Inelastic neutron scattering study of Ni-substituted Ce$_{0.5}$Fe$_4$Sb$_{12}$ skutterudite compounds

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Abstract. An inelastic neutron scattering study of the filled and partially-filled skutterudite compounds RFe$_4$Sb$_{12}$ and R$_{0.5}$Fe$_{2.75}$Ni$_{1.25}$Sb$_{12}$ (where R = Ce and La) was carried out to understand the nature of the spin dynamics. Strong magnetic scattering was observed in Ce$_{0.5}$Fe$_{2.75}$Ni$_{1.25}$Sb$_{12}$ at $\sim 5$ meV. The integrated intensity of this peak does not follow the Ce$^{3+}$ form factor, but exhibits a maximum at a momentum transfer ($|Q|$) of 2 Å$^{-1}$. We attribute this feature to a Ce$^{3+}$ crystal field excitation in the presence of magnetic exchange interactions. This picture is supported by thermodynamic and magnetic properties. Finally, we confirm the presence of a spin gap in CeFe$_4$Sb$_{12}$ suggested by our previous work.

Skutterudites of the MT$_4$X$_{12}$ type (M = rare earth or actinide, T = transition metal, X = Sb, P) which crystallize in a body centred cubic structure have attracted much attention because of their high thermoelectric efficiency. This is generally attributed to the reduction of the lattice thermal conductivity by the interaction between acoustic phonons of the framework and low-energy vibration modes of the rare-earth ions that are weakly bonded in oversized atomic cages [1,2]. Filled skutterudites are also of considerable interest in fundamental physics because of their various ground states: superconductivity, heavy fermion behaviour, magnetic ordering, metal-insulator transitions, hybridization gap semiconducting or non-Fermi liquid behaviour. These different ground states result from a competition between the intersite RKKY and the onsite Kondo interaction. When the Kondo interaction prevails, the hybridization between the 4f and conduction electrons may lead to the formation of a hybridization gap at the Fermi level ($E_F$) [3]. In CeFe$_4$Sb$_{12}$, both the Kondo effect and a
hybridization gap have been observed [4,5]. The relatively low specific heat, magnetic Grüneisen parameter and Kondo temperature and the presence of trivalent cerium [4,6-9] suggest that CeFe$_4$Sb$_{12}$ is situated between the limits of heavy fermion behaviour (as in CeAl$_3$) and intermediate valence behaviour (as in CeSn$_3$) [3,5]. In the partially-filled Ce$_{3/4}$Fe$_{4-x}$Ni$_x$Sb$_{12}$ skutterudites, however, no clear evidence for incoherent Kondo scattering was observed. This could be due to the much smaller charge carrier concentration in this latter system [7-9].

Therefore, in order to further understand the spin dynamics of this class of compounds, we have investigated Ce$_{0.5}$Fe$_{2.75}$Ni$_{1.25}$Sb$_{12}$ using inelastic neutron scattering (INS), heat capacity and magnetic measurements. Our study clearly shows strong magnetic scattering at 5 meV in Ce$_{0.5}$Fe$_{2.75}$Ni$_{1.25}$Sb$_{12}$, in strong contrast to the signal observed in CeFe$_4$Sb$_{12}$ at about 40 meV [5].

The synthesis details of the single phase polycrystalline samples were reported earlier [4-9]. INS measurements were carried out using the time-of-flight chopper spectrometer MARI at the ISIS Facility (UK). Samples were enclosed in aluminium foil and positioned with a hollow geometry in a thin wall Al sample can. An incident neutron energy of $E_i = 20$ meV was used for all the measurements. This gives an energy resolution of about 0.65 meV (FWMH) at the elastic scattering position. For details of the experimental set-up, see Ref. 10. All our results are normalized with a vanadium standard. The heat capacity was measured between 2 and 300 K using a microcalorimeter in a commercial PPMS apparatus from Quantum Design. The magnetic susceptibility was measured between 2 and 300 K under zero field cooling conditions with 0.5 T applied magnetic field in a vibrating sample magnetometer from Oxford.

