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Anomalous physical properties of cerium–lanthanum filled skutterudites

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Abstract

Thermoelectric materials generate an electromotive force when submitted to a thermal gradient with an efficiency scaled by the so-called figure of merit: $Z = \alpha^2\sigma/\kappa$, where α is the Seebeck coefficient, σ the electronic conductivity and κ the thermal conductivity. Theoretical considerations have shown that a large value of Z requires not only a small value of κ but also a large effective mass of charge carriers. The first condition is met in filled skutterudites, which have been studied extensively for this reason. The second condition suggests we focus our attention on skutterudites filled with an anomalous rare-earth element such as cerium, presenting heavy fermion characteristics. In this context, we report in this paper a study of the magnetic properties of $CeFe_4Sb_{12}$ and their evolution upon cerium dilution.

Keywords: Heavy fermions; Magnetic measurements; Neutron scattering

1. Introduction

Filled skutterudite compounds are promising new thermoelectric materials for intermediate temperature range applications [1,2]. They correspond to the formula RM_4X_{12}, where R is a rare-earth atom (Ce, La, Yb, Pr, etc.), M is a transition metal and X a pnictogene (P, As, Sb). Among these compounds, $CeFe_4Sb_{12}$ has been investigated in some details [3]. Analysis of X-ray absorption measurements shows that the cerium ion is trivalent in this compound at any temperature below 300 K [4]. The inverse magnetic susceptibility for $CeFe_4Sb_{12}$ is shown in Fig. 1. At low temperature, strong non-linear behavior is observed. Above 200 K, however, the Curie–Weiss law is satisfied from which we can infer an effective magnetic moment (μ_{eff}) of 3.36 μ_B. This value of μ_{eff} is in agreement with former results (see Ref. [3] and references therein), but larger than the free Ce^{3+} ion value (2.54 μ_B).

The large value of μ_{eff} has been interpreted in a localized ionic model by assuming three divalent and one trivalent Fe ion, the latter being in the d^5 low spin configuration with a total blocking of the orbital moment by the crystal field [4]. However, the theoretical μ_{eff} would then be 3.07 μ_B in this model, lower than the experimental value. Moreover, in the ionic model, one Fe out of four is assumed to have a valence different from the other Fe. This is hardly acceptable as all the Fe ions occupy the same crystallographic site and should be equivalent.

2. Experimental

The synthesis and characterization of the samples have been reported previously [1]. Magnetic experiments were performed on a 9 T vibrating sample magnetometer from Oxford Instruments, with a magnetic field of 0.5 T, from 2 to 300 K.

Inelastic powder neutron scattering experiments (INS) were performed at the Laboratoire Léon Brillouin (LLB) at Saclay (France) on a 3T1 three-axis spectrometer using a double nickel monochromator. As-cast samples were placed in an aluminum crucible. The experiments included energy transfer scans at constant Q and Q scans at constant transfer energy to determine the nature of the signal.

3. Results and discussion

In an attempt to separate the Fe and Ce contributions, we measured the magnetic susceptibility of $LaFe_4Sb_{12}$, also reported in Fig. 1 for comparison.

Up to 2 K, the compound does not order. Only a small deviation from linear behavior occurs below 50 K. In the

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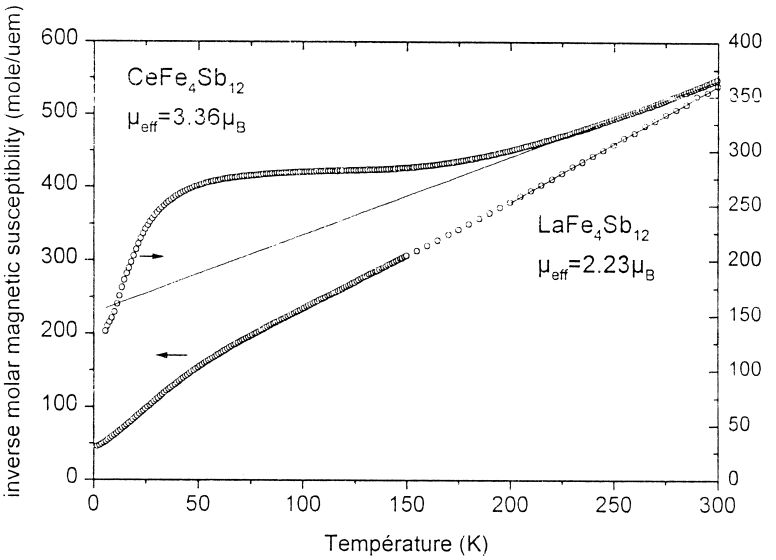

