Spin gap in $CeFe_4Sb_{12}$ studied by heat capacity and inelastic neutron scattering

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The magnetic properties of the skutterudite compound $CeFe_4Sb_{12}$ have been investigated by heat capacity and inelastic neutron scattering measurements. Heat capacity measurements reveal a broad peak centered at 125 K, whose magnitude is much larger than that expected from a Schottky anomaly due to a cubic crystal electric field. At 5 K, inelastic neutron scattering experiments clearly show the existence of a broad magnetic peak at 40(3) meV. The absence of quasielastic scattering at this temperature, together with the almost total account of the magnetic signal in the inelastic peak, shows that the excitation has a different origin than a splitting of the electronic levels due to crystal field energy. Instead, we propose a model in which the signal originates from inelastic excitations across two hybridization bands near the Fermi energy, usually referred to as a spin gap. A simple phenomenological two-level model can account for the peak in the specific heat, with a spin-gap energy of 36(2) meV, which is in very good agreement with the inelastic scattering data. Further, at 300 K, the inelastic response becomes purely quasielastic, which is in agreement with the theoretical calculations. Interestingly, the spin-gap energy in $CeFe_4Sb_{12}$ exhibits a universal scaling behavior with the Kondo temperature T_K. The relation between the spin-gap energy and the associated anomalies in the heat capacity or thermal expansion is discussed for a series of Ce- and Yb-based compounds.

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I. INTRODUCTION

For more than a decade, the filled skutterudite compounds with the general formula RM_4X_{12} (R=rare) or alkaline earth, actinide or alkaline metal, M=transition metal, and X=P, As, or Sb) have attracted considerable attention primarily because of their enhanced thermoelectric properties[1] and potential applications in future solid state devices. These compounds have generated a great deal of interest in the physics community due to their diverse and complex physical properties, as seen from the existence of many exotic ground states, notably, unconventional superconductivity,[2] quadrupolar ordering,[3] metal-insulator transition,[4] non-Fermi liquid behavior[5–7] and hybridization gap (or pseudogap) semimetal.[7–10] Among these properties, the hybridization gap is one of the most investigated phenomena in many Ce-based compounds, such as in $CeRu_4Sb_{12}$, $CeFe_4Sb_{12}$, and $CeOs_4Sb_{12}$.[7–10] A hybridization gap is a gap in the electronic density of states (DOS) near the Fermi energy (E_F), which opens due to the presence of strong hybridization between localized $4f$ electrons and conduction electrons. Interestingly, despite the existence of a hybridization pseudogap, these compounds exhibit a non-Fermi liquidlike (NFL) behavior at low temperatures.[6,7] We have previously shown that all the aforementioned Ce compounds have very similar physical properties,[7,10] although isolating the contribution of the Ce ion in $CeFe_4Sb_{12}$ was found to be difficult due to the large contribution of Fe to the physical properties at low temperatures, especially to the magnetic properties.[7]

Recently, both charge and spin pseudogaps have been detected in $CeRu_4Sb_{12}$ by optical spectroscopy and inelastic neutron scattering experiments, respectively, and have the same order of magnitude while having slightly different values.[8,9] Interestingly, the ratio between these values of energy agrees well with existing theories.[11] In optical studies, within a first order dipole approximation, one observes a direct gap at wave vector Q=0, while in inelastic neutron scattering studies, one normally observes an indirect gap with $Q \neq 0$. By going beyond the first order approximation (i.e., nondipolar) and invoking two phonon processes, one can also observe two gaps simultaneously, direct and indirect, through an optical study.[12] This is the case for $CeOs_4Sb_{12}$, for which both optical and inelastic studies reveal the presence of two energy gaps.[10,12] Currently, the physics of such spin/charge gap systems remains only partially understood, particularly the NFL behavior in the presence of a hybridization gap. In order to establish a more accurate picture and allow for theoretical developments, it is crucial to understand the nature of the hybridized bands near the Fermi level. In particular, it is extremely valuable to study systematically spin and charge gaps in various strongly correlated electron systems.

Very recently, we have observed an activation energy of about 25 meV in $CeFe_4Sb_{12}$ by Hall effect measurements.[7] The transport pseudogap of 50 meV deduced from these experiments agrees very well with the peak observed in the optical conductivity at 50 meV in $CeFe_4Sb_{12}$,[13] suggesting that the physics of this system is reminiscent of that found in its Os and Ru analogues, i.e., opening of a gap near E_F. In the present work, the presence of a transport gap in $CeFe_4Sb_{12}$ has been directly investigated by inelastic neutron scattering (INS) measurements. At low temperature, we observe a broad inelastic peak in the INS spectra, centered at

40(3) meV, as well as the absence of quasielastic scattering. The scattering intensity of the INS peak alone gives a full value of the paramagnetic effective moment of a degenerate $J=5/2$ manifold of the Ce^{3+} ions. This observation, together with the lack of quasielastic scattering, violates what is expected from a crystal electric field excitation and strongly supports the existence of a spin gap near E_F, as anticipated by earlier work.[7,13] We also show that a simple two-level phenomenological model for the spin gap allows us to account quantitatively for the anomaly observed in the heat capacity, in contrast to that calculated from a crystal electric field (CEF) model. An energy gap of 36(2) meV can be extracted from the heat capacity measurement, in very good agreement with the neutron work. Finally, by comparison with other Ce- and Yb-based compounds, we propose a universal behavior and we show that two scaling relationships between the spin gap and the macroscopic physical properties hold for a variety of systems.