![Figure 1](image1.png)

Figure 1 Magnetic response, obtained as explained in the text, for CeFe$_4$Sb$_{12}$ and Ce$_{3/4}$Fe$_{4-x}$Ni$_x$Sb$_{12}$ at 15 K and at low angle, $\phi_{avg}$ (wave vectors Q), (a) 8.1° (0.44 Å$^{-1}$) and (b) 21.5° (1.16 Å$^{-1}$). The thick solid lines represent the fit based on our CEF model, the thin lines its different components (see text).

![Figure 2](image2.png)

Figure 2 (a) Cerium contribution of the heat capacity of Ce$_{0.5}$Fe$_{2.75}$Ni$_{1.25}$Sb$_{12}$ and calculated heat capacity using the model described in the text. (b) Magnetic susceptibility of Ce$_{0.5}$Fe$_{2.75}$Ni$_{1.25}$Sb$_{12}$ with the calculated magnetic susceptibility using the model described in the text.

In Fig. 1 we show the magnetic part of the inelastic response at two different average scattering angles (or wave vectors Q), $\phi_{avg}= 8.1°$ (0.44 Å$^{-1}$) and 21.5° (1.16 Å$^{-1}$) for both CeFe$_4$Sb$_{12}$ and Ce$_{0.5}$Fe$_{2.75}$Ni$_{1.25}$Sb$_{12}$. At low Q, we see a strong inelastic response in Ce$_{0.5}$Fe$_{2.75}$Ni$_{1.25}$Sb$_{12}$ at about 5
meV that is absent in both CeFe$_4$Sb$_{12}$ and in the non-magnetic reference compound La$_{0.5}$Fe$_{2.75}$Ni$_{1.25}$Sb$_{12}$. The magnetic scattering was determined by subtracting the signal of LaFe$_5$Sb$_{12}$ and La$_{0.3}$Fe$_{2.73}$Ni$_{1.25}$Sb$_{12}$ from the signal of the respective Ce compounds. In addition, we accounted for the difference in total scattering cross-sections, $\sigma$(Ce compound) $-h\sigma$(La compound), where $h$ is 0.94 for CeFe$_4$Sb$_{12}$ and 0.97 for Ce$_0.5$Fe$_{2.75}$Ni$_{1.25}$Sb$_{12}$ (see Refs. 5 and 10 for details). When Q is increased above 2 Å$^{-1}$ (data not shown here), the difference between Ce$_0.5$Fe$_{2.75}$Ni$_{1.25}$Sb$_{12}$ and all other compounds decreases and becomes very small above 4 Å$^{-1}$ (see also discussion of Fig. 3). Hence, the observed Q dependence clearly indicates the presence of a strong magnetic contribution to the scattering in Ce$_0.5$Fe$_{2.75}$Ni$_{1.25}$Sb$_{12}$, because its intensity is maximal at low Q. The absence of a magnetic response for CeFe$_4$Sb$_{12}$ at low Q agrees with the previous observation of a spin gap at low energy for CeFe$_4$Sb$_{12}$ [5]. Because Ce$_0.5$Fe$_{2.75}$Ni$_{1.25}$Sb$_{12}$ has, like La$_{0.5}$Fe$_{4+x}$Ni$_{1.25}$Sb$_{12}$ [8,9,11] a low charge carrier concentration, we suggest that the magnetic peak at 5 meV corresponds to a crystalline electric field (CEF) excitation of the J = 5/2 ground state multiplet of the Ce$^{3+}$ ion, as previously observed in the cubic system CeSbNi$_x$ [12]. In skutterudites, we have the following CEF Hamiltonian for the Ce$^{3+}$ ion in T$_2$ point group symmetry:

$$H_{\text{CF}} = B_4^0 (O_4^0 + 5O_4^4)$$

where $B_4^0$ is the CEF parameter and $O_4^n$ are the Stevens operators [13]. Under the cubic (T$_2$) CEF potential the J = 5/2 multiplet of the Ce$^{3+}$ ions splits into a doublet ($\Gamma_7$) and a quartet ($\Gamma_8$), with energy eigenvalues of -240 $B_4^0$ and 120 $B_4^4$, respectively and therefore we have $\Delta_{\text{CEF}} = 360 B_4^0$ [13]. From the peak position alone, the sign of $B_4^0$ cannot be determined and thus it cannot be decided whether $\Gamma_7$ or $\Gamma_8$ is the ground state. However, this assignment is possible when also the intensities are taken into account. By fitting the peaks to the above CEF model, we obtain $B_4^0 = -14.3(6)$ µeV and -11.6(7) µeV for the best fit of the peaks for Q = 0.44 Å$^{-1}$ and 1.16 Å$^{-1}$, respectively; thus $\Gamma_8$ is the ground state according to this analysis. The slightly different value found for $B_4^0$ at the two Q positions is due to the unusual Q dependence of the intensity observed in the magnetic scattering.

