Possible undercompensation effect in the Kondo insulator (Yb,Tm)B$_{12}$


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The effects of Tm substitution on the dynamical magnetic response of Yb$_{1-x}$Tm$_x$B$_{12}$ (x = 0, 0.08, 0.15, and 0.75) and Lu$_{0.92}$Tm$_{0.08}$B$_{12}$ compounds have been studied using time-of-flight inelastic neutron scattering. Major changes were observed in the spectral structure and temperature evolution of the Yb contribution to the inelastic response for a rather low content of magnetic Tm ions. A sizable influence of the RB$_{12}$ host (YbB$_{12}$, as compared to LuB$_{12}$ or pure TmB$_{12}$) on the crystal-field splitting of the Tm$^{3+}$ ion is also reported. The results point to a specific effect of impurities carrying a magnetic moment (Tm, as compared to Lu or Zr) in a Kondo insulator, which is thought to reflect the “undercompensation” of Yb magnetic moments, originally Kondo screened in pure YbB$_{12}$. A parallel is made with the strong effect of Tm substitution on the temperature dependence of the Seebeck coefficient in Yb$_{1-x}$Tm$_x$B$_{12}$, which was reported previously.

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I. INTRODUCTION

Among strongly correlated electron systems, Kondo insulators are considered promising candidates for the design of high-performance low-temperature thermoelectric materials because of their rather high Seebeck thermoelectric power coefficient (TEP) coefficients (hundreds of microvolts per Kelvin) [1]. Recently a new series of Yb$_{1-x}$Tm$_x$B$_{12}$ solid solutions, based on the archetype Kondo insulator YbB$_{12}$, has been prepared [2]. It was shown that partial substitution of Yb by Tm ions results in a considerable enhancement of the thermoelectric power [2] in the temperature range 15–150 K, whereas no such effect is observed in the case of Lu substitution [3] (Fig. 1). Lu is isovalent to Tm but carries no magnetic moment owing to its filled f-electron shell. Therefore, the thermoelectric enhancement has to be somehow related to the magnetic moments of the substituent ions. Theoretical models or ab initio simulations are unfortunately not yet able to provide a quantitative description of these properties, even for undoped YbB$_{12}$. On the other hand, the microscopic behavior of the magnetic subsystem can be directly addressed by means of inelastic neutron scattering experiments.

The ground state of YbB$_{12}$ is a nonmagnetic singlet with dynamical antiferromagnetic correlations [4]. It transforms to a single-site spin-fluctuation regime above 60 K, with a characteristic spin-fluctuation temperature $T_d$ on the order of 100 K. The low-temperature regime is characterized by the existence of both a charge [5] and a spin [6] gap. In addition, a resonance mode (RM) of spin-exciton type with sizable dispersion was shown to exist at about 15 meV, below the spin-gap edge, for temperatures lower than about 40 K [7,8]. A cooperative state thus appears to form in this temperature range as a result of Kondo-like compensation effects in the strongly correlated electron system.
of ytterbium and thulium oxides performed under vacuum at 1700 °C. $^{11}$B isotope (99.5% or 99.3% enrichment) was used in order to reduce neutron absorption. The materials were subsequently remelted under Ar pressure using the traveling-solvent floating-zone technique. For $x = 0.15$ and 0.75, single crystals of satisfactory quality (few grains with a mosaic spread of 2.5 deg) with masses of a few grams could be grown by this method. In some cases, after checking by x rays, the samples were powdered and etched with nitric acid to remove the YbB$_6$ phase. X-ray diffraction measurements confirmed all compounds to have the fcc structure with the expected lattice parameter.

A Lu$_{0.92}$Tm$_{0.08}$B$_{12}$ sample was also prepared using the same method. In order to single out the influence of Tm ions on the original magnetic signal from Yb, a quantitatively reliable procedure is needed for subtracting the Tm contribution from total magnetic scattering intensity. This task is complicated by the strong neutron magnetic scattering cross section of Tm$^{3+}$, larger by about a factor of 3 than that of Yb$^{3+}$, and by the qualitative difference between their respective spectral shapes (narrow peaks for Tm and distributed for Yb). A direct measurement of the Tm contribution in a magnetically “inert” reference compound is therefore required.