II. EXPERIMENT

We have synthesized 20 g of polycrystalline samples of $LaFe_4Sb_{12}$ and $CeFe_4Sb_{12}$ by direct reaction at high temperature in a carbon-coated quartz tube. The starting materials were Ce, La (99.9%), Fe (99.9999%), and Sb (99.9999%). The reacting materials were heated at 1050 °C during 48 h, water quenched, and finally annealed for 4 days at 700 °C. The samples obtained were almost single phase with minor inclusion of $CeSb_2$ or $LaSb_2$, as indicated by x-ray diffraction and energy dispersive x-ray spectroscopy experiments.[5,7,14]

The magnetic susceptibility has been measured between 2 and 400 K in applied magnetic field of 7 T using a commercial MPMS superconducting quantum interference device magnetometer from Quantum Design. The heat capacity has been measured between 2 and 300 K using a microcalorimeter and a commercial PPMS apparatus from Quantum Design. Inelastic neutron scattering experiments have been carried out using the time-of-flight chopper spectrometer HET at the ISIS pulsed neutron source (UK) with incident energies (E_i) of 150 and 250 meV at 5 and 300 K. The observed scattering intensity was converted into absolute units of mb/sr/meV/f.u. by normalizing the measured scattering intensity to that from a standard vanadium sample.

III. RESULTS AND DISCUSSION

A. Magnetic susceptibility

In Fig. 1, we report the magnetic susceptibility of $CeFe_4Sb_{12}$ between 2 and 400 K. It is to be noted that the magnetic susceptibility was measured in an applied field of 7 T in order to suppress the signal of the residual free Fe impurity. This is the first determination of the magnetic susceptibility of this compound above 300 K. The results below 300 K are in good agreement with previous results in the literature.[7,14–18] We note that the broad hump around 125–150 K leads to an unreliable determination of both the Curie-Weiss temperature (μ_{eff}) and effective moment (θ_{CW}) using data only below 300 K because the Curie-Weiss law is not obeyed below 250 K. This can therefore explain why the values found in the literature for the effective paramagnetic moment and Curie-Weiss temperature are so different. Notably, the values found for μ_{eff} were between $2.4\mu_B$ and $4.15\mu_B$.[7,14–18] From the present measurements, we find $\mu_{\text{eff}}=3.45(1)\mu_B$ and $\theta_{\text{CW}}=-32(3)$ K for $250<T<400$ K). The value extracted here is in very good agreement with calculations since for $CeFe_4Sb_{12}$, contributions to the magnetic susceptibility from Ce and Fe must be taken into account. We therefore have used two methods for estimating the contribution of the Ce ions to the magnetic properties to check the reliability of our estimation. In the first method, we use the following formula:

$$\mu_{\text{eff}}(\text{Ce}) = \sqrt{[\mu_{\text{eff}}(\text{exp})]^2 - [\mu_{\text{eff}}(\text{Fe})]^2}, \quad (1)$$

where μ_{eff} (Ce) is the effective magnetic moment of Ce, μ_{eff} (Fe) is the effective magnetic moment of Fe and is estimated from the experimental value found for $LaFe_4Sb_{12}$ where only Fe is magnetically active, and μ_{eff} (exp) is the observed total experimental value for $CeFe_4Sb_{12}$. Taking μ_{eff} (Fe) $=2.26(11)\mu_B$ found for $LaFe_4Sb_{12}$,[5] we find μ_{eff} (Ce) $=2.60(10)\mu_B$ for the temperature range of 250–400 K. This value is in very good agreement with the theoretical value of $2.53\mu_B$ for Ce^{3+} with a total angular momentum of $J=5/2$.

In the second method, we have subtracted the magnetic susceptibility of $LaFe_4Sb_{12}$ (Ref. 5) from that of $CeFe_4Sb_{12}$ for the estimation of the Ce contribution χ(Ce) to the magnetic susceptibility in $CeFe_4Sb_{12}$. We have already used this procedure in a previous publication and have discussed that this was a reasonable procedure for $T>50$ K.[7] For $T>300$ K, we extrapolate the magnetic susceptibility of $LaFe_4Sb_{12}$ up to 400 K using the Curie-Weiss law determined for $LaFe_4Sb_{12}$ above 150 K.[5] In Fig. 1, χ(Ce) and its inverse are reported. We see that there is a clear maximum at

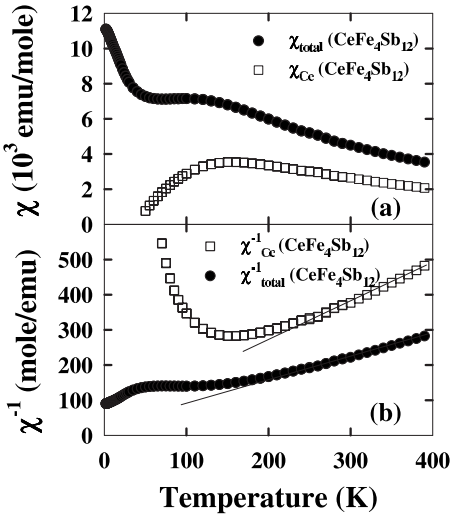

FIG. 1. (a) Magnetic susceptibility of $CeFe_4Sb_{12}$ measured at 7 T and its Ce contribution after subtraction of the iron contribution determined from the magnetic susceptibility of $LaFe_4Sb_{12}$ (see text for details). (b) Inverse of the magnetic susceptibility of $CeFe_4Sb_{12}$ measured at 7 T and its Ce contribution. The solid lines correspond to fitting of the experimental data with the Curie-Weiss equation.

