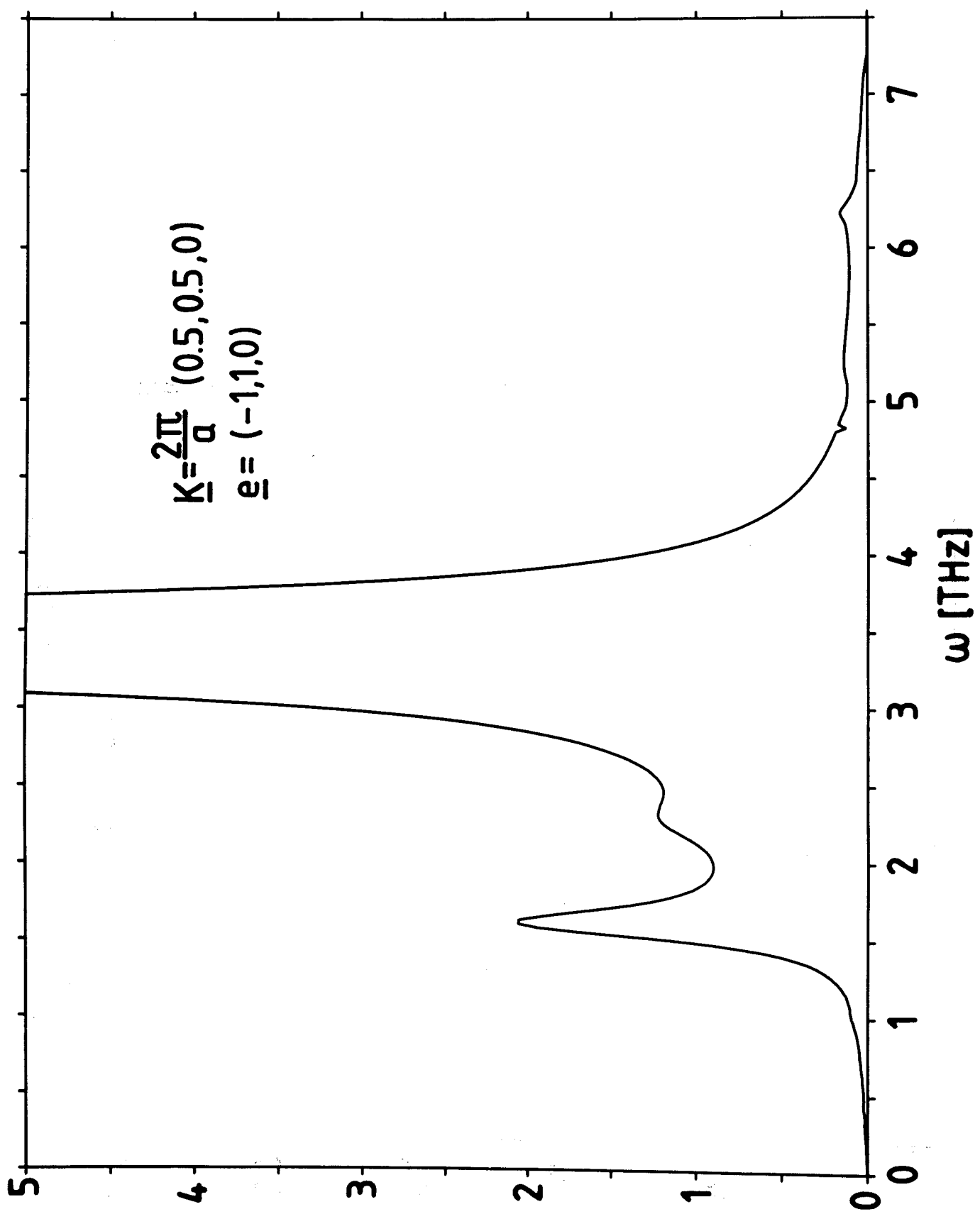


Fig. 10

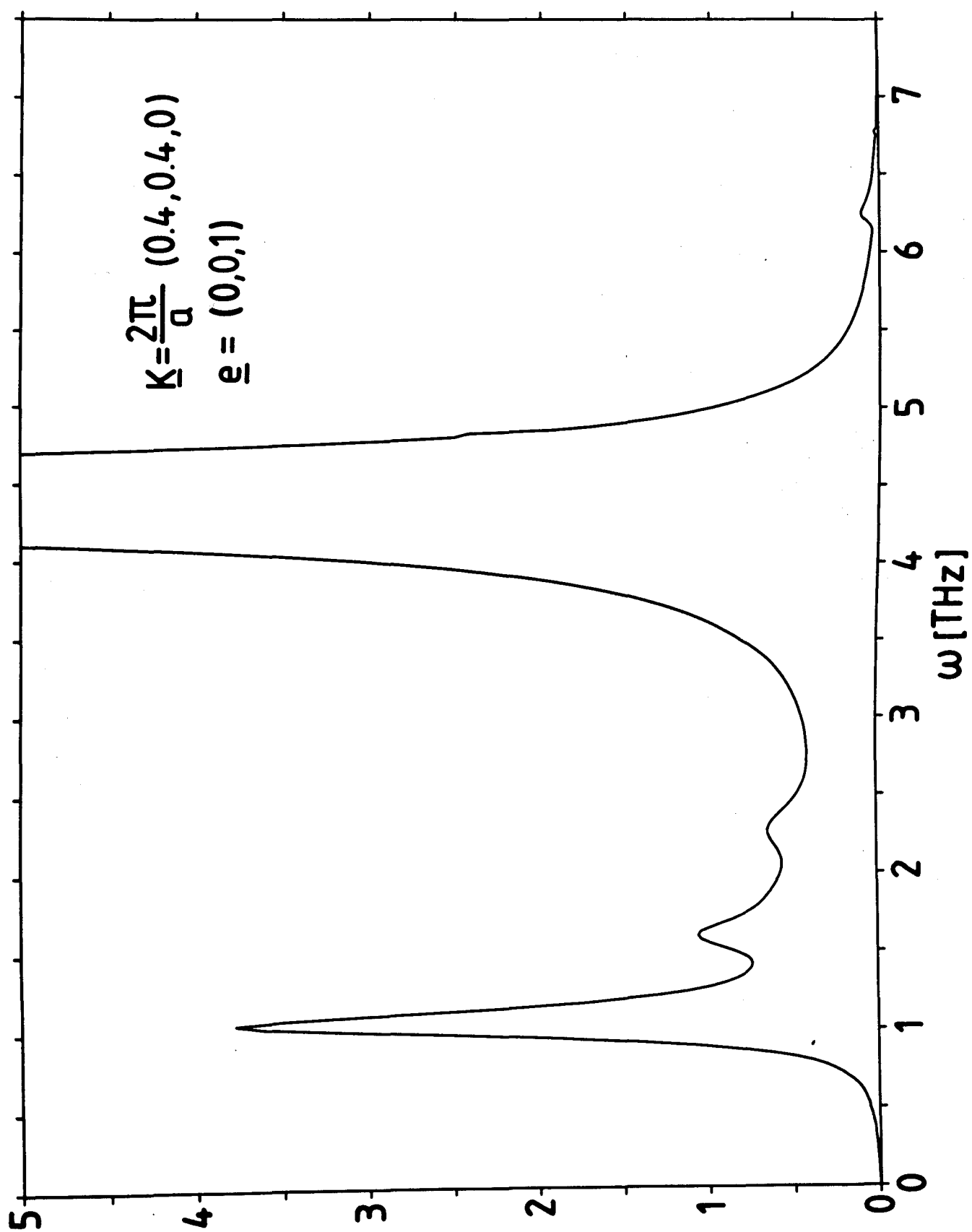