Measurements of Yb$_{12}$ and Lu$_{12}$ samples from previous studies [6] were repeated in the present experiments, mainly to allow comparisons between Tm-substituted and unsubstituted compounds to be performed on spectra obtained under identical conditions. Pure Lu$_{12}$ also served as a reference for subtracting phonon contributions when data could not be collected at sufficiently large momentum transfers ($\geq 7$ Å$^{-1}$).

**B. Experimental conditions**

A first series of neutron measurements was performed on the thermal-neutron time-of-flight spectrometer MERLIN at ISIS (RAL). This machine has a moderate resolution and a detector array covering a large solid angle, which allows collective effects to be studied using single crystals. In this experiment we have investigated the spin dynamics in Yb$_{1-x}$Tm$_x$B$_{12}$ ($x_{\text{Tm}} = 0.15, 0.75$) over a wide energy range, using incident neutrons of energy $E_i = 80$ meV (resolution $\Delta E = 5$ meV at zero energy transfer). The samples were single crystals with masses of 2.78 and 9.33 g, respectively (for $x_{\text{Tm}} = 0.75$ the sample actually consisted of two separate pieces). A LuB$_{12}$ powder specimen was used to estimate the nonmagnetic contribution to the measured spectra.

The measurements were carried out at $T = 6$, 75, 150, and 250 K for $x_{\text{Tm}} = 0.15$ by rotating the crystal around the vertical axis in order to collect the whole four-dimensional momentum-energy map. For $x_{\text{Tm}} = 0.75$, cooperative effects are expected to be less pronounced, owing to the lower Yb content, and the corresponding spectra were thus recorded only for one fixed sample rotation angle at two temperatures, $T = 7$ and 150 K.

To get more detailed information in the low-energy range (quasielastic region and near the spin-gap edge), we performed extensive measurements on the IN4C time-of-flight spectrometer at the ILL. Only powder samples with $x_{\text{Tm}} = 0$, 0.08, and 0.15 were used in that experiment. The incoming energy was $E_i = 36$ meV, giving an energy resolution $\Delta E = 1.75$ meV (pyrolytic graphite PG[002] monochromator) at zero energy transfer. Measurements were done in the temperature range $2 < T < 80$ K.

The powdered samples were enclosed in flat sachets folded from 28 μm thick Al foil, with a total area of 40 × 20 mm$^2$ and a controlled thickness of 2 mm. The total mass of powder was around 4 g for each sample, and the total amount of Al in the beam was less than 0.5 g, guaranteeing a low level of contamination by Al scattering. Separate measurements of the empty Al container and of a vanadium standard were used to correct the experimental spectra from the nuclear background and for detector calibration.

Because of the relatively low energy of incident neutrons on IN4C, the momentum transfer achieved for the largest accessible scattering angle was not sufficient to fully suppress the magnetic signal. The phonon background thus had to be determined indirectly from the corresponding LuB$_{12}$ spectra (see below). The uncertainty in extracting the magnetic signal was further reduced by restricting the data treatment to detector groups with low scattering angles, from $2\Theta = 13^\circ$ to $32^\circ$ ($2\Theta = 22^\circ$), for which the relative weight of phonon scattering is weakest.

After background subtraction and application of instrumental corrections (empty can contribution), the spectra were remapped on a linear energy scale and normalized to a fixed number of RB$_{12}$ formula units. Energy dependent transmission corrections for each sample were also applied. The transmission coefficient at zero energy transfer was within the limits of 0.70 to 0.75 for all samples measured.
III. RESULTS

A. Wide energy range (MERLIN)

In the single-crystal measurements we expected to observe some extra magnetic scattering near the $L$ point, $q = (1/2, 1/2, 1/2)$, reminiscent of the resonance mode previously observed in YbB$_{12}$ [4,7]. This expectation, however, was not fulfilled, even for the compound with the lower Tm content ($x_{\text{Tm}} = 0.15$). The experimental observation is that no emergence of an extra signal, besides the contribution from Tm, could be detected close to the $L$ point at low momentum transfer ($|Q| \sim 1 \, \text{Å}^{-1}$) with decreasing temperature.