Fig. 1. Thermal dependence of the inverse molar magnetic susceptibility of $LaFe_4Sb_{12}$ and $CeFe_4Sb_{12}$ ($H = 0.5$ T).

range 50–300 K, the Curie–Weiss law leads to an effective magnetic moment of 2.23 μ_B. Since La is non-magnetic, this magnetic moment comes from Fe only. This is, however, a value larger than predicted from the simple ionic model (1.73 μ_B). On the other hand, the effective magnetic moment of $CeFe_4Sb_{12}$ can now be expressed as the result of two additive magnetic contributions: that of the (free) Ce^{3+} ions and that of Fe deduced from the magnetic susceptibility of $LaFe_4Sb_{12}$. The theoretical value in this approach is very close to the experimental value. This corroborates that the 9% discrepancy obtained in the ionic model is not an artifact. The ionic model, proposed in the past, is thus not correct.

Instead, we propose an itinerant d-magnetic contribution of Fe in these skutterudites. In this context, the magnetic susceptibility of iron comes from the d band of iron with 0.25 hole. At 0 K, the magnetic susceptibility is then given by

$$\chi = \frac{1}{2} g^2 \mu_B^2 \frac{\rho_0}{1 - U\rho_0}$$

where U is the effective d–d Coulomb correlation interaction and ρ_0 the density of d-states at the Fermi level. As no magnetic ordering exists in $CeFe_4Sb_{12}$, the Stoner criterion is not fulfilled, i.e. $U\rho_0 < 1$. Assuming the density of d-states at the Fermi level is linearly temperature dependent and taking into account that $k_B T \ll U$ since U is the order of a few electron volts, the itinerant susceptibility takes a Curie—Weiss form

$$\chi = \frac{C_{\text{eff}}}{T - \theta}$$

with $C_{\text{eff}} = \rho_0 / U\alpha$ and $\theta = -(1 - U\rho_0)/U\alpha$. This linear dependence explains the Curie–Weiss-type behavior of the inverse magnetic susceptibility of $LaFe_4Sb_{12}$. Note that μ_{eff} associated with Fe in this case has still been defined by $C_{\text{eff}} = N\mu_{\text{eff}}^2/(3k_B)$ in the text, although C_{eff} is not related to the Curie constant associated with localized magnetism. In particular, μ_{eff} is not the local magnetic moment carried by an Fe atom. Actually, the condition $U\rho_0 < 1$ ensures that the magnetic moment carried by the Fe ion is zero and μ_{eff} is only related to the mean polarization of the d-electron conduction band upon application of the external magnetic field.

At low temperature ($T \leq 200$ K), the inverse magnetic susceptibility of $CeFe_4Sb_{12}$ presents a large deviation from the high temperature linear behavior (Fig. 1). The crystallographic site of Ce in $CeFe_4Sb_{12}$ is not octahedral, but the distortion with respect to octahedral symmetry is expected to be small enough to be neglected [5]. In this case, the cubic crystal field splits the $^2F_{5/2}$ ground state of the free Ce^{3+} ion into a Γ_7 doublet and a Γ_8 quartet separated by energy Δ. This energy is taken as positive (negative) if Γ_7 (Γ_8) is the new ground state. The magnetic susceptibility of Ce^{3+} in this cubic field has been determined by Jones [6]:

$$\frac{C}{\chi} - \theta = \frac{21T(1 + 2e^{-\delta})}{5 + 26e^{-\delta} + (32/\delta)(1 - e^{-\delta})}$$

with $\delta = \Delta / k_B T$. Fitting this formula to the experimental variation of χ^{-1} would lead to $\Delta = 350$ K. This high value is not realistic taking into account the large value of the characteristic lattice distances. For instance, in cubic CeTe or CeSb the crystal field splitting is of the order of 150 K for a lattice parameter of 6.4 Å [7]. Moreover, we have argued in the present work that Ce^{3+} in $CeFe_4Sb_{12}$ carry an effective magnetic moment roughly equal to that of the free ion at $T > 200$ K, not that of the Γ_7 or Γ_8 level only. The free ion value is restored only if both the Γ_7 and Γ_8

levels are occupied at such temperatures, i.e. $\Delta \approx 200$ K.