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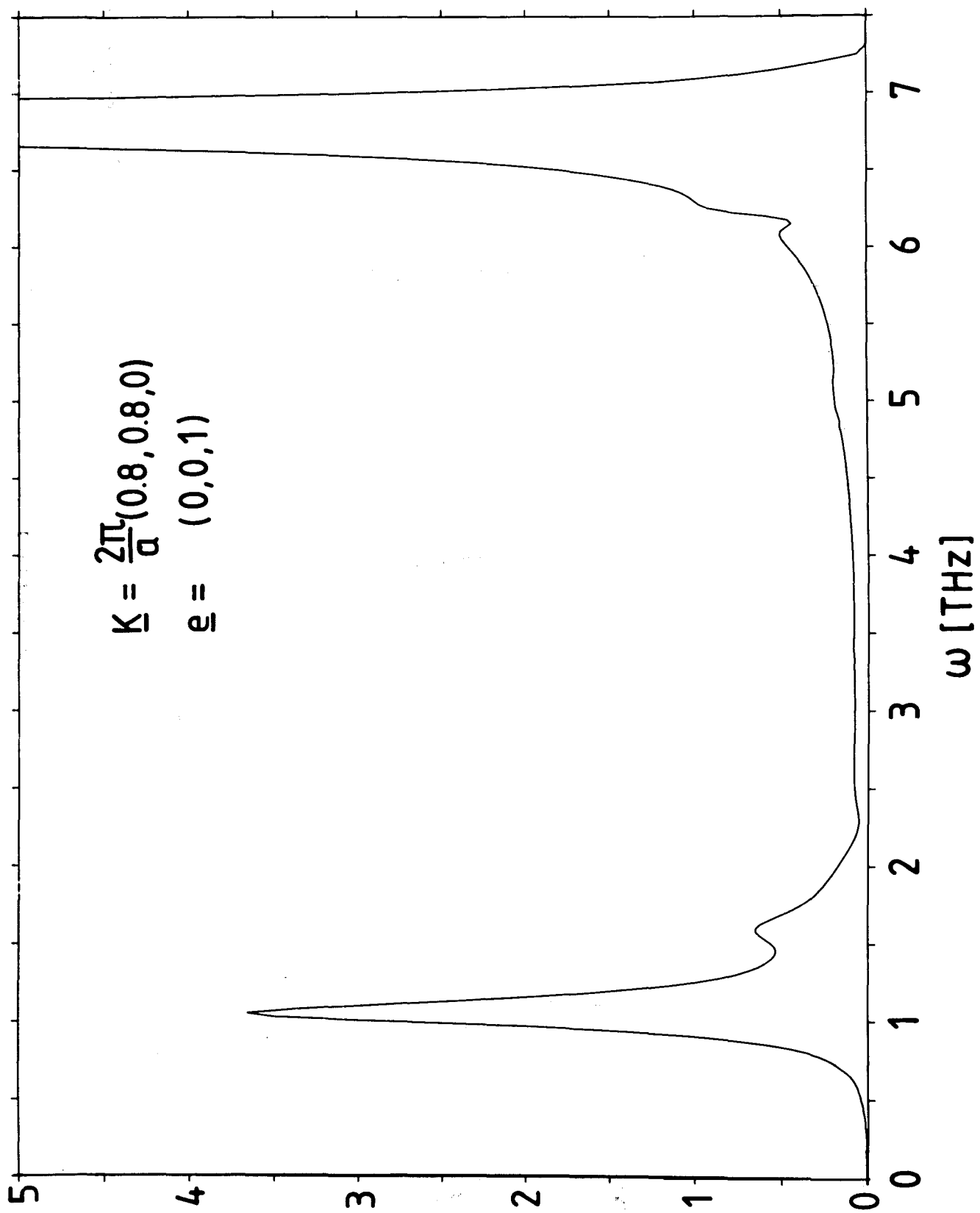