A preliminary analysis was thus done by averaging the spectra over all sample rotation angles and treating the result as polycrystal data [12]. The phonon contribution was then subtracted using the standard procedure for polycrystalline samples [13]. The obtained magnetic spectra are shown in Fig. 2. From this plot one sees that the Tm crystal-field (CF) contribution (total magnetic cross section $\sigma_{\text{mag}} = 35$ b) dominates in the spectra for Yb$_{0.25}$Tm$_{0.75}$B$_{12}$ (b), and still seems to give a sizable contribution in the case of Yb$_{0.85}$Tm$_{0.15}$B$_{12}$ (a). However, the most intense peaks are located at $E_1 \approx 7.5$ meV and $E_2 \approx 14$ meV, and the upper transition energy $E_3$ does not exceed 30 meV, in agreement with the results obtained for TmB$_{12}$ [11]. The magnetic signal above this limit thus arises from Yb alone and can be treated unambiguously.

At low temperature, both samples exhibit a pronounced broad peak at an energy of about 40 meV, similar to that previously reported for undoped YbB$_{12}$ [6]. In the latter compound, the peak was suppressed by increasing temperature to 60 K, giving place to a broad quasielastic signal. A similar effect seems to occur in Yb$_{0.85}$Tm$_{0.15}$B$_{12}$ [Fig. 2(a)]. For Yb$_{0.25}$Tm$_{0.75}$B$_{12}$ [Fig. 2(b)], on the other hand, the temperature evolution appears to be dominated by the effect of the detailed-balance factor for Tm-originated excitations in the region below 30 meV and perhaps for Yb-originated signal at higher energies.

To summarize this part, the general structure of the Yb magnetic excitation spectra above the energy range of Tm-related excitations seems to be similar to that observed in undoped YbB$_{12}$, despite the fact that no clear evidence of the dispersive RM-like excitation around $L$ point could be found in the present single-crystal study. Possible changes due to Tm substitution have to be searched for in the low energy transfer range. It is thus worthwhile to focus on the study of spin gap and near-edge region with increased resolution. Single-crystal measurements, on the other hand, may not be critical at this stage, especially if one recalls that, for pure YbB$_{12}$, the near-edge structure, and in particular the RM, were clearly identified in the powder experiments.

B. Spin-gap energy range (IN4C)

In this part of the work, a major experimental issue was the separation of the magnetic spectral response due to Yb from that due to the Tm CF transitions, which clearly dominates the inelastic neutron spectra. To this purpose, we have measured not only Yb$_{1-x}$Tm$_x$B$_{12}$ compounds with three different concentrations $x_{\text{Tm}} = 0, 0.08$, and 0.15, but also one Lu$_{0.92}$Tm$_{0.08}$B$_{12}$ and one pure LuB$_{12}$ sample, in order to determine the experimental magnetic signal from Tm under identical experimental conditions (same instrument, incident energy, energy resolution, etc.). The results of the measurements on LuB$_{12}$ and Lu$_{0.92}$Tm$_{0.08}$B$_{12}$ at 2 K are shown in Fig. 3, along with a fit of the phonon (for LuB$_{12}$ solid

![FIG. 2. (Color online) Magnetic spectral response of (a) Yb$_{0.85}$Tm$_{0.15}$B$_{12}$ and (b) Yb$_{0.25}$Tm$_{0.75}$B$_{12}$ measured on MERLIN (ISIS) with incident neutron energy $E_0 = 80$ meV and energy resolution $\Delta E_0 = 5$ meV at different temperatures, reduced to $Q = 0$ according to the Tm$^{3+}$ form factor. Arrows indicate the positions of the thulium CF excitations defined for TmB$_{12}$ at low temperature [9]. Inset in frame (b) same data plotted on an expanded scale.](image-url)

![FIG. 3. (Color online) Spectra obtained on IN4C (ILL) at incident neutron energy $E_0 = 36$ meV and scattering angle (2θ) = 22° for LuB$_{12}$ (open circles) and Lu$_{0.92}$Tm$_{0.08}$B$_{12}$ (closed circles) measured at $T = 2$ K; a vanadium spectrum ($T \sim 100$ K) is shown by open diamonds; the solid line denotes the fit to the LuB$_{12}$ spectrum, representing the phonon contribution to the scattering function. Inset: magnetic component of the Lu$_{0.92}$Tm$_{0.08}$B$_{12}$ spectra at 2, 50, and 100 K (dots, open squares, triangles, respectively), associated with the Tm$^{3+}$ CF excitations, after subtraction of the phonon contribution; the line is a fit to the spectrum at $T = 2$ K by Gaussian line shapes.](image-url)
line in the main frame) and magnetic (for Lu0.92Tm0.08B12 solid line in the inset) components. The temperature dependence of the magnetic signal is shown in the inset for the range between 2 and 80 K. One clearly distinguishes three transitions between CF levels, in good correspondence with the only results reported so far for pure TmB12 [11], and there is no significant shift or broadening of the CF peaks in the temperature range studied. It can be noted that the strongest two CF excitations for Tm3+ occur, respectively, deep within the spin gap (≈7 meV) and close to the energy (≈14 meV) of the first peak in the phonon density of states, as well as to that of the RM in the magnetic response of YbB12.

