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# Quasielastic and low-energy inelastic neutron scattering study of $\text{HoCrO}_3$ by high resolution time-of-flight neutron spectroscopy

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In order to understand the origin of the huge quasielastic magnetic scattering observed previously with a back-scattering neutron spectrometer we have re-investigated the low energy excitations in  $\text{HoCrO}_3$  by inelastic neutron scattering in a much wider energy range with time-of-flight neutron spectrometers. The inelastic signals are due to the excitations between the ground state doublet of the Ho ion. The quasielastic signal is due to the fluctuation of the disordered Ho moments. At low temperature the intensity of quasielastic scattering is small. It starts increasing as the temperature increases above 30 K. At the same temperature the elastic intensity due to Ho moment ordering decreases in a similar way. This observation strengthens the hypothesis that the quasielastic scattering is due the fluctuations of the disordered Ho moments. The time scale of fluctuations has been determined from the quasielastic scattering and was found to vary from about 22 ps at  $T = 70$  K to about 2.5 ps at  $T = 160$  K. The stretched exponential line shape indicates a distribution of decay rates at low temperatures.

## INTRIODOUCTION

The structure and properties of transition metal oxides  $\text{ABO}_3$  ( $A = \text{rare earth R or Y}$ ,  $B = \text{Ti, V, Cr, Mn, Fe, Co, Ni and Cu}$ ) with distorted perovskite structures and their layered variants have been investigated quite intensively for more than half a century. The discovery of high- $T_c$  superconductivity in 1986 in doped layered-variant cuprate perovskite materials gave a big boost to this research [1–3]. This was then followed by the discovery of colossal magnetoresistive manganites [4] and subsequently several multiferroic [5, 6] materials suitable for potential applications in magnetic and spintronic devices. Apart from potential industrial applications the research revealed a wealth of complex phenomena arising due to the interplay among charge, orbital, spin and lattice degrees of freedom. Among all these transition metal compounds the chromites  $\text{RCrO}_3$  are relatively less investigated probably because of the difficulty of their synthesis and especially their crystal growth. However, in recent years there have been some reports of possible multiferroic behavior [7–17]. The presence of two magnetic sublattices also give rise to several interesting phenomena like weak ferromagnetism and spin reorientation transitions. Here we have investigated low energy magnetic excitations in  $\text{HoCrO}_3$  by inelastic neutron scattering with the time-of-flight neutron spectroscopy. The initial impetus of this work was our previous study of hyperfine interaction [18] by high-resolution back-scattering neutron spectroscopy that revealed the existence of hyperfine signals at about  $\pm 22 \mu\text{eV}$  at low temperature. However while studying its temperature dependence we observed appearance of huge quasielastic scattering at

higher temperature in which the relatively weak hyperfine signals at about  $\pm 22 \mu\text{eV}$  were completely buried and could not be studied further. The hyperfine study was done with a spectrometer energy window of about  $\pm 100 \mu\text{eV}$  and therefore the evolution of the quasielastic scattering could not be studied at higher temperatures at which its width became larger than the energy window and therefore the most of the signal went outside the window. In order to understand the origin of the observed quasielastic scattering in  $\text{HoCrO}_3$  we have carried out the present investigation with two time-of-flight neutron spectrometers with somewhat reduced energy resolution but with a much larger energy window. This has allowed us to investigate the origin of the quasielastic scattering.

$\text{HoCrO}_3$  crystallizes with the orthorhombically distorted perovskite structure in the space group  $D_{2h}^{16} - Pbnm$  and has four formula units per unit cell. The magnetic properties of  $\text{HoCrO}_3$  have been studied by magnetization and neutron diffraction in the second half of the last century. The exchange coupling between nearest-neighbor  $\text{Cr}^{3+}$  ions is predominantly antiferromagnetic and these ions order magnetically [19–21] below  $T_N \approx 142$  K. Below this temperature  $\text{HoCrO}_3$  exhibits weak ferromagnetic moment [21]. The magnetic structure of the Cr sublattice [21] is  $G_z F_x$  in the notation of Koehler et al. [22] and Bertaut [23]. At lower temperature Ho ions order and also due to strong interaction between Cr and Ho moments, spin canting phenomena take place [24–26]. The recent interest [7, 27–30] in  $\text{HoCrO}_3$  and other rare-earth chromites is due to the possibility of coupling between the magnetic and ferroelectric properties leading to multiferroic behavior and potential device applications. There have been several reports of the fer-