Fig. 12

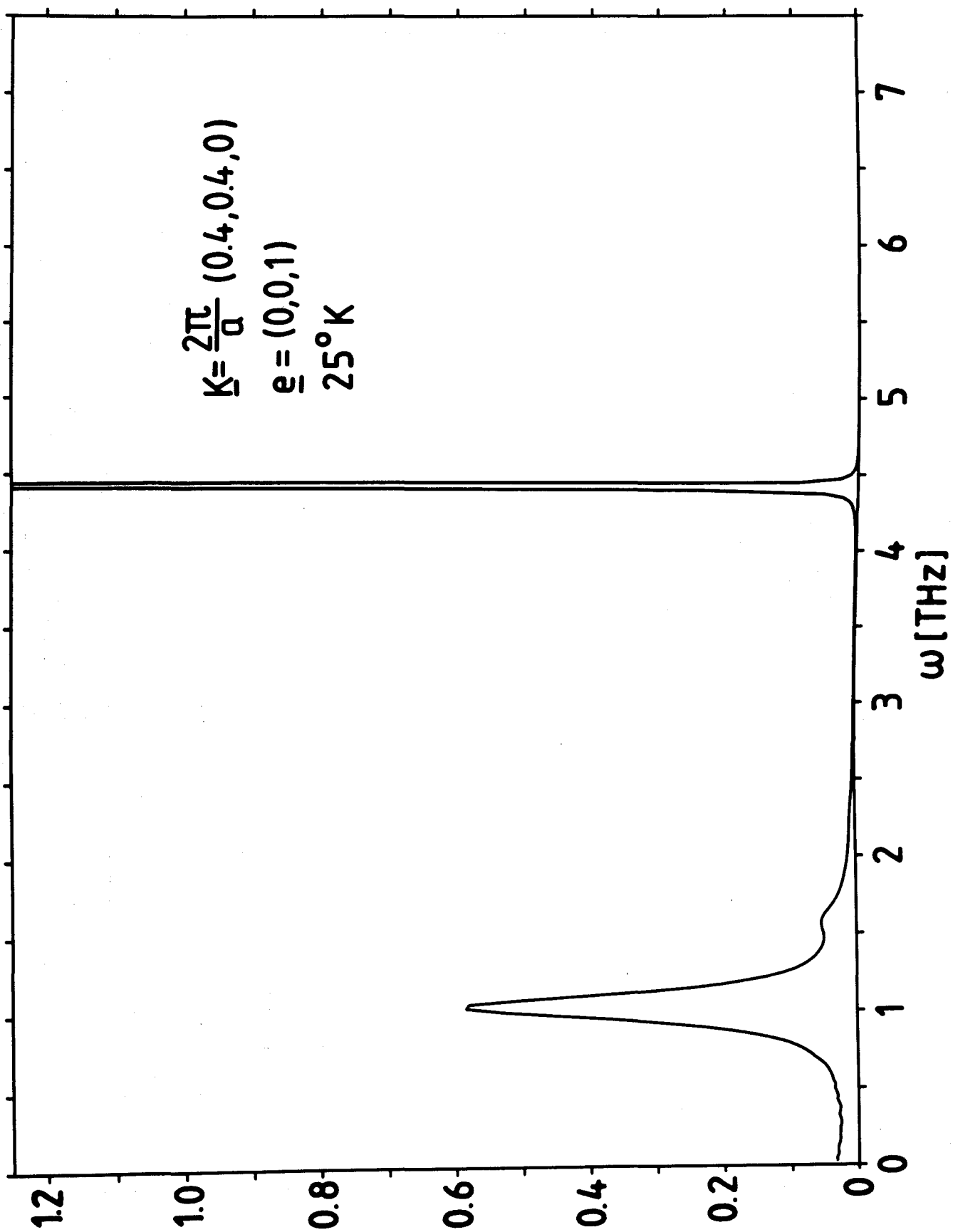


Fig. 13