The phonon contribution to the Yb1−xTmxB12 spectra was calculated from the LuB12 spectra measured at temperatures from 2 to 100 K. It is well established, from a previous lattice dynamics study [14], that the RE nuclear scattering cross section is responsible for the phonon peak at 15 meV in the phonon density of states of YbB12. In the incoherent approximation, the intensity of this peak reflects the total scattering cross section of the RE ion. Therefore, the scaling factor corresponding to the ratio of the total RE cross sections (σ tot[Lu:TM:Yb] = 1.09 3.25) was applied only to the amplitude of the 15 meV phonon peak in the smoothed scattering function of LuB12, in order to reconstruct a spectrum representing the estimated phonon contribution in Yb1−xTmxB12.

Figure 4 shows the magnetic components in Lu0.92Tm0.08B12 and Yb1−xTmxB12 for T = 2 K. Unexpectedly, a systematic shift of the Tm3+ CF peaks is observed between the Lu- and Yb-based compounds. Furthermore, the amplitude of this shift increases almost linearly with the excitation energy, according to a fit of the first two (strongest) peaks, with a relative shift ΔE/E, averaged over the three main peaks, of about 4%. It also appears to be independent of the Tm concentration and of the measuring temperature, at least up to 80 K, which is the range of interest here.1 In these materials the Tm3+ ions serve as a probe of the intrinsic CF potential in the LuB12 or YbB12 matrix, and clearly feel the difference between the two.

In the magnetic scattering spectra at T = 2 K is presented for pure YbB12 and the two Yb1−xTmxB12 solid solutions. The spectra basically consist of strong, resolution-limited, CF excitations from Tm3+, superimposed on a wide gapped spectrum similar to that of YbB12. To separate out the signal from Yb, one must subtract the (strong) Tm CF excitations and the (much weaker) phonon background.

The results, normalized to the number of Yb ions, are presented in Figs. 6(a)–6(c) for xTm = 0, 0.08, and 0.15. Several observations can be made from these plots. The first one is that, in YbB12, the narrow peak associated with the RM at 15 meV is already strongly suppressed when temperature is raised to no more than 30 K, i.e., just before the spin gap begins to fill. This is in good agreement with our recent single-crystal data [8], which demonstrated the complete suppression of the RM at q = (1/2, 1/2, 1/2) above 40 K, without a significant shift in its energy [Figs. 7(a) and 7(b)]. It also confirms a previous study of the temperature evolution of the magnetic spectral response in YbB12 powder [8,15], which concluded to a filling of the gap by a quasielastic signal [Fig. 7(c)].

In Figs. 6(b) and 6(c)2 the spectra exhibit some residual structure near 15 meV. However, its intensity represents less than 10% of that of the RM peak in pure YbB12, as shown in Fig. 6(a). Furthermore, the effect appears more pronounced in the compound with the larger Tm concentration, which is clearly unphysical. It could result from uncertainties in subtracting out the phonon background, or in separating the Yb magnetic signal from the strong Tm CF excitations. However, if one estimates the magnitude of this latter effect from the

1Above this temperature the Yb magnetic response is almost completely transformed from gaplike to spin-fluctuation-like (see Introduction).

2See also Figs. 8(c) and 8(d) below.
FIG. 6. (Color online) Yb contribution to the magnetic scattering spectra for Yb₁₋ₓTmₓB₁₂, obtained by subtracting phonon scattering and the Tm contribution (a) YbB₁₂, (b) Yb₀.₉₂Tm₀.₀₈B₁₂, and (c) Yb₀.₈₅Tm₀.₁₅B₁₂ at different temperature in the range 2–80 K. Measurements performed on IN4C (ILL), at incident energy E₀ = 36 meV (energy resolution ΔE₀ = 1.75 meV).

residual oscillation it causes in the quasielastic part of the Yb spectrum around E = 7.5 meV (the energy of the lowest Tm³⁺ CF peak), it seems that it cannot account entirely for the observed intensity. Another possible origin could be the existence of mixed excitation modes, in a spectral range where different types of interactions are involved in the excitations probed by neutrons. In any case, the striking result is that the RM peak at 15 meV is essentially suppressed by Tm substitution for such low concentrations as xTm = 0.15, and even xTm = 0.08.