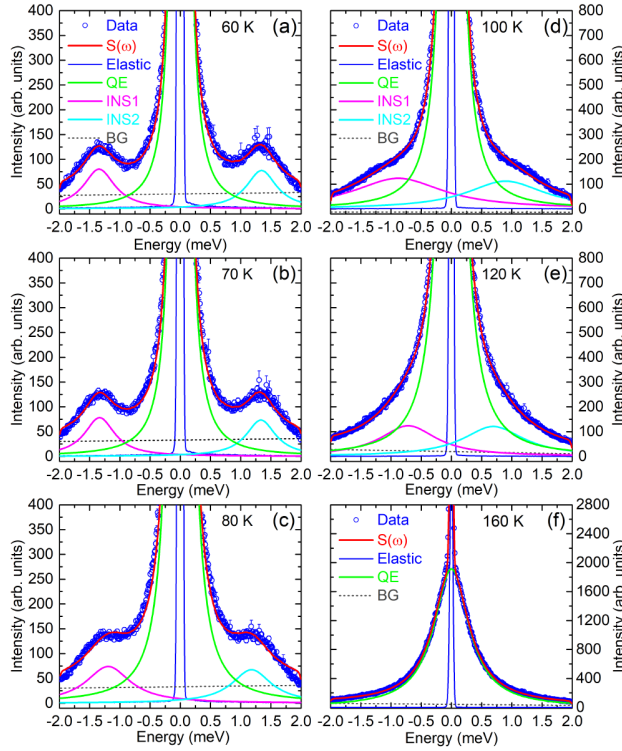


FIG. 1. Inelastic spectra of  $\text{HoCrO}_3$  at  $T = 60, 70, 80, 100, 120, 160$  and  $200$  K measured on the CNCS spectrometer at both energy loss and gain sides fitted by convoluting instrumental resolution function  $R(\omega)$  determined from vanadium with one delta function  $\delta_{el}(\omega)$  for the elastic peak and with two Lorentzian functions,  $L_{ins}(\Delta, \omega)$  for the two inelastic peaks and a Lorentzian function  $L_{qe}$  for the quasielastic scattering. These components are shown by continuous curves of different colors indicated by the legends. The data have been averaged over the  $Q$ -range from  $Q_{min} = 0.7 \text{ \AA}^{-1}$  to  $Q_{max} = 1.7 \text{ \AA}^{-1}$ .

roelectric polarization in  $\text{HoCrO}_3$  and other rare earth chromites [14, 16, 17]

## EXPERIMENTAL METHODS

Polycrystalline  $\text{HoCrO}_3$  samples were synthesized by the solid state reaction of  $\text{Ho}_2\text{O}_3(3\text{N})$  and  $\text{Cr}_2\text{O}_3(4\text{N})$  in stoichiometric ratio [25]. The precursors were mixed intimately and subsequently heat treated at  $1100^\circ\text{C}$  for 48 h. The resulting material was then reground and annealed again at  $1200^\circ\text{C}$  for 24 h. The phase purity of the synthesized powder sample was then confirmed by powder X-ray diffraction with  $\text{CuK}\alpha$  ( $\lambda = 1.54059 \text{ \AA}$ ) radiation, using a Huber X-ray diffractometer (Huber G670) in transmission Guinier geometry. Specific heat, magnetization and also neutron diffraction measurements showed that the sample orders below  $T_N \approx 142 \text{ K}$ .