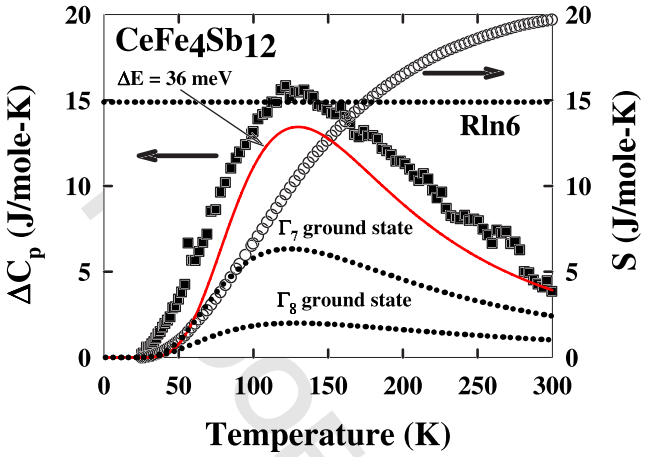

FIG. 2. (Color online) Ce contribution to the heat capacity of $CeFe_4Sb_{12}$ (filled symbol). The lines represent the theoretical calculations based on the pseudogap model (solid line) and on the crystal electric field models (dotted lines). Right: thermal variation of the entropy corresponding to the Ce contribution of the heat capacity of $CeFe_4Sb_{12}$ (open symbols).

about 140–150 K, in agreement with our previous results.[7] Moreover, if we fit χ^{-1}(Ce) between 290 and 400 K, we find μ_{eff} (Ce)=2.65(2)μ_B and θ_{CW}=−30(7) K. This result is in good agreement with the one obtained from the first method. Therefore, this indicates that the contribution of the Fe to the magnetic properties is the same in $CeFe_4Sb_{12}$ and in $LaFe_4Sb_{12}$, at least at high enough $T(T>50$ K). It is to be noted that the data of χ(Ce) at low temperatures (below 50 K) are not reliable due to the strong contribution of the Fe ion, as seen from the susceptibility of $LaFe_4Sb_{12}$,[7] and hence not given in Fig. 1.

B. Heat capacity

Figure 2 shows the Ce contribution of the heat capacity of $CeFe_4Sb_{12}$, which has been obtained by subtracting the heat capacity of $LaFe_4Sb_{12}$ from that of $CeFe_4Sb_{12}$. As explained in our preliminary report,[7] and similarly to what is observed for the magnetic susceptibility, the heat capacity of $LaFe_4Sb_{12}$ is larger than that of $CeFe_4Sb_{12}$, below 25 K. This is probably due to the larger density of states at low temperature in the La compound than in the Ce compound[19] and to the larger contribution of spin fluctuations related to iron in the La compound, as can be deduced from the larger Sommerfeld coefficient in $LaFe_4Sb_{12}$.[5,7,20,21]

In Fig. 2, we observe a Schottky-type anomaly with a maximum close to 125 K. This can be explained in three ways:

- by considering the effect of the cubic CEF splitting on the sixfold $J=5/2$ multiplet of the Ce^{3+} ion into a doublet (Γ_7) and a quartet (Γ_8),
- interaction between the CEF and the Kondo effect, as we have proposed in our preliminary report,[7,22,23] and
- the presence of a hybridization gap (or pseudogap), as observed in other Ce-based skutterudites.[10,11,24]

First, we consider the simple case of a Schottky anomaly arising from the cubic CEF effect alone (i.e., considering a hypothetical system where T_K is negligible with respect to the CEF energy gap Δ_{CEF}). Calculations (dotted lines) using either a doublet (Γ_7) or a quartet (Γ_8) ground state fail to reproduce the experimental result, particularly the magnitude of the peak in the specific heat measurement, as seen in Fig. 2. This behavior is consistent with our earlier work[7] showing that T_K and CEF would have the same temperature. This argument is reinforced by inspecting the variation of the entropy with temperature, found to be continuous without appearance of plateau at values of $R\ln 4$ or $R\ln 2$. This indicates that the low temperature Kondo temperature and the CEF splitting have the same order of magnitude.

As to the second case, there are some reports on the heat capacity of Kondo systems in the presence of CEF.[22,23] However, no simple analytical results have been reported, and the calculations show that the position of the heat capacity peak is related both to the value of the CEF splitting and to the Kondo temperature with a complex form. The case was considered by Kawakami and Okiji for the cubic symmetry[22] and by Desgranges and Rasul for a lower symmetry.[23] The thermal variation of the heat capacity is very close to the case where we can neglect the CEF [this is the case for which the ratio of the CEF splitting Δ_{CEF} and the high temperature Kondo temperature T_K (or T_0 symbol used in Ref. 22) for $J=5/2$ is between 0 and 1 and tends to 0], i.e., the case for the fully degenerate multiplet of Ce^{3+} ion with $J=5/2$. However, there is no analytical expression available for the temperature dependence of the heat capacity in this case, for both the modes discussed here, so we have not analyzed our data based on this approach. Further, the numerical calculations show that the peak height remains almost the same or reduces with the increase in the ratio of Δ_{CEF}/T_K, which suggests that this case is also not appropriate to explain the observed heat capacity data of $CeFe_4Sb_{12}$.