**Figure 3** Contour plot of the momentum (Q) and energy (E) transfer of magnetic scattering $S_{\text{m}}(Q,E)$ from Ce$_{0.5}$Fe$_{2.75}$Ni$_{1.25}$Sb$_{12}$ at 15 K.

**Figure 4** The Q-dependence of the inelastic peak intensity integrated over energies from 2 to 6 meV (symbols).

To test the above model, we have measured the heat capacity and the magnetic susceptibility of Ce$_0.5$Fe$_{2.75}$Ni$_{1.25}$Sb$_{12}$ (see Fig. 2). The Ce contribution of the heat capacity of Ce$_0.5$Fe$_{2.75}$Ni$_{1.25}$Sb$_{12}$, obtained by subtracting the phonon part estimated from the measured heat capacity of the La reference, is shown in Fig. 2-a. The agreement between the data and the theoretical curve calculated with the above $B_4^0$ values is much better than in the case where the ground state is $\Gamma_7$. Note that the electronic heat capacity of the non-magnetic reference La$_{0.5}$Fe$_{2.75}$Ni$_{1.25}$Sb$_{12}$ is quite low (about 7 mJ/mole.K$^2$). For the magnetic susceptibility, the above CEF model is insufficient to reproduce the
experimental data at low temperature quantitatively whatever the ground state used in the calculation. The discrepancy points to the limit of the model and might be due to additional magnetic interactions. The absence of a peak in the magnetic susceptibility shows the absence of a hybridization gap.

In Fig. 3 and 4, we show a contour plot of the magnetic scattering at 20 K as a function of energy transfer and $|Q|$, and the integrated intensity of the magnetic scattering (integrated between 2 and 6 meV energy transfer) as a function of $|Q|$, respectively. A peak appears at $Q \sim 2 \, \text{Å}^{-1}$, which is a very unusual behaviour that has been observed so far only in two Ce-based compounds (CeFe$_4$Sb$_{12}$ [5] and Ce$_3$Pd$_{20}$Si$_6$ [14]). For magnetic excitations of either crystal field or spin gap type, one expects that the $Q$ dependence of the peak intensity follows the square of the magnetic form factor of a free Ce$^{3+}$ ion (see solid line in Fig. 4, where we use the $F(Q)^2$ obtained by P. J. Brown’s method [15]). "Unusual" magnetic scattering, with departure from the Ce$^{3+}$ free-ion form factor only at low $Q$, was observed in the intermediate-valence compound CeSn$_3$ [16]. This was interpreted as a contribution from the polarization of the Ce 5d electrons. It may be that the same mechanism acts in Ce$_{0.5}$Fe$_{2.75}$Ni$_{1.25}$Sb$_{12}$. In the case of Ce$_3$Pd$_{20}$Si$_6$ [14], this was interpreted as due to quantum critical fluctuations.

In conclusion we observe magnetic scattering in Ce$_{0.5}$Fe$_{2.75}$Ni$_{1.25}$Sb$_{12}$ and attribute it to a CEF excitation. The fact that such excitation is absent in CeFe$_4$Sb$_{12}$ is believed to be due to its larger charge carrier concentration and stronger 4f-conduction electron hybridization that broaden the 4f levels and thus collapses the CEF excitations [5]. A further conclusion can also be drawn from our present results: the CEF splitting is relatively small in Ce based skutterudites as proposed earlier [4-8]. We would like to thank K. A. McEwen, S. M. Bennington, J. Lorenzana, J.-G. Park and Dr E.A. Goremychkin, for fruitful discussions. S. P. acknowledges financial support from the Austrian Science Fund (project P19458-N16).

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