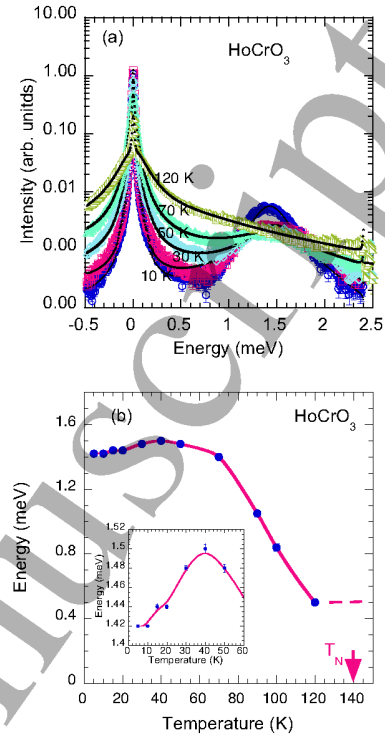


FIG. 2. (a) Inelastic spectra from  $\text{HoCrO}_3$  measured on the OSIRIS spectrometer at different temperatures. The black continuous curves are the fit to the data with the convolution of the instrumental resolution function with a delta function and a Lorentzian for the elastic and the quasielastic peak plus a Lorentzian for the inelastic peak. The data have been averaged over the  $Q$  range from  $0.3$  to  $1.1 \text{ \AA}^{-1}$ . (b) Temperature variation of the energy of the excitations due to transition between the accidental doublet of the crystal field levels of the  $\text{Ho}^{3+}$  ions in  $\text{HoCrO}_3$ . In the inset the low temperature part is shown. The continuous red curves are just guides to the eye.

## INELASTIC AND QUASIELASTIC NEUTRON SCATTERING

Inelastic and quasielastic neutron scattering investigations were done on the Cold Neutron Chopper Spectrometer [31] (CNCS) at the Spallation Neutron Source (SNS) of the Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA and also on the OSIRIS spectrometer [32, 33] of the ISIS Facility at Chilton, Didcot, UK. Incoming energies  $E_i = 3, 5.8$  and  $12 \text{ meV}$  were used for the measurements on CNCS. The runs on the indirect time of flight backscattering spectrometer OSIRIS utilized an end energy of  $1.845 \text{ meV}$  and the elastic energy resolution was  $25 \mu\text{eV}$  and the inelastic one at  $1.4 \text{ meV}$  energy transfer was about  $28 \mu\text{eV}$ .

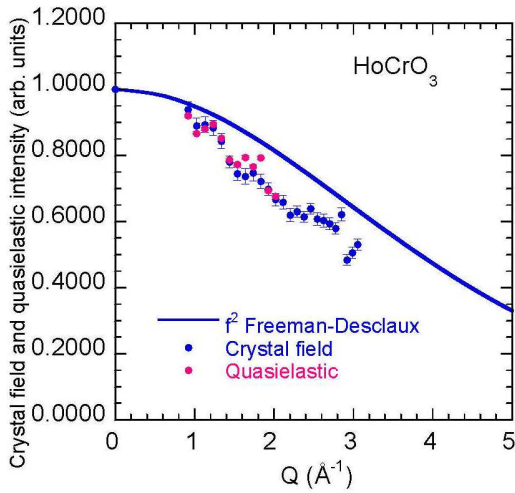


FIG. 3.  $Q$  dependence of the energy integrated intensity of the inelastic (crystal field) and quasielastic peaks of  $\text{HoCrO}_3$  measured on the OSIRIS spectrometer of the ISIS Facility. The intensity of the inelastic peak was measured at  $T = 10$  K and the quasielastic intensity was measured at 160 K in order to avoid disturbance of magnetic peaks in the covered  $Q$ -range. The continuous line is the square of the form factor [35] of  $\text{Ho}^{3+}$ . In order to compare with the  $\text{Ho}^{3+}$  form factor, the crystal field and quasielastic intensities are scaled to give the value 1 at  $Q = 0$ .

Fig. 1 shows the inelastic spectra of  $\text{HoCrO}_3$  at  $T = 60, 70, 80, 100, 160$  and  $200$  K measured on the CNCS spectrometer with  $E_i = 3$  meV on both energy loss and gain sides. We see clearly the presence of inelastic peaks on the energy loss and energy gain sides at  $\pm 1.4$  meV. The inelastic peaks are due to the transitions from the ground state doublet of the  $\text{Ho}^{3+}$ . With the present resolution of the spectrometer we of course do not see the hyperfine peaks at  $E = \pm 22 \mu\text{eV}$  previously observed by us [18] on the back-scattering neutron spectrometer BASIS. These inelastic signals are here inside the central quasielastic peak. The spectra were fitted by convoluting instrumental resolution function  $R(\omega)$  determined from vanadium with one delta function  $\delta_{el}$  for the elastic peak and with two Lorentzians  $L_{ins}$  for the two inelastic peaks and a Lorentzian function  $L_{qe}$  for the quasielastic scattering. We have fitted the spectra measured on CNCS