In the third case, where we consider that the Schottky-type anomaly is due to a hybridization gap (or pseudogap), we have the following simple phenomenological two-level model with a Schottky anomaly:[24]

$$\Delta C = Nk_B\left(\frac{\Delta E}{k_BT}\right)^2\frac{(2J+1)e^{\Delta E/k_BT}}{(2J+1+e^{\Delta E/k_BT})^2}, \qquad (2)$$

where ΔE is the hybridization gap energy. Assuming a full degeneracy of the ground state, $J=5/2$, we can reproduce well the experimental results, leading to $\Delta E=36(2)$ meV (solid lines in Fig. 2). This value is to be compared with the value of the gap $2E_g=50$ meV found from the Hall effect experiment.[7] When considering $J=3/2$ or $1/2$, the calculated height of the heat capacity peak is too small, which again suggests that the physics of $CeFe_4Sb_{12}$ is governed by full degeneracy of the sixfold $J=5/2$ multiplet. This simple phenomenological two-level model has the advantage of its simplicity, but does not take into account the detailed structure of the density of states, such as the width of the upper and lower hybridized bands as well as a finite residual DOS in the gap. However, this simple model has been successfully used to explain the heat capacity behavior in some Kondo semiconductors.[24] Further, we note that the analysis of the heat capacity presented here assumes that the gap energy is

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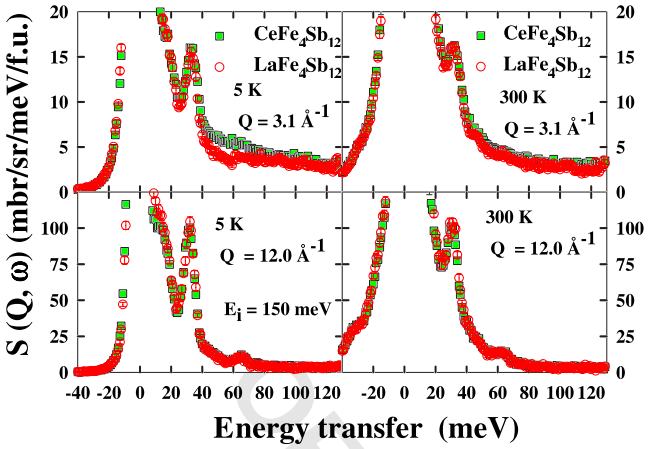


FIG. 3. (Color online) Inelastic neutron scattering spectra of $CeFe_4Sb_{12}$ and $LaFe_4Sb_{12}$ at 5 and 300 K, respectively. Data have been recorded with an incident neutron energy E_i=150 meV and are shown for different fixed Q values.

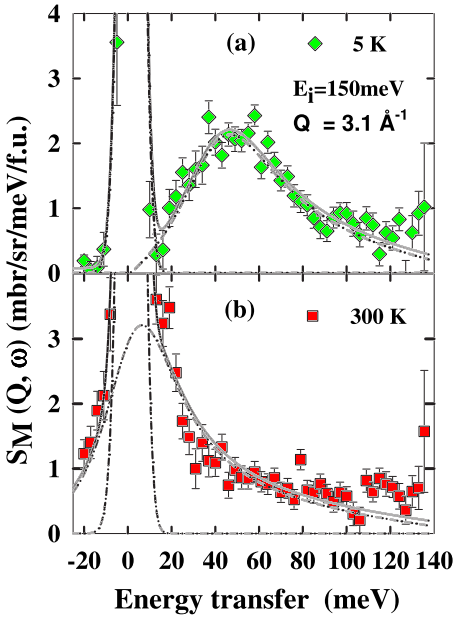


FIG. 4. (Color online) Inelastic neutron scattering spectra showing the Ce magnetic response for $CeFe_4Sb_{12}$ after subtraction of the nonmagnetic scattering at 5 and 300 K. The solid line represents the result of the refinement (see text for details). Dash-dotted lines show the separated contributions of the elastic, inelastic, and background signals.

independent of the temperature, in contrast to what is evidenced by inelastic neutron scattering experiments and discussed in the next section. At least, we cannot exclude that the formation of a hybridization gap could be influenced by its interaction with the CEF and the Kondo effect. Noticeably, in a theoretical work on the periodic Anderson model including the CEF effect, Hanzawa studied the role of the CEF effect on the formation of hybridization pseudogap[25] and discussed various cases depending on the relative strengths of the CEF and gap energy. When the gap and CEF energies are similar, it was found that some residual density of states exists in the pseudogap, leading to a semimetallic behavior with a large value of the Sommerfeld coefficient, as observed for CeNiSn (Ref. 26) and here in $CeFe_4Sb_{12}$.[7]

C. Inelastic neutron scattering

Figure 3 shows the inelastic neutron scattering spectra of $CeFe_4Sb_{12}$ and $LaFe_4Sb_{12}$ for low Q(3.1 Å^{-1}) and high Q(12 Å^{-1}); here Q is the magnitude of the wave vector transfer ($|Q|$) at 5 and 300 K. We can see that at 5 K and at low Q, between 40 and 90 meV energy transfer, the scattering intensity for $CeFe_4Sb_{12}$ is higher than that for $LaFe_4Sb_{12}$. This clearly indicates the presence of magnetic scattering above 40 meV and at 5 K in $CeFe_4Sb_{12}$. Furthermore, the scattering intensity at high Q is almost identical in both $CeFe_4Sb_{12}$ and $LaFe_4Sb_{12}$. It is to be noted that the intensity of magnetic scattering will decrease with increasing Q following the magnetic form factor squared, $F^2(Q)$, while the intensity of phonon scattering will increase with Q as Q^2. The observed similar scattering at high Q in both $CeFe_4Sb_{12}$ and $LaFe_4Sb_{12}$ indicates that they have similar phonon scattering contributions, as expected. The magnetic scattering in $CeFe_4Sb_{12}$ has been extracted using a method described in Ref. 9,

