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Gap-like magnetic excitation in the neutron-scattering response of $\text{Ce}_3\text{Bi}_4\text{Pt}_3$

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Abstract

$\text{Ce}_3\text{Bi}_4\text{Pt}_3$ is a mixed valence compound with a gap in its electronic excitation spectrum. An Arrhenius plot of resistivity gives $\rho \sim \exp(-\Delta/T)$, where $\Delta \approx 5$ meV. Inelastic neutron scattering experiments on $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ and also the isostructural lanthanum analogue reveal a gap in the spin-spin correlation function of $\text{Ce}_3\text{Bi}_4\text{Pt}_3$. At low temperatures the magnetic gap $\Delta_m = 12$ meV. Above 50 K the gap fills, becoming indiscernible at 150 K.

1. Introduction

Most of the heavy fermion or intermediate valence compounds have a metallic ground state which is either paramagnetic, antiferromagnetic or superconducting, and only a few 4f compounds show insulating behaviour at low temperature with a small energy gap Δ in the electronic excitation spectra. $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ appears to be intermediate valence and belongs to the insulating group [1]. The static susceptibility χ_{stat} is typical for an intermediate valence compound, *i.e.* at high temperatures it has Curie-Weiss behaviour, goes through a broad maximum at $T = 80$ K and reaches a finite value for $T \rightarrow 0$ (see Fig. 1). The Curie tail at low temperatures may be attributed to sample impurities and/or defects. Thermal expansion measurements support the classification of $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ as a possibly intermediate valence compound [2]. The linear coefficient γ of the specific heat for $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ is only $3.3 \text{ mJ (mol Ce)}^{-1} \text{ K}^{-2}$, which is three times smaller than that of $\text{La}_3\text{Bi}_4\text{Pt}_3$ and considerably smaller than the γ value expected from Bethe *ansatz* analysis of the static susceptibility ($\gamma_{\text{Bethe}} = 75 \text{ mJ (mol Ce)}^{-1} \text{ K}^{-2}$) [1]. The semi-conducting ground state of $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ explains the absence of a significant electronic contribution to the specific heat. Below 50 K the resistivity rises sharply and is clearly non-metallic [1]. Altogether, the transport properties can be described with an activation energy Δ of the order of 5 meV. Other 4f compounds with insulating ground states are TmSe ($\Delta \approx 2$ meV) [3], SmB_6

Fig. 1. Bulk susceptibility of $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ vs. temperature as measured in a SQUID magnetometer (full curve). The full circles are the susceptibility values calculated from the neutron data, scaled to the magnetometer value at $T=100$ K.

($\Delta \approx 3\text{--}4$ meV) [4], YbB_{12} ($\Delta \approx 6$ meV) [5], $\text{CeFe}_4\text{P}_{12}$ ($\Delta \approx 130$ meV) [6], CeNiSn ($\Delta \approx 0.5$ meV) [7] and CeRhSb ($\Delta \approx 0.4$ meV) [8]. Some of these compounds are intermediate valence.

The magnetic excitation spectra of 4f compounds with a metallic ground state have been intensively studied, but until recently there have been few neutron data available of 4f compounds with an insulating ground state.

2. Experimental details and analysis

$\text{Ce}_3\text{Bi}_4\text{Pt}_3$ and $\text{La}_3\text{Bi}_4\text{Pt}_3$ grow in small single crystals ($1 \times 1 \times 5$ mm³) from a bismuth flux. In this experiment we used about 30 g of powdered single crystals. The cubic ($I\bar{4}3d$) symmetry, with lattice constants $a_0 = 10.051$ and 10.130 Å for the cerium and lanthanum samples respectively [2], was verified by X-ray diffraction. The static susceptibility was measured on a number of single crystals from our samples to assure that the magnetic properties are identical to the ones previously reported [1].

The inelastic neutron-scattering measurements were performed at the Institut Laue–Langevin in Grenoble on the time-of-flight spectrometers IN4 and IN6. These enabled us to investigate the inelastic and quasi-elastic parts of the spectrum with different resolutions. Three different incident energies were used, $E_0 = 69$ and 17 meV on IN4 and $E_0 = 3.1$ meV on IN6. The respective energy resolutions are $\Delta E/E = 4.5\%$ on IN4 (full width at half-maximum, FWHM) and 3% on IN6 at the elastic position. The IN4 resolution function does not vary with the energy transfer; the IN6 resolution can be considered as constant within an energy window of ± 2 meV. For the data correction we measured the empty sample holder, cadmium, and a vanadium standard in the sample position. All data shown are corrected for background, absorption and detector efficiency and are scaled to absolute units of cross-section by the vanadium standard. The momentum transfer Q varies with the energy transfer and the data points of the magnetic spectra are *not*

corrected for the magnetic form factor $f(Q)$. However, fits to the magnetic spectra take the Ce^{3+} form factor into account for each time-of-flight channel and detector (*i.e.* before the detector grouping). In the spectra we always give the momentum transfer at the elastic position. The non-magnetic, isostructural compound $\text{La}_3\text{Bi}_4\text{Pt}_3$ was measured at the same temperatures and energies as the cerium sample in order to subtract the phonon scattering as accurately as possible.