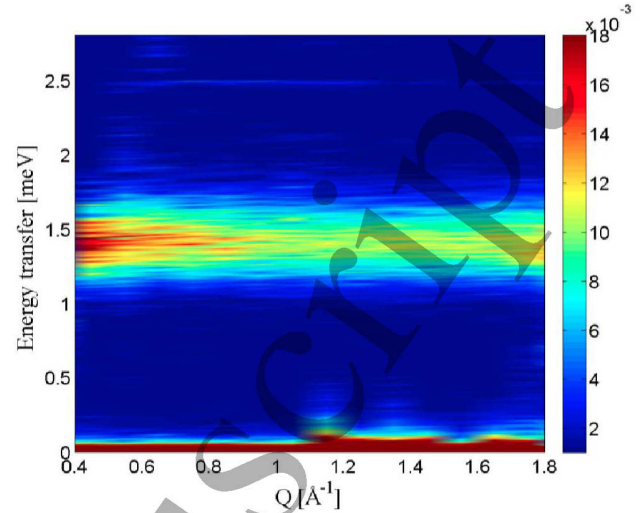


FIG. 4. Typical  $S(Q, \omega)$  plot of  $\text{HoCrO}_3$  measured at  $T = 7$  K on the OSIRIS spectrometer of the ISIS Facility. The results indicate the magnetic origin of the inelastic excitation.

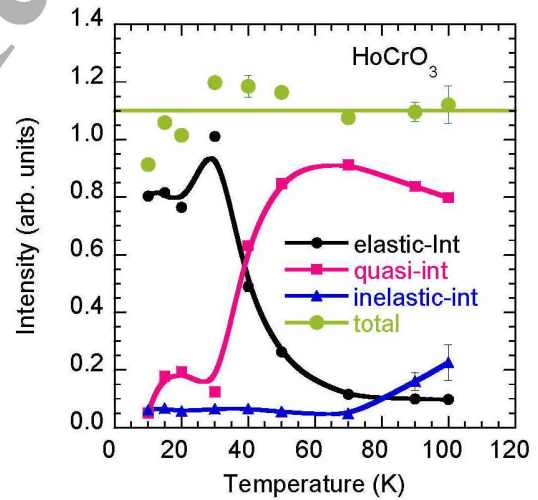


FIG. 5. Temperature variation of the  $Q$ -integrated ( $Q$  in the range from  $0.3$  to  $1.1 \text{ \AA}^{-1}$ ) intensity of the elastic, quasielastic and the inelastic signals from  $\text{HoCrO}_3$  and their sum as measured on the OSIRIS spectrometer of the ISIS Facility. The lines are only guides for the eyes.



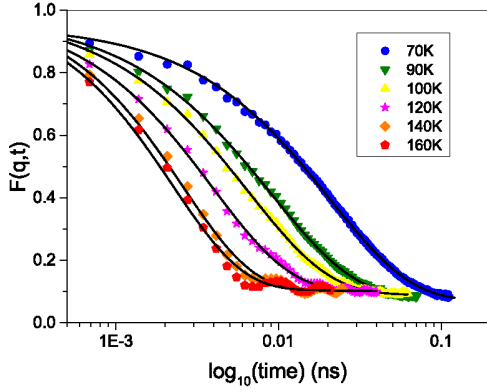


FIG. 6. Fourier transformed quasielastic data and their fit with a stretched exponential function (line) at different temperatures

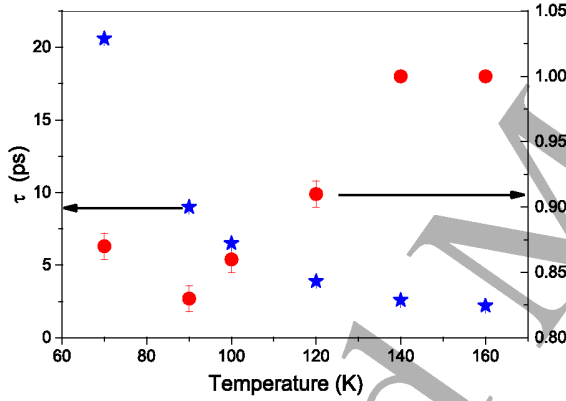


FIG. 7. Temperature dependence of the power of stretched exponential function  $\beta$  and the relaxation time  $\tau$ .