$$S(Q,\omega)_{\mathrm{mag}} = S(Q,\omega)CeFe_4Sb_{12} - S(Q,\omega)LaFe_4Sb_{12}\alpha,$$

where α=0.94 is the ratio of the total scattering cross section of $LaFe_4Sb_{12}$ and $CeFe_4Sb_{12}$. Figure 4 shows the estimated magnetic scattering in $CeFe_4Sb_{12}$ at 5 and 300 K. Interestingly, at 5 K, we can see a broad inelastic peak centered around 50 meV, while at 300 K, the magnetic response becomes clearly of the quasielastic type. This kind of temperature dependence of the magnetic signal has been observed in other skutterudite compounds such as $CeRu_4Sb_{12}$ (Ref. 9) and $CeOs_4Sb_{12}$ (Ref. 10) and also in the Kondo semiconductor $Ce_3Bi_4Pt_3$ (Ref. 27) and the metallic Kondo compound $YbAl_3$.[28] This observed temperature dependence of inelastic response is in agreement with the theoretical calculations of the dynamical susceptibility for Kondo insulators.[24] Furthermore, it is interesting to note the value of the threshold energy is ~16 meV and that of the peak position is ~50 meV; the latter is nearly three times the former. We will discus this point in more detail later in this section. We have fitted the broad magnetic inelastic peak at ~50 meV in the magnetic response of $CeFe_4Sb_{12}$ at 5 K using a Lorentzian spectral function that allows a determination of the energy of the inelastic peak, referred to as spin-gap energy Δ_{spin} =40(3) meV, and the linewidth [half-width at half maximum (HWHM)] of about 27(3) meV. At 300 K, the response is better fitted with a quasielastic peak (centered at zero energy) with a linewidth of 20(3) meV. It is interesting to compare the value of the susceptibility estimated through inelastic neutron scattering measurements with that determined using a conventional magnetometer. Using the sum rule for the uniform bulk susceptibility [the so-called Kramers-Krönig relation,[28] $\int \chi''(\omega)/\omega d\omega = \chi'(0)$], we have determined $\chi'(0)$ =2.8(4)$\times 10^{-3}$ emu/mole (see Fig. 1) at 5 and 2.7(2) $\times 10^{-3}$ at 300 K. These values are very close to the value of 2.4×10^{-3} emu/mole estimated from the Ce bulk magnetic susceptibility χ(300 K). Furthermore, a paramagnetic effec-

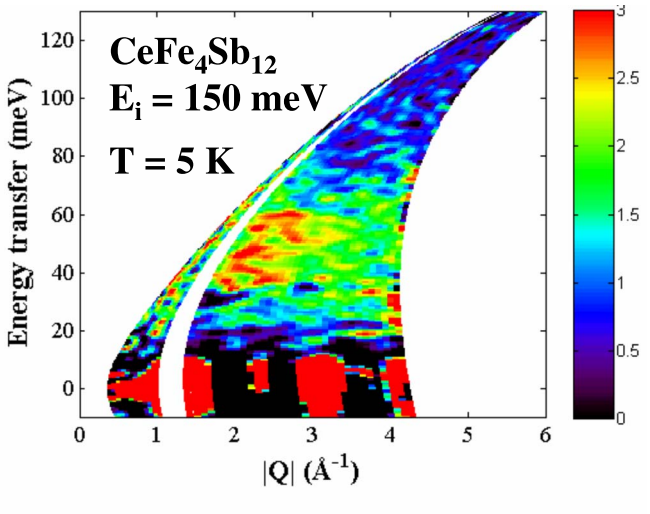
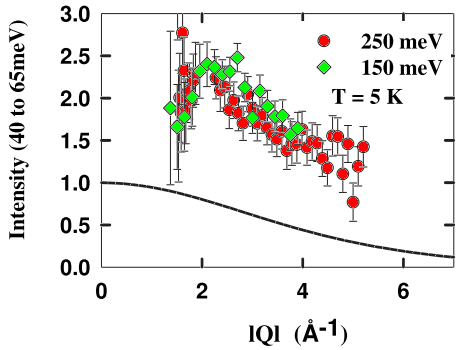


FIG. 5. (Color online) Contour map of the magnetic scattering for $CeFe_4Sb_{12}$ at 5 K plotted as a function of energy transfer (E) and wave vector transfer $|Q|$. The scattering intensity is color coded.

tive moment of $\mu_{\text{eff}}=2.3(1)\mu_B$ has been extracted using the second sum rule of $S(Q,\omega)$, $\int S(q,\omega)/F^2(Q)d\omega=48.8\mu_{\text{eff}}^2$ using the 5 K data. This is in good agreement with that estimated from the bulk susceptibility, as discussed previously.