3. Results

In Fig. 2 spectra of $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ are shown for small momentum transfers and several temperatures between 2 and 150 K. An $\text{La}_3\text{Bi}_4\text{Pt}_3$ spectrum for the same momentum transfers is shown in Fig. 3. The lanthanum data contain only nuclear scattering, *i.e.* incoherent elastic and phonon scattering, whereas the cerium data contain magnetic scattering in addition. The lanthanum

Fig. 2. $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ spectra for several temperatures at small scattering angles ($2\theta = 8.4^\circ$). The full curves include the nuclear intensities, *i.e.* incoherent elastic and phonon scattering.

Fig. 3. $\text{La}_3\text{Bi}_4\text{Pt}_3$ data for $T = 5$ K at small scattering angles ($2\theta = 8.4^\circ$). The other temperatures will be shown elsewhere [14].

spectra at low Q (Fig. 3) and the high Q data establish that most of the phonon scattering occurs at energy transfers smaller than 20 meV; the high energy tail is probably due to multiple phonon scattering. Owing to the Bose factor, the phonon intensities increase slightly with increasing temperature. In order to separate the magnetic from the nuclear scattering in the cerium data, the incoherent elastic peak has been described by the resolution function (vanadium) and the phonon scattering has been determined as follows. Comparison of the cerium and lanthanum data at high Q shows that the positions and widths of the phonon peaks are the same for both samples. Therefore we could fix the phonon positions and widths for the low Q cerium data from fits to the lanthanum data. The phonon intensities in the low Q cerium data were determined with reference to the low Q data of the lanthanum sample, allowing for the difference in the averaged nuclear scattering length ($\sigma_{\text{av}}(\text{Ce}) \approx 0.8 \sigma_{\text{av}}(\text{La})$). The result of the nuclear description is visualized by the full curves in Figs. 2(a)–2(f). After subtracting the nuclear intensities, we are left with the purely magnetic spectra (see Figs. 4(a)–4(f)). Since the elastic peak is about 25 times higher than the inelastic signal, this subtraction yields huge error bars in the elastic region (see open circles).

According to Fig. 4(a), the magnetic intensity at 2 K is zero for energy transfers smaller than 12 meV. Between 12 and 20 meV the intensity rises sharply and then falls off smoothly beyond. Neither the spectrum's shape nor the width of the magnetic gap, $\Delta_m \approx 12$ meV, changes when warming up to 25 K (Figs. 4(b) and 4(c)). At 50 K the magnetic gap is already partially filled whereas the intensity at the high energy edge of the spectrum starts to decrease (Fig. 4(d)). Generally the intensity shifts towards smaller energy transfers upon warming. At 100 and 150 K the spectra appear almost like a broad quasi-elastic distribution (Figs. 4(e) and 4(f)).

Since the observation of a gap in the magnetic excitation spectrum for $T \leq 25$ K and the rapid change of the spectrum between 25 and 100 K is a rather unusual result, we wanted to underpin the data presented above. We performed measurements with smaller incident energies, *i.e.* with better resolution, in order to rule out the chance that we missed magnetic intensity within the resolution width. In Fig. 5 spectra of $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ (full circles) and $\text{La}_3\text{Bi}_4\text{Pt}_3$ (open squares) are shown, measured with an incident energy of 17 meV at the same temperatures as the 69 meV data. Here we have not subtracted any nuclear scattering; the differences in the cerium and lanthanum spectra represent the magnetic intensity (the lanthanum data should be multiplied by the ratio of the nuclear scattering lengths to be more accurate). These data are consistent with the 69 meV data, *i.e.* below 25 K the magnetic intensity is zero within the displayed energy window (12 meV or less) and increases between 50 and 150 K. Additional measurements with even better resolution ($E_0 = 3.1$ meV) confirm that there is no magnetic intensity between 0.1 and 1.8 meV for temperatures below 25 K.

The ability of the data to yield the bulk susceptibility χ_{bulk} is a good verification of magnetic neutron results. The paramagnetic scattering function $S(Q, \omega)$ is related to the imaginary part of the dynamic susceptibility

Fig. 4. $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ spectra at small scattering angles ($2\theta = 8.4^\circ$) after subtraction of the nuclear scattering (areas under the curves in Figs. 2(a)–2(f)). The open circles mark the elastic peak, of which the error bars are enormous owing to the subtraction.