spectrometer by the equation

$$S(\omega) = [p_0\delta_{el}(\omega) + p_1L_{ins}(\Delta, \omega) + p_2L_{ins}(\Delta, \omega) + p_3L_{qe}(\Delta, \omega)] \otimes R(\omega) + B \quad (1)$$

where delta function  $\delta_{el}$  represents the elastic peak respectively. The Lorentzian function  $L$  represents the quasielastic component, and the  $L_{ins}(\Delta, \omega)$  Lorentzian function represents the inelastic peaks. The above mentioned terms are all convoluted numerically with the experimentally determined resolution function,  $R(\omega)$ .  $B$  is the flat background term and  $p_0, p_1, p_2, p_3$  are scaling factors. The delta function for the elastic peak and the two Lorentzian functions for the inelastic peaks when convoluted with the experimentally determined instrumental

resolution function reproduces these three peaks quite well. We have also included the Lorentzian function to take into account for any quasielastic scattering. We note that increasingly strong quasielastic scattering does arise at higher temperatures.

Fig. 2 (a) shows the inelastic spectra from  $\text{HoCrO}_3$  obtained on the OSIRIS spectrometer at different temperatures. The OSIRIS data have been fitted by a model comprising a sum of a elastic delta function and two Lorentzian function plus the background. One Lorentzian for the inelastic contribution and one for the emerging quasielastic intensity. A linear background was taken into account. The whole model was then numerically convoluted with the resolution function. Within the Levenberg-Marquardt fit all three intensity parameters, the peak position of the excitation and the line widths of the two Lorentzians have been varied. Fig. 2 (b) shows the temperature dependence of the inelastic peak obtained by the fits shown in Fig. 2(a). The energy of the inelastic peak is  $E = 1.420 \pm 0.001$  meV at  $T = 5$  K. It increases at first with temperature to about  $E = 1.500 \pm 0.005$  meV. The energy then decreases continuously with temperature to about  $E = 0.50 \pm 0.02$ . It was not possible to fit the inelastic peak at higher temperatures due to the large width of the signal of the inelastic peak. The optical absorption Zeeman spectroscopy [34] shows that the energy eventually becomes about  $E \approx 0.5$  meV at  $T_N \approx 140$  K and remains constant at higher temperature. These three steps in the temperature variation of energy can be understood by assuming that the constant value of energy attained at  $T \geq T_N \approx 140$  is the energy of splitting of the ground doublet due to the crystal field alone. At lower temperature the splitting increases with decreasing temperature down to about 40 K due to increase of the field by ordered Cr ions on the Ho site. Below  $T = 40$  K the Ho ions become polarized and put on Ho ion an effective field that decreases somewhat with lowering temperature. The continuous red curves shown in Fig. 2 (a) and also its inset are just guides to the eye.

The above results referred to Q-integrated intensities. We have also investigated the Q dependence of the energy integrated intensities of the quasielastic and inelastic excitations. Fig. 3 shows the Q dependence of these intensities. The Q dependence of the square of the  $\text{Ho}^{3+}$  form factor [35] is also shown by the continuous line in the figure. Both these intensities decrease strongly with increasing Q showing that these scatterings are of magnetic origin. We expect these intensities decrease as a function Q following the square of the  $\text{Ho}^{3+}$  form factor. Both these intensities do decrease with increasing Q but the dependences do not follow exactly the form factor. The reason for this deviation may perhaps be explained by the uncertainty in the evaluation process but may have more fundamental reasons as well. For making more definite conclusion one needs further detailed studies. We

also show a typical  $S(Q, \omega)$  map of  $\text{HoCrO}_3$  at  $T = 7$  K in Fig. 4 obtained from the OSIRIS spectrometer. It clearly indicated the magnetic origin of the inelastic excitation due to the decay in intensity. Furthermore it does not show any evidence for a dispersion of the excitation with  $Q$ .