The presence of an inelastic magnetic scattering signal near 40 meV indicates the formation of a spin gap (Δ_{spin}) in the hybridized bands near the Fermi level in $CeFe_4Sb_{12}$; thus, it would be interesting to see its Q dependence. The contour plot as a function of energy transfer versus $|Q|$ shown in Fig. 5 for the magnetic scattering in $CeFe_4Sb_{12}$ at 5 K reveals a broad inelastic peak near 50 meV, whose position is nearly independent of Q. This may indicate a single ion Kondo-type response. However, the Q dependence of the energy integrated intensity between 40 and 65 meV for both the incident energies of 150 and 250 meV exhibits a broad maximum near $Q\sim 2$ Å^{-1}. This behavior is different from that expected for the magnetic form factor of Ce^{3+}: For comparison, we have also plotted the Ce^{3+} magnetic form factor squared $[F^2(Q)]$ in Fig. 6 (solid line). At present, we do not have any clear explanation for the observed Q dependence behavior of the intensity. One of the possibilities is that it may be due to the presence of weak short range exchange



AQ: #7 FIG. 6. (Color online) Q dependence of the energy integrated intensity between 40 and 65 meV at 5 K for an incident energy of 150 meV (green diamond) and of 250 meV (red circle).

interactions between the Ce and Fe ions, as discussed in the next section.

Here we will give a detailed discussion of how the threshold energy (E_{thr}-E_f) is related to the peak position (E_{peak}-E_f) observed in inelastic neutron scattering. Here, E_f is the position of the f quasiparticle peak (just above the Fermi energy or the middle of the gap in the DOS). In the quasiparticle limit (i.e., low temperature and low energy limit), the f-DOS should be given in terms of the (unhybridized) conduction band density of states, derived from the slave boson theory of the Anderson lattice model, assuming k-independent hybridization matrix elements,[24] via

$$\rho_f(E)=\left(\frac{V}{E-E_f}\right)^2\rho_c\left[E-\left(\frac{V^2}{E-E_f}\right)\right], \quad (3)$$

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where V is the renormalized hybridization matrix element. Further, the threshold energy is given by setting the argument of ρ_c to its extremal values $\pm W$, where W is the width of the conduction band, or, in other words, the smallest value of the hybridization gap is caused by hybridization with conduction band states at either the top or the bottom of the conduction band. So, one has

$$\left[E-\left(\frac{V^2}{E-E_f}\right)\right]=\pm W, \quad (4)$$

which gives the band edges at

$$E=E_f+\frac{\pm W-E_f}{2}\pm\left(\sqrt{\left(\frac{\pm W-E_f}{2}\right)^2+V^2}\right). \quad (5)$$

So, one expects the threshold energy in the f-DOS to be given by

$$(E_{\text{thr}}-E_f)=\frac{V^2}{W}. \quad (6)$$

However, the peak in the f-DOS is given by

$$\frac{\partial\rho_f}{\partial E}=0 \quad (7)$$

or

$$(E_{\text{peak}}-E_f)=\frac{2}{\left[1+\left(\frac{V}{E-E_f}\right)^{-2}\right]}\left(\frac{\rho_c}{\frac{\partial\rho_c}{\partial E}}\right), \quad (8)$$

where $\rho_c\propto(E\pm W)^\alpha$ at the band edges, so $\alpha=1/2$. On solving this, one finds that the peak position is given by

$$(E_{\text{peak}}-E_f)=\frac{(2+\alpha)}{2}\left(\frac{V^2}{W}\right). \quad (9)$$

So, with $\alpha=1/2$, we have

$$(E_{\text{peak}}-E_f)=\frac{5}{4}\left(\frac{V^2}{W}\right). \quad (10)$$

Thus, Eq. (10) shows that the peak energy ($E_{\text{peak}}-E_f$) is 5/4 times the threshold energy ($E_{\text{thr}}-E_f$)=(V^2/W), which is smaller than what we have seen in Fig. 4 for $CeFe_4Sb_{12}$. This

could change if one introduces a k-dependent hybridization or if there is a Van Hove singularity in the conduction band density of states nearby.

Now, we discuss on the various origins of the magnetic signal at 40 meV in $CeFe_4Sb_{12}$. There are two main possibilities. Firstly, we are dealing with a CEF transition very much broadened by the Kondo spin fluctuations. Indeed, a similar inelastic signal has been observed at low temperatures for the Kondo systems $CeNi_2Ge_2$ (Ref. 29) and $CeRu_2Si_2$ (Ref. 30), where T_K is about 20 K and the CEF splitting is about 300 K. However, in $CeRu_2Si_2$, a quasielastic peak is also observed with a HWHM of about 1 meV.[31] Thus, the case of these compounds is different from the present case for which we have not observed any quasielastic peak in the high-resolution INS experiment on the time-of-flight spectrometer IN4.[32] To further confirm the absence of any magnetic scattering at low energy, we have also carried out high-resolution INS measurements on $CeFe_4Sb_{12}$ and $LaFe_4Sb_{12}$ on the MARI spectrometer at ISIS with E_f = 20 meV at 15 K. We found a similar scattering in both the compounds for Q values between 0.75 and 5 $Å^{-1}$ (data not shown here). This again supports the absence of the quasielastic scattering in the spin gap of $CeFe_4Sb_{14}$. This observation is in agreement with our estimation of $\mu_{\text{eff}} \sim 2.3(1)\mu_B$, which is close to the full theoretical value of $2.54\mu_B$, from the integrated intensity of the 50 meV peak. This suggests that most of the integrated intensity expected from the sum rules is tied up in the high energy response, and hence there is little intensity left to assign at low energy and low Q. Thus, our second explanation for the magnetic signal observed in $CeFe_4Sb_{12}$, and its temperature dependence, is the observation of a spin gap, as mentioned previously, similar to that observed in skutterudite compounds $CeRu_4Sb_{12}$ (Ref. 9) and $CeOs_4Sb_{12}$,[10] in the Kondo semiconductor $Ce_3Bi_4Pt_3$,[27] and in intermediate valence systems (IVSs) such as $YbAl_3$.[28]