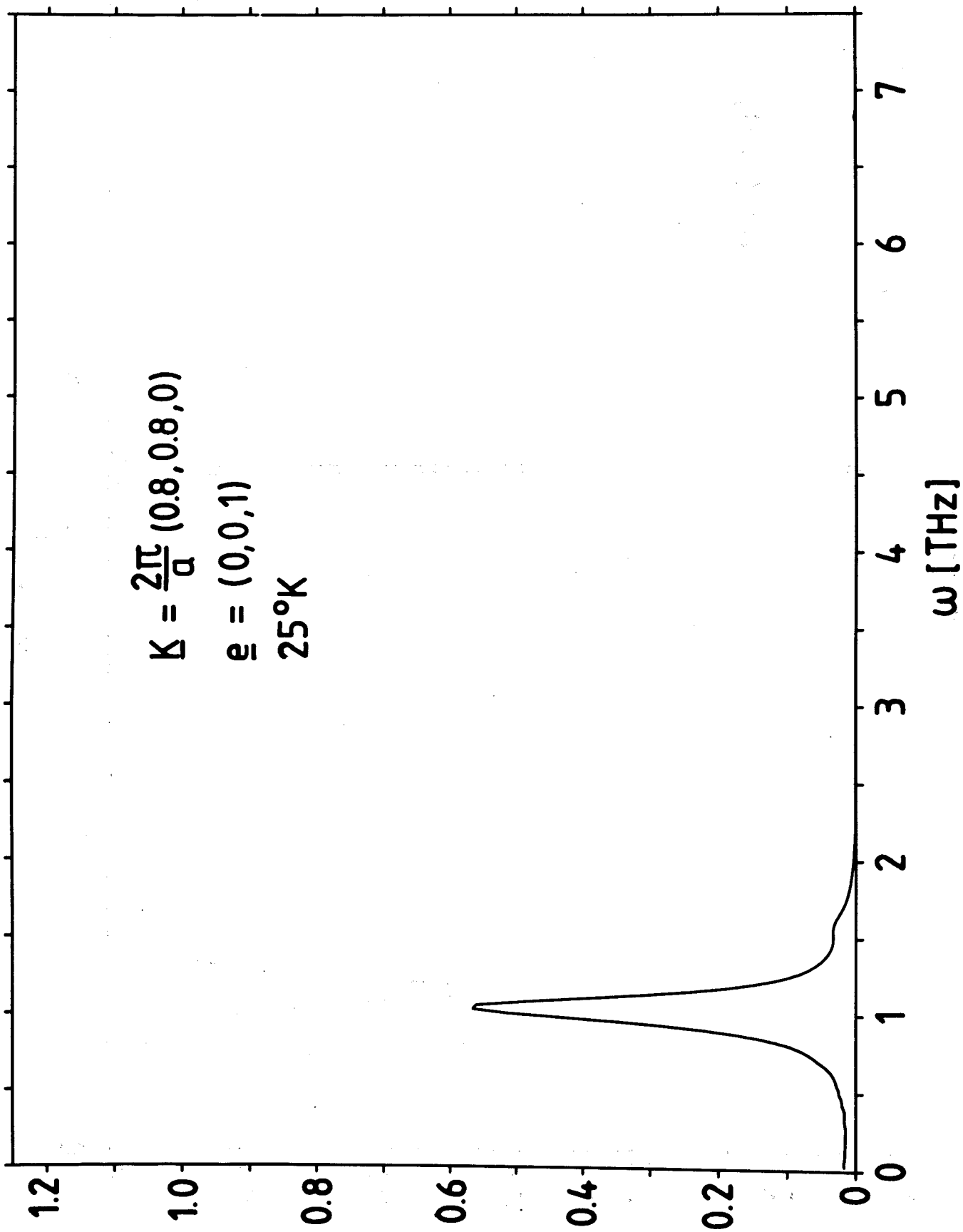


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