Fig. 5 shows the temperature variation of the  $Q$ -integrated ( $Q$  in the range from 0.3 to 1.1  $\text{\AA}^{-1}$ ) intensity of the elastic, quasielastic and the inelastic signals from  $\text{HoCrO}_3$  and their sums as measured on the OSIRIS spectrometer of the ISIS Facility. We note that although the individual intensities vary considerably with temperature their sum remains more or less constant. Most spectacular is the temperature variation of the elastic and quasielastic intensities that have just opposite tendencies. As the temperature is raised above 30 K the elastic intensity decreases whereas the quasielastic intensity shoots up dramatically at the same time. The elastic intensity decreases due to the disordering of Ho moments and quasielastic scattering increases due to the fluctuations of disordered Ho moments. It is known from the diffraction experiments [24, 25] that the intensities of the 100, 011 and 101 reflections grow immensely below about 30 K due to the ordering of the Ho moments. So the origin of the huge quasielastic scattering in  $\text{HoCrO}_3$  at higher temperature is in fact scattering due to the disordered fluctuating Ho moments. The inelastic scattering due to the crystal field excitations is much smaller compared to the elastic and quasielastic intensities. We also note an increase in intensity of the inelastic peak above about 80 K. We do not consider this small increase to be real but is perhaps due to the increasing difficulties of the least squares fit procedure when the inelastic peak energy became very small and almost merge to the central elastic peak.

In order to get the time scale of fluctuations of the disordered Ho moments we Fourier-transformed the quasielastic data and fitted the intensity by a stretched exponential function

$$F(Q, t) = B + A \exp[-(t/\tau)^\beta] \quad (2)$$

where  $B$  is the background and  $\tau$  and  $\beta$  are the relaxation time and power of the stretched exponential function. Fig. 6 shows the fit of these data at different temperatures. The resulting temperature dependences of the parameters  $\tau$  and  $\beta$  are shown in Fig. 7. We note that time scale of fluctuations of the disordered Ho magnetic moment varies from about 22 ps at  $T = 70$  K to about 2.5 ps at  $T = 160$  K. The power of stretched exponential function  $\beta$  varies from 0.6 at  $T = 70$  K to about 1.0 at  $T = 160$  K. The stretched exponential line shape indicates a distribution of decay rates at low temperatures. However, at high temperatures the decay transforms to a pure exponential decay.

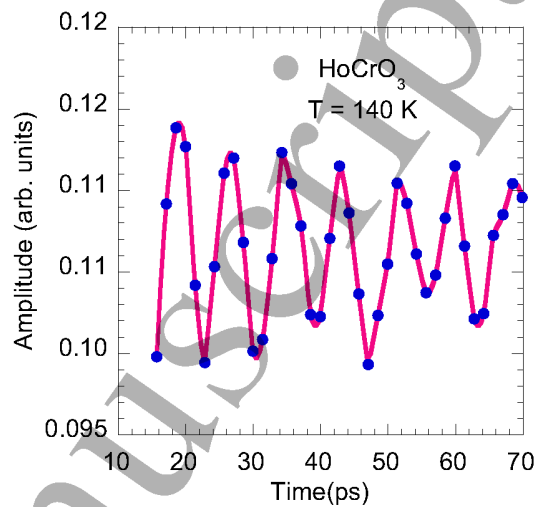


FIG. 8. Oscillations in the background of the Fourier transformed quasielastic data at  $T = 140$  K. The period of the oscillations is about 8 ps corresponding to the energy  $E \approx 0.5 \text{ meV}$

## DISCUSSIONS

We discuss first the origin of the inelastic peak at  $E = 1.4 \text{ meV}$  observed at about 5 K and shown in Fig. 1 and 2. The two lowest crystal field states of the free ion term  $^5I_8$  are singlets, split by an energy of about  $D = 0.5 \text{ meV}$  in paramagnetic state of  $\text{HoCrO}_3$ , are well below the next excited crystal field state [25, 26, 34, 36] which has an energy of 10 meV and is much higher than  $D = 0.5 \text{ meV}$ . Thus the two lowest energy singlet states can be treated as an accidental ground doublet or just doublet for brevity. This is because the doublet splitting energy is small and is of the order of magnetic exchange interaction the ground doublet may be described in an effective spin formalism with  $S = 1/2$ . The energy of the excitations increases continuously as the temperature is decreased in the ordered magnetic state because of the increasing magnetic field of ordered Cr ions at lower temperature. At  $T = 40$  K the splitting decreases due to the magnetic field of the polarized  $\text{Ho}^{3+}$  ions.