Lastly, the spin-gap filling behavior differs depending on Tm concentration. Substituting 8% Tm results in a visible decrease of the temperature at which this process takes places. With 15% Tm, the spectrum changes qualitatively even at the lowest temperature, Tₘᵡᵢₙ = 2 K, the gap is already partly filled, and the filling is almost completed near 40 K.

IV. DISCUSSION

The experimental neutron scattering study performed in IN4C at low energy transfer and with improved energy resolution has revealed (i) the difference in the CF potential of YbB₁₂ with respect to those of LuB₁₂ and (from the data in Ref. [11]) TmB₁₂, which seem very close to each other, and (ii) the strong influence of the Tm impurities on the magnetic excitation spectrum of Yb in YbB₁₂, affecting its structure as well as its temperature evolution. We will now discuss these two points separately.

A. Thulium as a probe of CF potential in RB₁₂

The Tm magnetic excitation spectra are well described by a standard CF model for a site with cubic point symmetry. The
present data for $x_{\text{tm}} = 0.08, 0.15, \text{and } 0.75 \text{ are in very good agreement with the CF splitting scheme, with a } \Gamma_5 \text{ triplet ground state, suggested in Ref. [11], which corresponds to the set of parameters } W = 0.102 \text{ meV, } X = -0.063 \text{ in Lea, Leask, and Wolff’s (LLW) notations [16]. This triplet has strong transition matrix elements with the lower two excited states which are doublet } \Gamma_3 \text{ (the strongest) and triplet } \Gamma_4, \text{ at energies of about 7 and 14 meV, and much weaker ones with another triplet } \Gamma_3 \text{ and a doublet } \Gamma_3 \text{ at higher energies } (\sim 21 \text{ and } 28 \text{ meV). At low temperature, the magnetic triplet ground state with a large magnetic moment of about } 4.7 \mu_B \text{ naturally leads to a long-range order in pure TmB$_{12}$). The large magnetic moment in the CF ground state of Tm$^{3+}$ is also important to understand the effect of Tm impurities substituted on the Yb sublattice in YbB$_{12}$.}

In the present measurements, a remarkable difference in the energies of the Tm CF transitions has been observed between Lu- and Yb-based solid solutions. As noted in Sec. III, the shift amounts to a decrease by approximately 4% in the energy of each excited level (see, for instance, [16]), and it is related to the radial extension of the 4$f$ electron wave function of the ion and can be found in the literature, whereas $A_n$ depends only on the value and spatial distribution of charges around the RE site, thus being directly related to the CF potential from neighbor ions and conduction electrons. The values of $A_n$ associated with the observed splitting of the Tm$^{3+}$ multiplet ($J = 6$ in YbB$_{12}$ or LuB$_{12}$ (neglecting the above-mentioned 4% difference) are $A_4 \approx -9$ meV $\text{Å}^{-4}$, and $A_6 \approx -29$ meV $\text{Å}^{-6}$, in good agreement with those derived in Ref. [15] from the CF splitting of Er$^{3+}$ impurities in YbB$_{12}$ ($A_4 \sim -11$ meV $\text{Å}^{-4}$, and $A_6 \sim -22$ meV $\text{Å}^{-6}$). If, on the other hand, one tries to estimate the overall CF splitting in Yb$^{3+}$ based on the above results, the predicted value is only $\delta_{\text{CF}} \approx 11$ meV. This is about two times less than the energy of the single broad inelastic peak observed in the “high temperature” ($T > 70$ K) spectra of YbB$_{12}$, which is thought to reflect CF effects within the incoherent spin-fluctuation regime ($T_{\text{ch}} \sim 100$ K). It thus appears that the hybridization of the Yb $f$-electron states with conduction electron states in the intermediate valence state of YbB$_{12}$ results not only in a reduction of the effective CF potential acting on the Tm ion impurities but also in a strong increase of the energy splitting of the Yb atoms forming the host lattice.