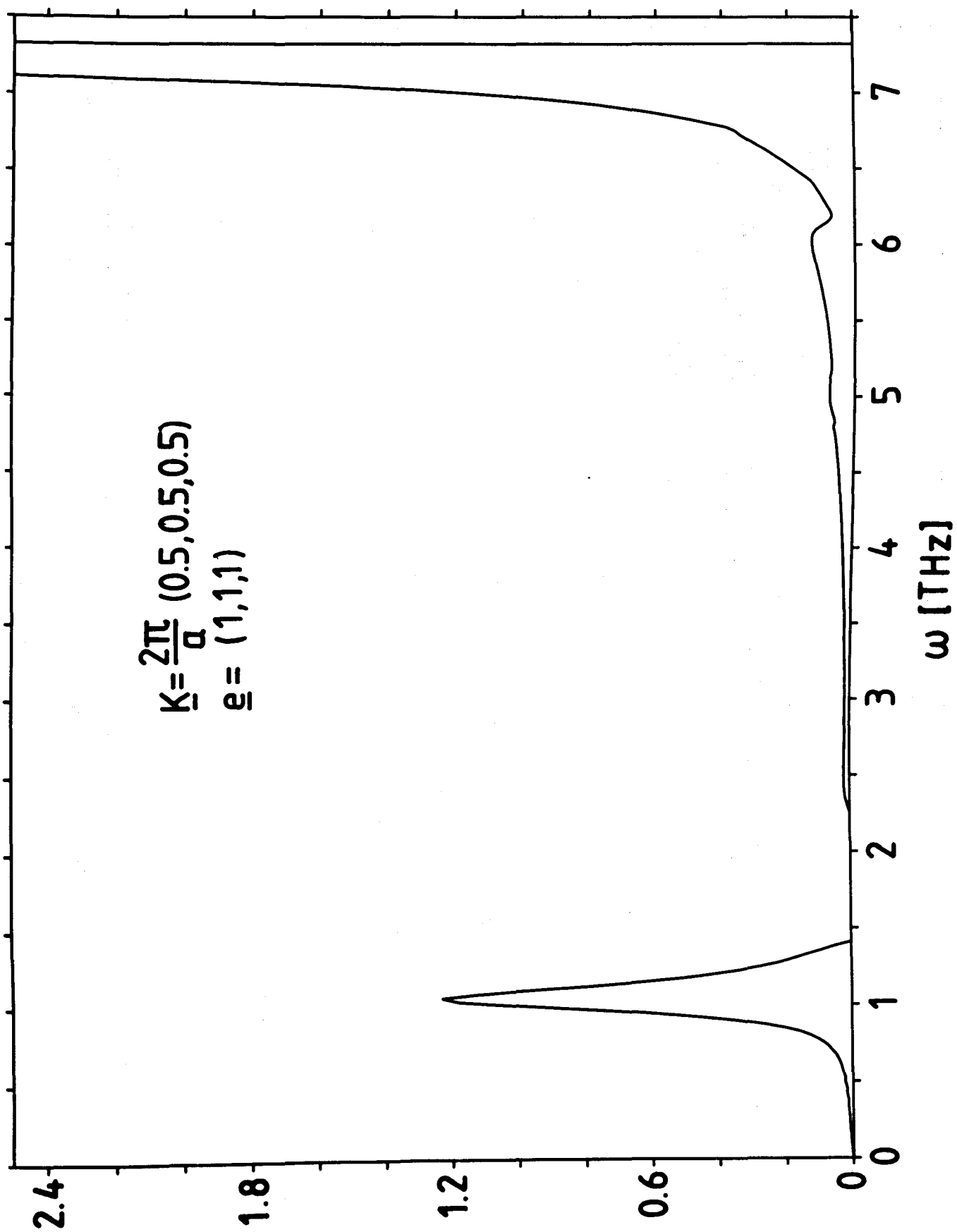