We consider next the quasielastic scattering under the elastic peak which develops as the temperature is increased above about 30 K. The increase in quasielastic

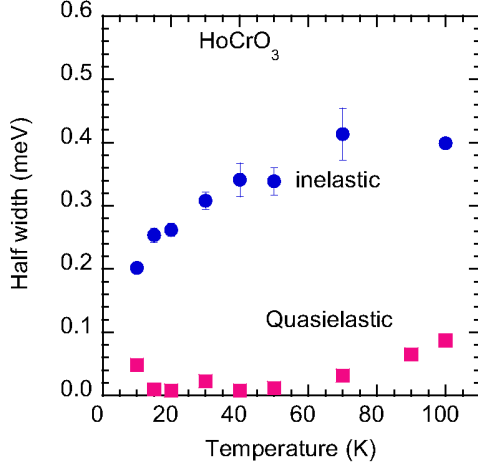


FIG. 9. Temperature dependence of the half-width at half-maximum of the inelastic and quasielastic peaks.

scattering is accompanied by the decrease of elastic intensity as shown clearly in Fig. 5. The elastic peak is mostly due to the ordering of  $\text{Ho}^{3+}$  ions. The elastic intensity increases with decreasing temperature due to the ordering of Ho magnetic moments and it decreases above about 30 K. The temperature dependence quasielastic intensity is just the opposite as shown in Fig. 5. The increasing quasielastic intensity above about 30 K is due to the fluctuations of the disordered moments. The time scale of these fluctuations is determined to be about 8-20 ps in the temperature range investigated as shown in Fig 7.

We note that in the Fourier transformed quasielastic data shown in Fig. 6 the plot shows oscillations in the background for time higher than 15 ps for  $T = 140$  and 160 K. This is shown in a more favorable scale in Fig. 8. The continuous line shows just the interpolation of the data and not any fit. The oscillation period is about 8 ps which corresponds to an energy of about 0.5 meV. This is exactly the energy of the crystal field levels at about  $T_N = 142$  K and also at higher temperatures. In order to make sure that this oscillation has nothing to do with the truncation error of Fourier transformation we analyzed the Fourier transformed data at  $T = 10$  K and

we found again oscillation corresponding to the energy  $E = 1.4$  meV of the inelastic peak at this temperature.

Finally we wish to discuss the large width of the inelastic peak shown in Fig. 2. Also Fig. 9 shows the temperature variation of the widths of inelastic and quasielastic peaks determined from the data from OSIRIS spectrometer. The width of the inelastic peak at all temperatures is much larger than the instrumental energy resolution [37] which is  $\text{FWHM} = 28 \mu\text{eV}$ . There may be several reasons for the broadening for the inelastic peak. There may be coupling of phonon with the crystal field or some other similar coupling processes. To be certain we need detailed investigation on single crystals.

## CONCLUSION

In conclusion we point out that the huge quasielastic scattering, which observed in  $\text{HoCrO}_3$  in our previous study [18] of the hyperfine structure at temperatures above about 30 K is due to the fluctuations of the increasingly disordered Ho moments. We also concluded the same in the previous study [18]. However at higher temperatures the quasielastic scattering went beyond the dynamic window of the backscattering BASIS spectrometer and therefore could not be investigated in details properly. In the present investigation with the CNCS and OSIRIS spectrometers with somewhat lower resolution but with much higher dynamic ranges we could investigate the temperature dependence of the quasielastic scattering in detail more accurately. We have also studied in addition the temperature evolution of low energy crystal-field excitations between accidental ground doublet of  $\text{Ho}^{3+}$  ion. The energy width of the crystal-field excitation is much larger than the instrumental resolution function. The increased width can be due to the coupling of phonons with the crystal field or due to other similar coupling processes. This is still an open issue and needs further detailed single crystal investigations.

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