It is known that the valence mixing can strongly affect the CF potential acting on paramagnetic impurities. This has been observed, for instance, in neutron experiments on (Ce,Pr)Al$_3$ [17], where Ce exhibits a very high degree of $f$-electron delocalization. Another limiting case is the heavy-fermion compound (Ce,Pr)Al$_3$ [17,18]. In the latter system the CF splitting of the Ce ions varies by as much as 20% when the heavy-fermion state forms with decreasing temperature, but no significant change occurs in that of paramagnetic Pr impurities.

Therefore, the present case of (Yb,Tm)B$_{12}$ seems closer to that of heavy-fermion systems, but with some incipient $f$-electron delocalization, which is weak but sufficient to produce a 4% decrease in the CF splitting of the impurity, together with a rather strong (100% instead of 20%) in the case of a classical heavy-fermion compound) renormalization of the CF splitting of the “host” atom.

One additional remark can be made in connection with the possibility of a structural distortion in LuB$_{12}$ (and YbB$_{12}$ as well) at temperatures below 80 K, which was suggested in a recent publication [19]. The CF is quite sensitive to such effects, as was shown in a variety of situations (amorphization of RE intermetallics, ionic substitution in solid solutions, etc.). Therefore, a very small lattice distortion occurring in the vicinity of a CF-sensitive ion may have drastic effects.

$^1$In particular there should be no mixing between the $f$-electron density and the surrounding charge distribution.

$^2$In such systems CF transitions are usually observed only for impurities, not for the host rare-earth ions, which are dominated by spin-fluctuation effects.
The limit of experimental accuracy (10% or less).

The inelastic part of the data for two inelastic peaks (plus the RM peak for \( \text{Tm} \langle \text{c}, \text{d} \rangle \)) is 

moment (the moment in the CF ground state of Yb3

of the gap at the higher \( \text{Tm} \) concentration. This can be seen with our previous measurements [6]. For \( \text{Tm} \langle \text{c}, \text{d} \rangle \), the RM excitation is known to exhibit

a strong effect on the RM of isoelectronic magnetic impurities (TM+) provides incentives for developing more realistic models.

Even before the beginning of our work on YbB12, a sharp low-energy excitation had been identified in the well-known mixed-valence system SmB6 [26]. This compound is currently undergoing a strong revival of interest as a possible example of a “topological insulator.” A detailed inelastic neutron scattering study of that excitation in isotopically enriched, single-crystal SmB6 and its solid solutions documented its dependence on the momentum transfer and the Sm valence state [26,27]. These experiments were recently revisited in the light of our work on YbB12 [8]. As in the latter compound, the excitation can be interpreted as an in-gap resonance mode, associated with the spin gap forming at low temperature in the KI regime. However, the physical origin may differ between the two systems [8]. Further understanding of the RM in SmB6 could likely be gained by studying the effect of magnetic impurity substitution, as was done in the present study for YbB12.

The evolution of the quasielastic signal is summarized in Fig. 9. The data points shown in this plot represent the integrated intensity of the quasielastic Lorentzian line shape used for fitting the spectral response in the spin-fluctuation regime [see, for example, Figs. 8(b) and 8(d)], when the suppression of the singlet ground state restores a magnetic density of states within the gap. This approach was used in previous work to represent the temperature evolution of the magnetic excitation spectrum in pure YbB12 and in Lu-substituted solid solutions. In the (Yb,Tm)B12 series, the half-width of quasielastic signal \( \Gamma_{\text{sf}}/2 \) stayed close to the value determined for YbB12 [21], on the order of 9 to 11 meV. This value represents the spin-fluctuation energy \( E_{\text{sf}} = k_{B}T_{\text{sf}} \) of the system.

The influence of a low concentration of TM ions on the Yb magnetic excitation spectrum is rather strong in comparison to that previously reported for other types of YbB12-based solid solutions [15,21,22]. Only in the case of Zr [22] was the effect comparable in magnitude (20% of nonmagnetic Zr comparable to 15% of Tm). In that case, however, the temperature evolution became slower in comparison with YbB12, and the spin-gap suppression process extended to rather high temperatures, whereas Tm substitution results in the spin gap being suppressed at lower temperature than in pure YbB12. With isoelectronic Lu substitution, which can be viewed as a mere dilution of Yb magnetic moments, the gap was not significantly reduced up to more than 50% Lu concentration [23]. We also recall that the application of an external magnetic field of up to 10 T (Fig. 7) produced no significant change either in the properties of the RM or in the temperature evolution of the spin gap [8].