Fig. 5. 17 meV spectra of $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ (full circles) and $\text{La}_3\text{Bi}_4\text{Pt}_3$ (open squares) for several temperatures at small scattering angles ($2\theta = 8.4^\circ$). The difference in intensity between the cerium and lanthanum spectra is due to magnetic scattering.

$\chi''(Q, \omega)$, and the latter in turn can be expressed in terms of the bulk susceptibility via the Kramers–Kronig relation:

$$S(Q, \omega) \approx \left[1 - \exp\left(\frac{-\hbar\omega}{kT}\right) \right]^{-1} \chi''(Q, \omega) \\ \approx \pi\hbar\omega \left[1 - \exp\left(-\frac{\hbar\omega}{kT}\right) \right]^{-1} |f(Q)|^2 P(Q, \omega) \chi_{\text{bulk}} \quad (1)$$

$P(Q, \omega)$ is a spectral function which has to fulfil the normalization requirement $\int_{-\infty}^{\infty} P(Q, \omega) d\omega = 1$. In this particular case there is no straightforward spectral function for describing the magnetic data. At low temperatures the spectrum is certainly not lorentzian and above 50 K the spectra cannot be described by one line either (compare 17 and 69 meV spectra in Figs. 4 and 5). However, for the calculation of the static susceptibility the scattering function

has to be brought within parameters according to eqn. (1). We did that by fitting the spectra with several empirical inelastic lines, with the sole restriction that the same parameters had to describe the 17 and 69 meV data. The static susceptibility, calculated from the neutron data, reproduces the temperature dependence of the bulk susceptibility (see full circles in Fig. 1). Since the neutron susceptibilities in absolute units exceed the susceptometer values by about 15%, we have scaled them to the 100 K value of the bulk susceptibility. However, the integrated magnetic intensity in absolute units of cross-section underestimates the Ce^{3+} cross-section by 30%. Having in mind that the integrated magnetic intensity is given by $\sigma_{\text{mag}} = 4\pi \int_{-\infty}^{\infty} S(Q, \omega) d\omega$ (more or less the area under the spectra) and that the static susceptibility takes into account magnetic intensities according to $1/\omega$ (the bigger the energy transfer, the smaller is the contribution to χ), we draw the following conclusion: we have correctly determined the magnetic intensity in the energy window covered (60 meV or less) but have possibly missed intensity at energy transfers beyond 60 meV.

4. Discussion

The broad structureless magnetic response of $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ beyond 20 meV compares well with the spectra of metallic intermediate valence compounds [9]; however, a magnetic gap, as found in $\text{Ce}_3\text{Bi}_4\text{Pt}_3$, has not yet been reported for any cerium compound. Therefore we will present a brief comparison of our neutron-scattering results and those of related compounds that exhibit a gap in their electronic spectrum. To our knowledge only neutron data of TmSe [10] and SmB_6 [11] have been published. TmSe is not well suited for a comparison since in thulium, as opposed to cerium, samarium and ytterbium, two magnetic 4f configurations are involved, and for SmB_6 no statement can be made concerning the existence of a magnetic gap from the existing data [14]. However, the behaviour found in $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ seems to be confirmed by preliminary CeNiSn [12] and YbB_{12} [13] data. In both cases a gap appears to be present in the magnetic excitation spectrum and $\Delta_m \geq 2\Delta$.

To address the possible appearance of a gap in the spin-spin correlation function and its relationship to the transport gap, we have developed a simple model which will be presented elsewhere [14]. The dynamic susceptibility $\chi(Q, \omega)$ has been calculated within the framework of the spin- $\frac{1}{2}$ Anderson lattice model and we are able to show that gaps in the magnetic spectrum with $\Delta_m > 2\Delta$ can occur. However, in order to be more quantitative, the model would have to contain more realistic assumptions, *e.g.* a temperature-dependent hybridization. For a direct comparison between theory and experiment it will be essential to determine experimentally the Q dependence of Δ_m .

5. Summary

Static susceptibility and thermal expansion measurements indicate that $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ is mixed valent like, whereas transport measurements reveal a gap of $\Delta \approx 5$ meV in the electronic excitation spectrum. We report the magnetic response of $\text{Ce}_3\text{Bi}_4\text{Pt}_3$, at temperatures between 2 and 150 K, determined with incident neutron energies of 3.1, 17 and 69 meV. The isostructural, non-magnetic reference compound $\text{La}_3\text{Bi}_4\text{Pt}_3$ was also studied at the same temperatures and energies so that phonon contributions could be subtracted accurately. At 2 K a gap $\Delta_m \approx 12$ meV is present in the magnetic excitation spectrum: the 3.1, 17 and 69 meV data consistently show that the magnetic intensity is zero for energy transfers less than 12 meV, rises sharply between 12 and 20 meV and falls off smoothly beyond. Above 50 K the gap in the spin-spin correlation function starts to fill. The neutron results reproduce the temperature dependence of the bulk susceptibility.

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