To determine Δ, we performed neutron inelastic scattering experiments on diluted compounds (dilution is useful to identify the observed inelastic lines unambiguously). We then used $La_{1-x}Ce_xFe_4Sb_{12}$ with $x = 0.02$, 0.3, 0.7 and 1 (Fig. 2).

All spectra were recorded at 10 K. All the INS spectra are similar. Two peaks are observed at 1.8 and 2.8 THz. The magnitude of the first peak does not change with composition. Q scans at fixed energy (1.8 THz) demonstrate that this peak corresponds to phonon excitations (intensity increases as Q^2). The nature of the second peak is more difficult to determine. However, theoretical considerations demonstrate that the cross section (and therefore the intensity) for magnetic excitation is proportional to the square of the magnetic form factor $F^2(Q)$. $F(Q)$ decreases for increasing modulus of the scattering vector Q. This property allows for dissociation between the magnetic and phonon signals. Although the intensity of the 2.8 THz peak includes a phonon mode (Q scans reveal an increasing intensity for high values of Q while decreasing intensity at low values), we observe a reinforcement of the signal when the cerium concentration increases. Therefore, this line is associated with the crystal field excitation. The frequency of 2.8 THz corresponds to an energy splitting of 140 K. This value of the crystal field splitting is consistent with magnetic properties ($\Delta \approx 160$ K) and also in agreement with resistivity measurements [8].

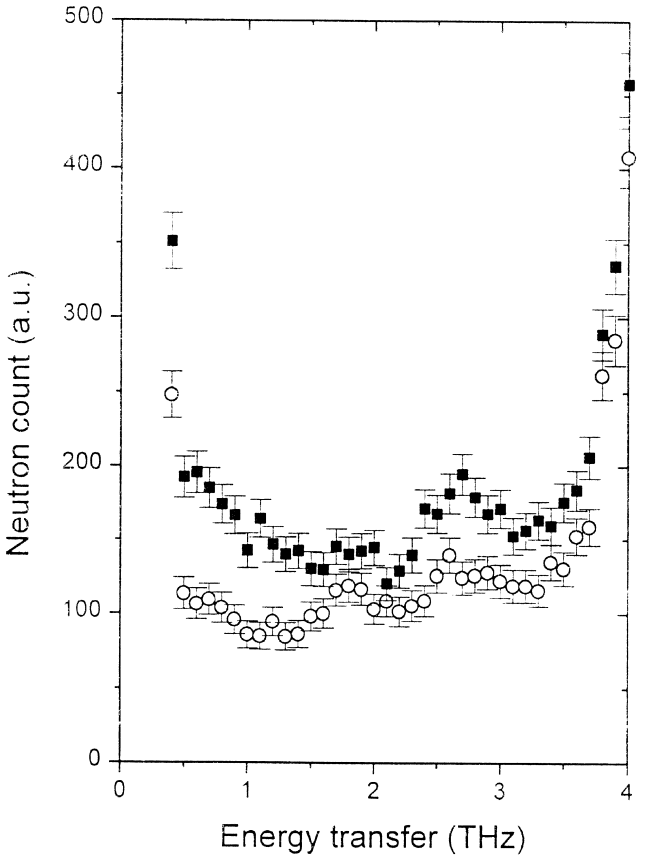

Fig. 2. Inelastic neutron scattering spectrum for $CeFe_4Sb_{12}$ (■) and $LaFe_4Sb_{12}$ (○) at 10 K and $Q = 1.5$ Å^{-1}.

As stated above, this value is not high enough to account for the abnormal behavior of χ^{-1} at low temperature. Actually, some authors present $CeFe_4Sb_{12}$ as a heavy fermion system. Indeed, the lack of any magnetic ordering of Ce at low temperature is indicative of Fermi liquid behavior. The deviations of the magnetic properties at low temperature are then attributable to the transition into a non-magnetic Kondo-type state.

4. Conclusion

In this paper, we have shown that the anomalous magnetic properties of $CeFe_4Sb_{12}$ cannot be interpreted within a localized ionic model. Indeed, the contribution of iron to the magnetic properties, which is far from negligible, has been analyzed in the framework of an itinerant magnetism theory. Our determination of the crystal field energy by neutron inelastic scattering analysis is consistent with the magnetic and transport properties and gives support to the hypothesis of heavy fermion behavior in $CeFe_4Sb_{12}$.

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