It is interesting to compare the absolute value of the spin-gap energy obtained from the various different techniques in $CeFe_4Sb_{12}$ and also to compare the spin-gap value with other compounds. The value found for the spin gap from the heat capacity (36 meV) agrees very well with the value extracted [40(3) meV] from the Lorentzian spectral fit to the INS data. This good agreement is thus a further support of our simple model for the heat capacity. Furthermore, it is very interesting to note that the value of the charge gap $\Delta_{\text{char}} \sim 50$ meV observed in the optical experiment in $CeFe_4Sb_{12}$ (Ref. 13) is similar to the spin-gap energy of $\Delta_{\text{spin}} \sim 40-50$ meV found here for the inelastic neutron scattering and Hall effect experiments.[7] Thus, here the ratio between the charge gap and the spin gap is about $\sim 0.8-1$. A very similar ratio of the charge gap to spin gap has also been observed in the case of another skutterudite compound, $CeOs_4Sb_{12}$.[10] The absolute value of the spin gap observed in $CeFe_4Sb_{12}$ is larger than the spin-gap value of 30 and 27 meV observed in $CeRu_4Sb_{12}$ and $CeOs_4Sb_{12}$, respectively, which indicates the presence of stronger hybridization in the former compound.

Now, we want to check the general validity of this phenomenological model for IVS and Kondo semiconductors. Because there are some compounds with different values of J (1/2, 5/2, or 7/2), we have plotted the position of the inelastic neutron scattering peak E_{INS} in meV (see Refs. 27, 28, and 34–47) versus the temperature of the maximum to the Ce contribution of the heat capacity T^C_{max} or thermal expansion, if the heat capacity data are not available, for the different compounds found in the literature (see Refs. 33, 34, 46, and 48–61)This is shown in Fig. 7, where we can see that the majority of the compounds are around a straight line for which we have E_{INS} (in kelvin) equal to about four times T^C_{max}. In a solid line, we have also plotted the case where Eq. (2) is applied for different values of the kinetic moment J. It is interesting to note that the calculations of Hanzawa[25] of the specific heat for the different kinetic moments $J=5/2$ and 7/2 lead to almost the same ratio (about 3.5) between the value of the spin gap ΔE (equal here to E_{INS}) and the temperature of the maximum of the heat capacity in using the periodic Anderson model rather than our phenomenological two-level model. This provides further support for using the simple phenomenological model in our heat capacity data analysis. However, we note that there are some disagreements for CeNi, $Ce_3Bi_4Pt_3$, and $CePt_2Si_2$. For $CeFe_4Sb_{12}$, we have used the value of E_{INS} from the fit in Fig. 4 that gave a good agreement between the heat capacity and INS experiments. Obviously, the deviations observed from the straight line should be due to the too great simplicity of our phenomenological model because it ignores the details of the DOS around the hybridization gap. Clearly, it would be very interesting to make the heat capacity and/or thermal expansion measurements up to 300 K on $CeRu_4Sb_{12}$ and $CeOs_4Sb_{12}$ to

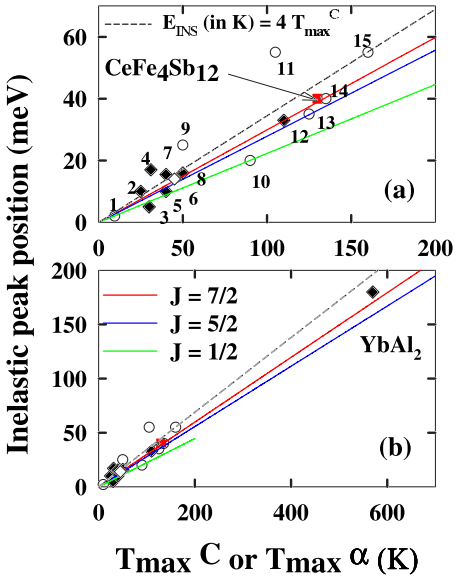

FIG. 7. (Color online) [(a) and (b)] Maximum of the INS peak E_{INS} (see Refs. 23, 24, and 36–49) vs maximum of the heat capacity T^C_{max} and of the thermal expansion T^{α}_{max} (see Refs. 27, 35, 39, and 49–62) in the intermediate valence systems, Kondo semiconductors. 1: CeNiSn, 2: YbCuAl, 3: $YbPd_2Si_2$, 4: $YbCu_2Si_2$, 5: $YbCu_4Ag$, 6: SmB_6, 7: YbB_{12}, 8: $Yb_{0.75}Lu_{0.25}B_{12}$, 9: $Ce_3Bi_4Pt_3$, 10: $CePt_2Si_2$, 11: CeNi, 12: $YbAl_3$, 13: CeRhSb, 14: $CeSn_3$, and 15: $CePd_3$ The dashed line represents the equation E_{INS} (in K)=4 T^C_{max}, while the solid lines show the calculations corresponding to the ratio between ΔE and T^C_{max} in a simple two-level phenomenological model for various J values (see text for details). The symbols used in (b) have same meaning as in (a).