The narrow in-gap mode found in YbB12 was initially interpreted within Riseborough’s simple spin-exciton picture [20]. Subsequent theoretical work focused on YbB12 considered additional effects from the crystal field [24], or from interactions between rare-earth ions [25]. The observation of a strong effect on the RM of isoelectronic magnetic impurities (TM+) provides incentives for developing more realistic models.

The second effect of Tm substitution is to gradually destabilize the spin gap. Initially (\( \text{TM} = 0 \) to 0.08) the temperature of the transition from the gap state to the spin-fluctuation regime goes down. Further increasing the concentration (\( \text{TM} = 0.15 \)) results in the replacement of the gap by a pseudogap down to the lowest temperature of the measurements (\( \text{T}_{\text{min}} = 2 \) K).

This is illustrated in Fig. 8, which presents selected spectra for \( \text{Yb}_{1-x}\text{Tm}_{x}\text{B}_{12} \) (\( \text{TM} = 0, 0.08, 0.15 \)) at \( T = 2 \) K [Figs. 8(a), 8(c), and 8(d)], and for pure \( \text{YbB}_{12} \) at \( T = 80 \) K [Fig. 8(b)]. The inelastic part of the data for \( T = 2 \) K can be fitted using two inelastic peaks (plus the RM peak for \( \text{TM} = 0 \)). At \( T = 80 \) K the \( \text{YbB}_{12} \) spectrum exhibits a clear Lorentzian quasielastic component, together with a single inelastic peak, in accordance with our previous measurements [6]. For \( \text{TM} = 0.15 \), the quasielastic component still exists at \( T = 2 \) K [Fig. 8(d)].

The main difference between the spectra for \( \text{TM} = 0.08 \) and 0.15 at \( \text{T}_{\text{min}} = 2 \) K thus turns out to be the partial filling of the gap at the higher TM concentration. This can be seen in Fig. 8(e), where the two data sets could practically be superimposed, within the limits of error bars, after subtracting out the residual quasielastic signal, represented by a Lorentzian line shape, from the \( \text{TM} = 0.15 \) spectrum.
FIG. 8. (Color online) Magnetic scattering spectra for YbB$_{12}$ at $T = 2$ K (a) and 80 K (b), and for Yb$_{1-x}$Tm$_x$B$_{12}$ (Tm contribution subtracted) at $T = 2$ K [$x = 0.08$ (c) and $x = 0.15$ (d)]. The dash-dotted line in frames (b) and (d) corresponds to a fit of the spin-fluctuation contribution by a quasielastic Lorentzian line shape (half-width $\Gamma_{qe}/223c \approx 9$ meV), taking into account the detailed balance factor. The dashed lines represent the decomposition of the inelastic magnetic signal into different contributions according to our previous interpretation of the magnetic response in YbB$_{12}$ [6,7], namely one narrow peak at 15 meV and two broad peaks at 20 and 40 meV at low temperature, and one single broad peak at about 25 meV at high temperature. (e) Compares the result obtained by subtracting a spin-fluctuation contribution associated with the in-gap density of states (represented by a quasielastic Lorentzian spectral function) from the experimental pseudogap spectrum of Yb$_{0.85}$Tm$_{0.15}$B$_{12}$ (closed squares) to the as-measured spectrum for Yb$_{0.92}$Tm$_{0.08}$B$_{12}$ (open circles).

To understand how such dramatic changes can occur over a narrow range of Tm concentrations, one can refer to a recent study [28] of another strongly correlated insulator FeSi, belonging to the family of transition metal silicides TSi ($T = $ Fe, Mn, Co). The substitution of Mn for Fe corresponds to the introduction of magnetic ions on the $d$-element sublattice (contrary to FeSi, MnSi exhibits long-range helimagnetic order at low temperature). It was found that a few percent of Mn change the physical (magnetic and transport) properties drastically. In Ref. [28] this was taken to demonstrate the possibility of achieving a non-Fermi-liquid behavior through the so-called “under-compensated Kondo effect,” in which there are too few mobile electrons to compensate the spin of unpaired electrons localized on impurity atoms. Similarly, in case of Tm impurities introduced on the Yb sublattice of YbB$_{12}$, the Tm$^{3+}$ magnetic moments can remain uncompensated, even at low temperature, causing inelastic scattering of the electronic carriers, while disrupting the coherent character of the ground state intrinsically connected to band electrons.