Fig. 15

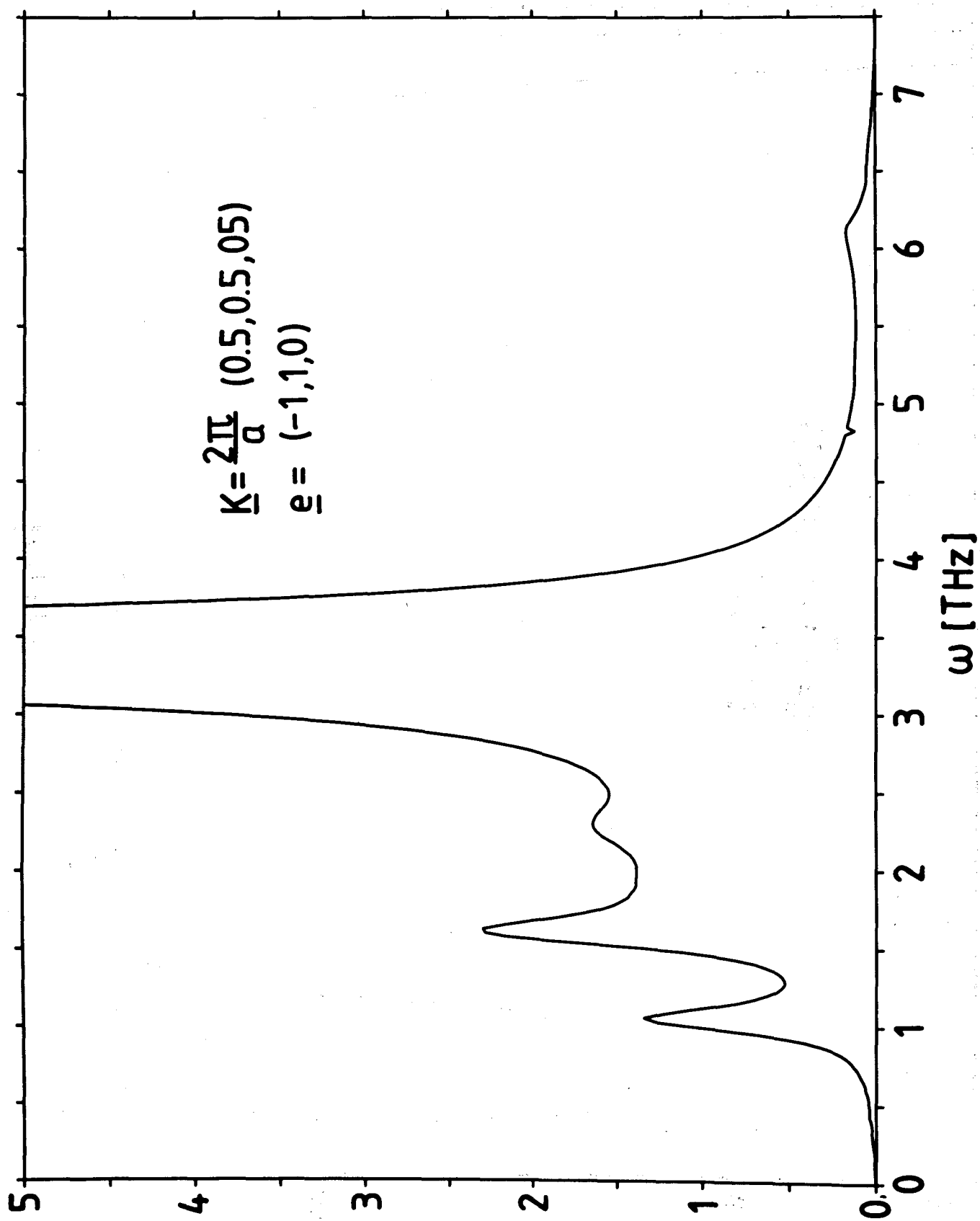


Fig. 16

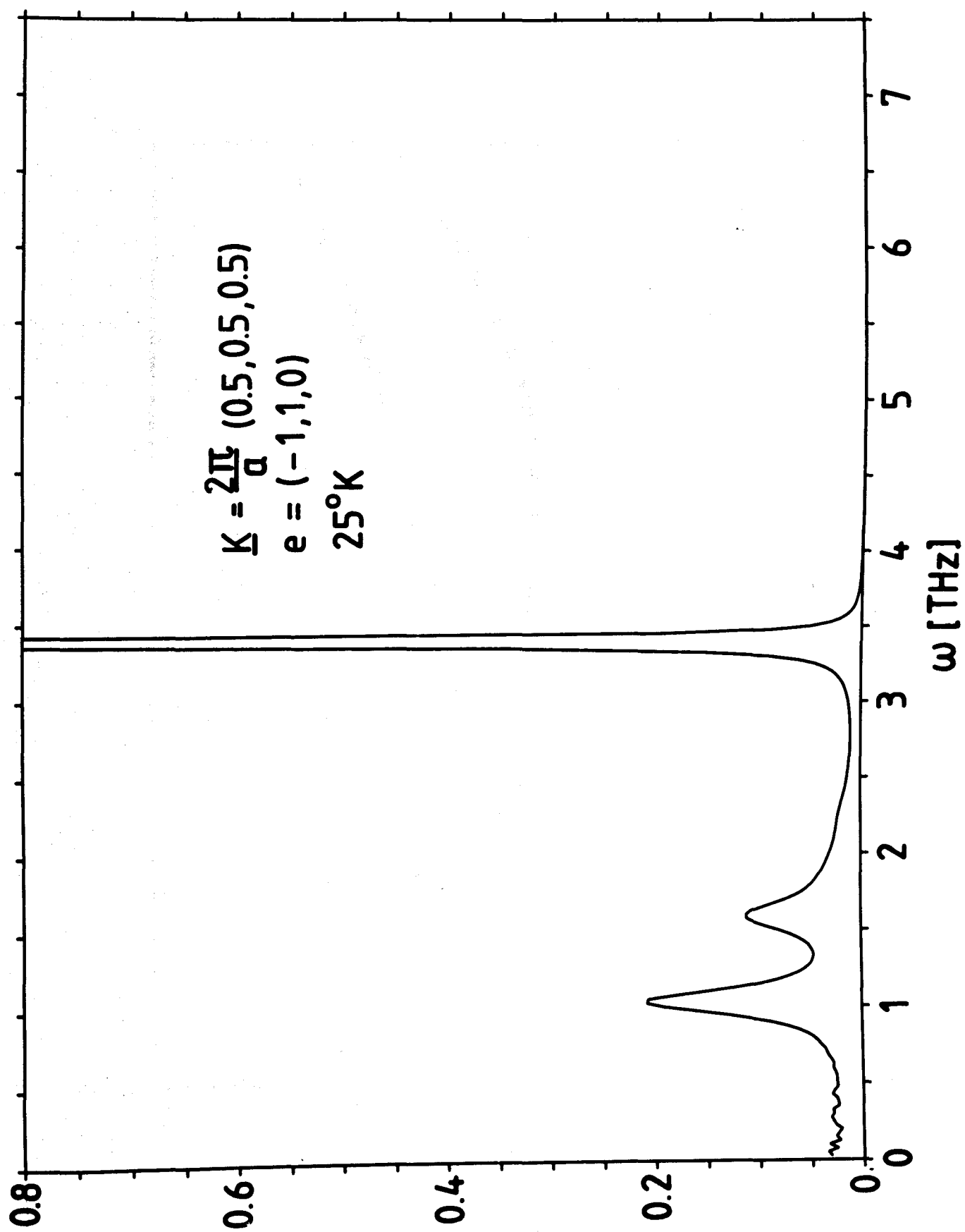