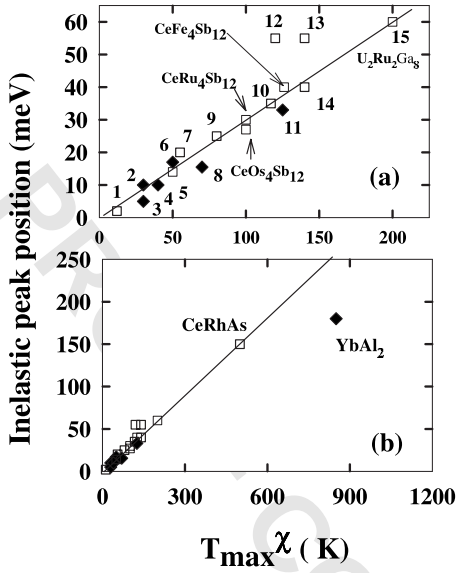

FIG. 8. [(a) and (b)] Maximum of the INS peak E_{INS} (see Refs. 27, 28, 34–46, 65, and 66) vs maximum of the magnetic susceptibility T_{max}^{χ} (see Refs.27, 28, 34–47, 65, and 66) in the intermediate valence systems, Kondo semiconductors. 1: CeNiSn, 2: YbCuAl, 3: $YbPd_2Si_2$, 4: $YbCu_2Si_2$, 5: SmB_6, 6: $YbCu_4Ag$, 7: $CePt_2Si_2$, 8: YbB_{12}, 9: $Ce_3Bi_4Pt_3$, 10: CeRhSb, 11: $YbAl_3$, 12: $CePd_3$, 13: CeNi, 14: $CeSn_3$, and 15: U_2RuGa_8. The solid line is a guide to the eyes. The symbols used in (b) have the same meaning as in (a).

test whether our simple phenomenological model also works in this case.

According to the single impurity model,[62] we can estimate the high temperature Kondo temperature T_K through the maximum $T_{max}(\chi)$ in the bulk susceptibility as $T_K = 3T_{max}(\chi)$. Therefore, it would be interesting to show a universal relation between the inelastic peak position (or spin-gap energy) and the high temperature Kondo temperature T_K or $T_{max}(\chi)$, as shown in Ref. 10 In Fig. 8, we have plotted the peak position of the inelastic neutron scattering versus $T_{max}(\chi)$ for many Ce- and Yb-based intermediate valence compounds. We can see that the excellent universal scaling relation is observed between $T_{max}(\chi)$ or T_K (Refs. 24, 28, 33, 36, 39, 50, 51, 55, 60, and 63–66) and the inelastic peak position corresponding to the spin gap (see Refs. 27, 28, 34–47, and 63–66) in all these compounds, notably for the case of three different CeM_4Sb_{12} (M=Fe, Ru, and Os) skutterudite compounds.

IV. CONCLUSIONS

We have carried out magnetic susceptibility, heat capacity, and inelastic neutron scattering measurements on $CeFe_4Sb_{12}$ in order to understand the nature of $4f$ electrons in this compound and especially to find out whether there exists a spin gap or not. Our inelastic neutron scattering study clearly reveals the presence of spin gap $\Delta_{spin} \sim 40(3)$ meV in $CeFe_4Sb_{12}$, which is also supported through our heat capacity measurements as well as published Hall effect measurements.[7] Further, we found that the spin-gap energy is independent of Q, which indicates that single-ion-type interactions play an important role in the spin-gap formation. On the other hand, the energy integrated magnetic intensity between 40 and 65 meV shows a broad maximum at $Q \sim 2$ Å^{-1}, which might suggest the presence of some weak intersite correlations. The fact that Ce-Ce distances are larger (7.91 Å) in $CeFe_4Sb_{12}$ and that the maximum in the susceptibility of $Ce_{1-x}La_xRu_4Sb_{12}$ is independent of La concentration[7] furthermore supports the single impurity-type behavior of the Ce ions. Thus, it is likely possible that weak intersite correlations may exits between the Ce and Fe atoms, due to the shorter Ce-Fe distance (3.95 Å) as well as the paramagnetic nature of the Fe ion in $CeFe_4Sb_{12}$, which are most likely responsible for the observed Q-dependence intensity. We have also found a universal scaling relation between the spin-gap energy and the temperature, at which the bulk susceptibility and also the heat capacity (or thermal expansion) exhibit a maximum for many Ce and Yb compounds. We have presented theoretical calculations showing a relation between the threshold energy and the peak position observed in the inelastic response of spin-gap systems.

An important role of the Fe ion in $CeFe_4Sb_{12}$ can be seen when we compare the value of spin-gap energy of 40–50 meV, which are larger than 30 meV in $CeRu_4Sb_{12}$ and 27 meV in $CeOs_4Sb_{12}$. This is also true for the Pr-based skutterudite superconductors: PrT_4Sb_{12} (T=Fe, Ru, and Os) all having a singlet ground state.[67–69] The Pr compounds with T=Os and Ru are superconducting with $T_c \sim 1.9$ and 1 K, respectively, but no superconductivity has been observed in the T=Fe compound. This observation again suggests the special role played by the Fe ion in both the Ce- and Pr-based skutterudite compounds.

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AUTHOR QUERIES —

#1 pls. check definition of EDX.
#2 pls. spell out MPMS, PPMS, HET.
#3 pls. check insertion of ″was.″
#4 pls. spell out MARI.
#5 pls. check change from ″45″ to ″46″
#6 pls. check insertion of ″rather.″
#7 Pls. be aware that although a caption makes reference to color online, figures in print will appear in black and white.
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