The extra scattering channels for charge carriers, along with the changes produced in the magnetic excitation spectrum, can have drastic effects on the thermoelectric properties of Yb$_{1-x}$Tm$_x$B$_{12}$. It was shown recently, in an extensive review article [29], that CF splitting and Kondo effect could contribute...
to the thermopower in different temperature ranges for Kondo systems. Assuming $\Delta_{\text{CF}}$ to be much larger (up to an order of magnitude) than the Kondo temperature $T_K$, two peaks can be observed in the temperature dependence of the thermoelectric coefficient a maximum, due to the CF contribution, at a temperature $T_1$ which is comparable to, or somewhat smaller than $\Delta_{\text{CF}}$, and a second peak at about $T_2 \sim T_K/2$, i.e., far below $\Delta_{\text{CF}}$.

In YbB$_{12}$, $T_1$ and $T_2$ can be roughly estimated, from the neutron scattering data, to be about $T_1 \sim 100–200$ K ($\Delta_{\text{CF}} \sim 230$ K) and $T_2 \sim 40–50$ K ($T_K$, $T_{\text{sd}} \sim 100$ K). As can be seen in Fig. 1, three notable features are present in the temperature dependence of the Seebeck coefficient $S(T)$ (i) one shoulder close to, or slightly above, 100 K, (ii) a peak at about 30–40 K, and (iii) another peak at 10 K. The first two are in qualitative agreement with the above estimates of $T_1$ and $T_2$. The third one appears to be less stable against Tm and, to some extent, Lu substitution, and could be related to the formation of the spin-exciton state responsible for the RM, which fully develops only below 30 K.

As shown above, increasing the Tm impurity concentration first suppresses the RM in the neutron spectrum. Accordingly, the feature in the TEP ascribed to the $T_{\text{sd}}$ energy scale and the spin-gap opening can expand with decreasing temperature, without interference from the RM (in-gap) mode formation. This effect is seen in Fig. 1, for $0 < x_{\text{Tm}} \leq 0.2$, as the suppression of peak (iii), together with a dramatic enhancement of peak (ii). At larger Tm concentrations ($x_{\text{Tm}} > 0.2$), hybridization effects and, consequently, the spin gap itself, are gradually suppressed, resulting in a fast decrease in the amplitude of peak (ii). Finally, only a broad negative minimum, likely related to the CF splitting of Yb, survives in the Tm-rich compounds ($x_{\text{Tm}} = 0.5–0.7$) in the vicinity of the insulator-metal transition in (Yb,Tm)B$_{12}$ (closing of the conductivity gap).

These considerations on a possible relationship between the magnetic excitation spectra and the temperature dependence of the Seebeck coefficient are only qualitative. No detailed theoretical model is currently available. We simply wanted to point out the intriguing correspondence between the effect of Tm and Lu impurities on the TEP, on the one hand, and on magnetic excitation spectra, on the other hand.

### V. CONCLUSION

The effect of isoelectronic substitution of magnetic Tm$^{3+}$ on the energy structure and temperature dependence of the dynamical magnetic response in Yb$_{1-x}$Tm$_x$B$_{12}$ solid solutions has been studied using inelastic neutron scattering. The spin-exciton-like resonance mode near 15 meV is steeply suppressed at the lowest measured Tm concentration of $x_{\text{Tm}} = 0.08$. The spin gap is replaced by a pseudogap at concentrations lower than 0.15. This is thought to reflect the presence of magnetic moments on Tm ions, even at the lowest temperature, because of their triplet CF ground state. The introduction of extra scattering centers for the band electrons results in a loss of coherence causing a modification, then the complete suppression, of the gapped excitation spectrum characteristic of the Kondo-insulator ground state in pure YbB$_{12}$. This effect bears interesting similarities to the “undercompensated Kondo effect” invoked to explain the influence of magnetic impurities in another well-known strongly correlated insulator FeSi. A correspondence was suggested between the concentration dependence of the magnetic response observed in this work and that of the TEP coefficient $S(T)$.

It was also found that the CF potential is different in YbB$_{12}$ from that in LuB$_{12}$ and in TmB$_{12}$. A plausible explanation is a change in the contribution of conduction electrons to the CF potential due to mixed-valence state of Yb, associated with a significant hybridization between localized $4f$ and conduction-band electrons.

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