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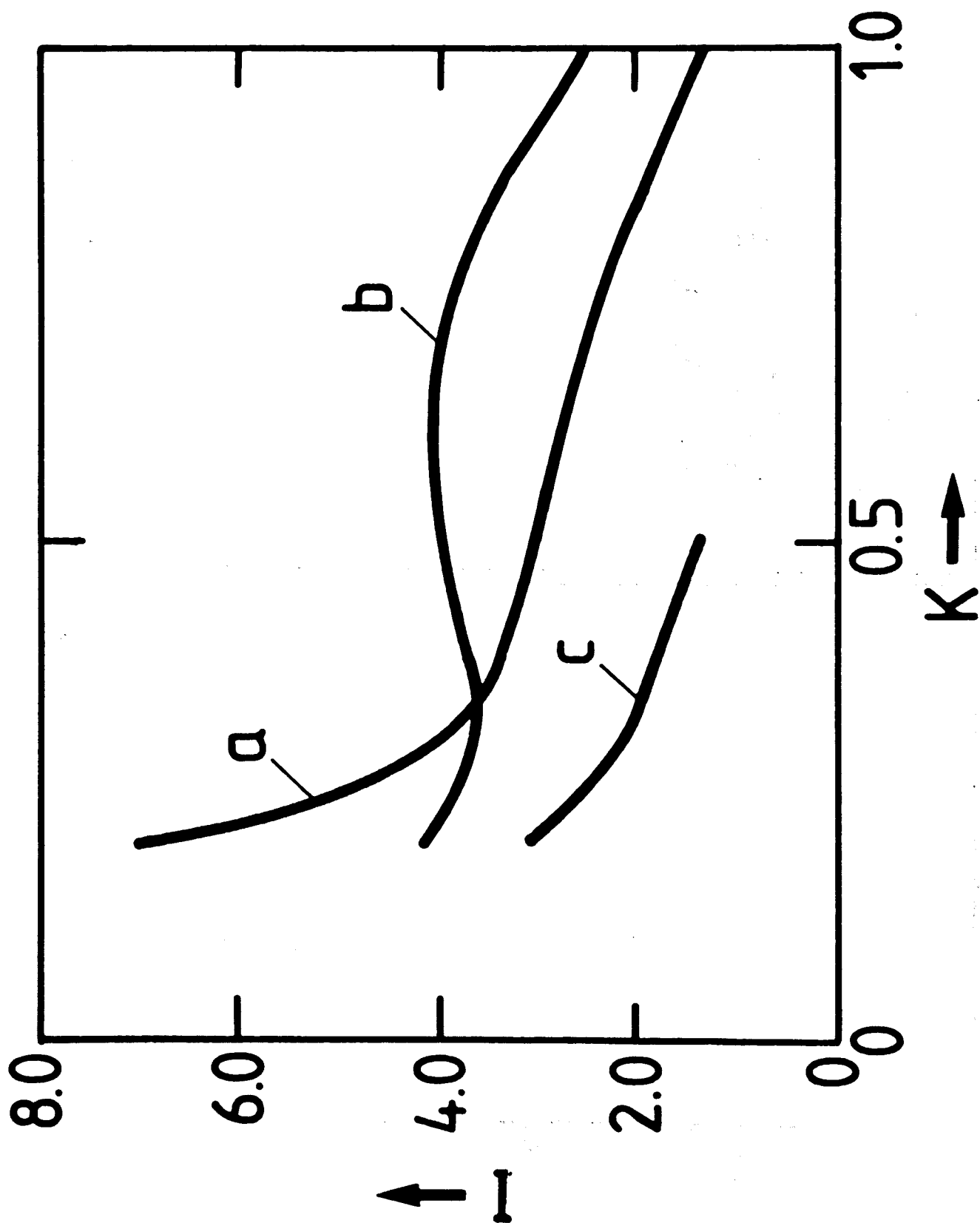


Fig. 18

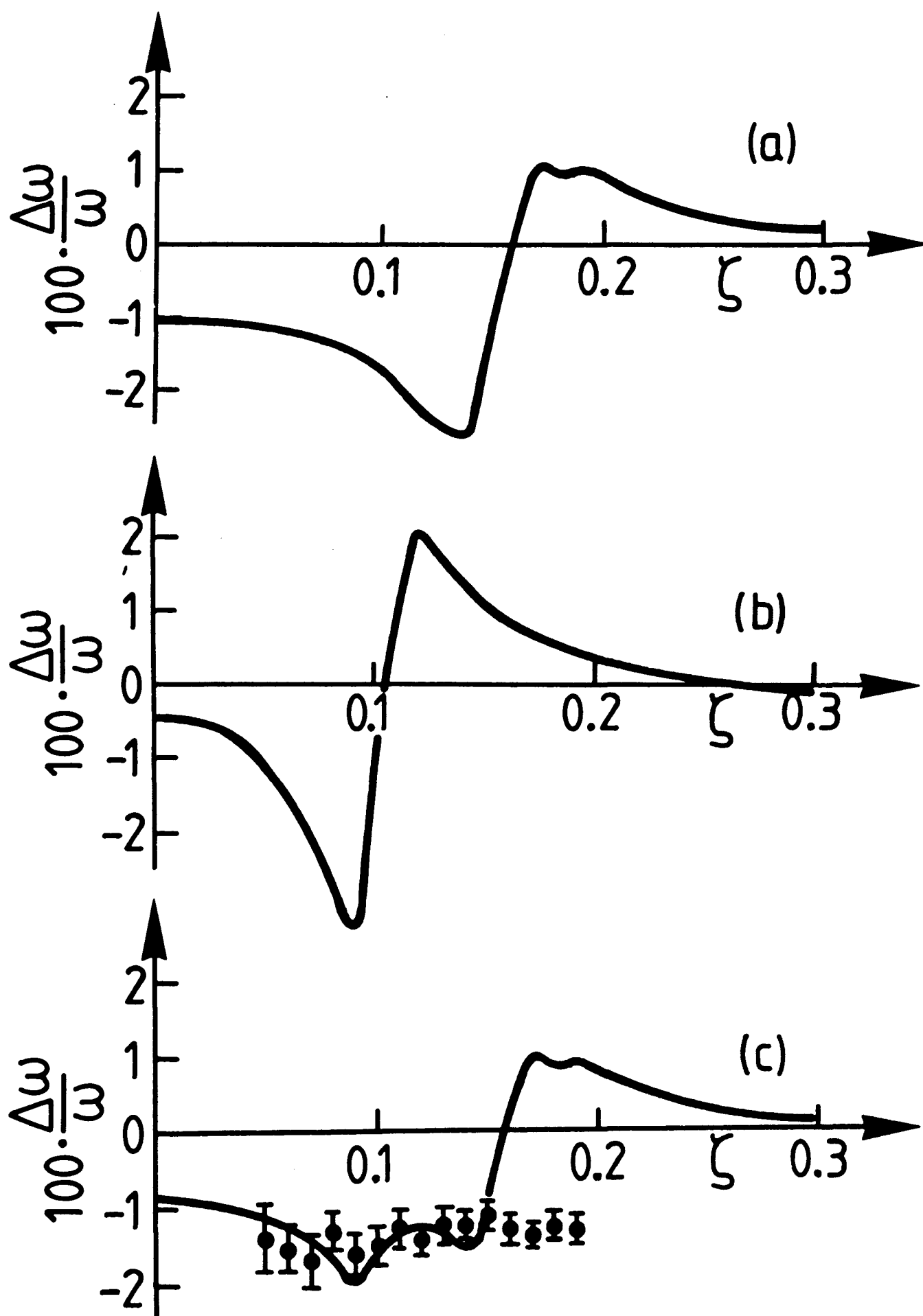


Fig. 19