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N Magnani[1], A Paoluzi[2], L Pareti[2] and J A Stride[3]

[1] European Commission, Joint Research Centre, Institute for Transuranium Elements, Postfach 2340, Karlsruhe, Germany
[2] Consiglio Nazionale delle Ricerche, Istituto dei Materiali per l'Elettronica e il Magnetismo, I-43010 Fontanini (PR), Italy
[3] School of Chemistry, University of New South Wales, Sydney, NSW 2052, Australia

E-mail: Nicola.Magnani@ec.europa.eu

Abstract

Inelastic neutron scattering measurements have been performed on the intermetallic compounds $Pr_2Co_{12}Fe_5$ (and $Y_2Co_{12}Fe_5$) on the IN4 time-of-flight spectrometer at the Institut Laue-Langevin, Grenoble. The data on the yttrium-based compound have been used to estimate the phonon scattering. A broad peak is detected at 18 meV, whose deduced Q dependence (when only the magnetic contribution is considered) is consistent with the form factor of Pr^{3+} ions; in the high-Q region, the same peak displays a clear phononic character. The experimental results are analysed by a molecular field model including exchange and crystal-field contributions, and the derived value for the exchange parameter is consistent with the trend inferred by studying Pr_2Co_{17} and Pr_2Fe_{17}. A possible mechanism for the generation of the large volume magnetostriction, to be checked by further experiments, is suggested.

1. Introduction

Rare-earth and transition-metal intermetallic compounds are the ideal physical systems to study the rich phenomenology caused by the simultaneous presence of itinerant (3d) and localized (4f) electrons [1]. The interplay between the magnetic properties of d and f electrons gives rise to an outstanding variety of magnetic field and temperature-induced magnetic transitions. $Pr_2Co_{12}Fe_5$ is almost unique amongst its family of compounds, in that it displays two distinct temperature-induced spin reorientations (SRTs) and a series of field-induced first-order magnetic transitions which survive up to 300 K and above [2]; moreover, a very large volume magnetostriction is present near the low-temperature SRT, whose physical mechanism remains unexplained [3].

Inelastic neutron scattering (INS) is by far the most direct experimental method to determine the crystal-field (CF) potential and the intersublattice exchange field H_{ex} in rare-earth intermetallic compounds [4]. Both the above interactions significantly affect the physical properties: for example, the largest part of the magnetic anisotropy is generated by the CF acting on the 4f moment of the rare-earth ion, while its thermal decay is mainly governed by the exchange interaction [5]. We have performed INS experiments on the time-of-flight spectrometer IN4 at the Institut Laue-Langevin, Grenoble, with the aim of obtaining the value of the exchange interaction in $Pr_2Co_{12}Fe_5$ and, eventually, to find hints about the reason for its anomalous magnetostrictive properties.

2. Experimental results

Several batches of $Pr_2Co_{12}Fe_5$ and $Y_2Co_{12}Fe_5$ were obtained from high-purity (99.99%) elements by arc-melting technique; the ingots were then remelted three times to ensure homogeneity, wrapped in Ta foil, annealed under Ar atmosphere at 1220 K for three days, and quenched in water. The resulting compounds were found to be single-phase by x-ray diffraction and thermomagnetic analysis; finally, powders were obtained by hand-crushing and put into a hollow cylindrical Al container suitable for INS experiments.

The Hamiltonian which describes the RE quantum state in these compounds is

$$\hat{H}_{RE} = \Lambda \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} + 2\mu_B \mathbf{H}_{ex} \cdot \hat{\mathbf{S}} + \sum_{k,q} B_{kq} \hat{C}_q^{(k)}, \qquad (1)$$

where the first term on the right-hand side is the spin–orbit coupling, the second is the mean-field exchange term and
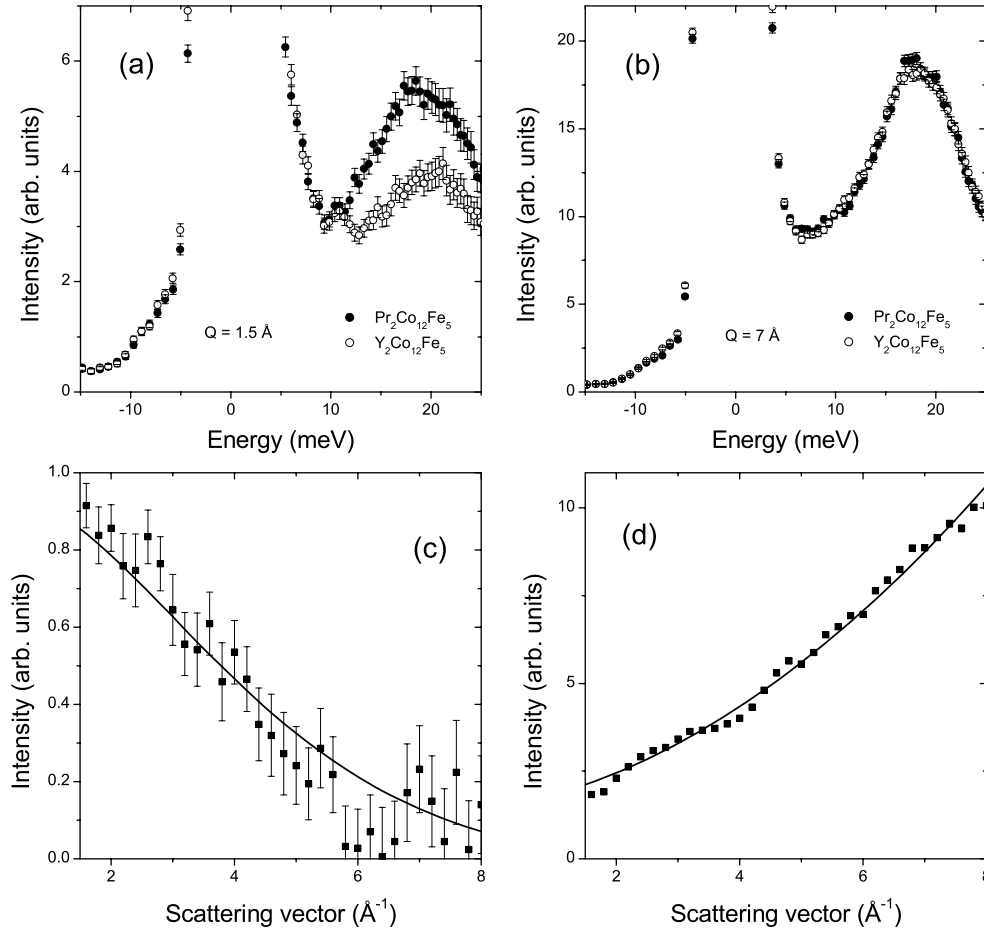
Figure 1. (a) Inelastic neutron scattering spectra of Pr$_2$Co$_{12}$Fe$_5$ (●) and Y$_2$Co$_{12}$Fe$_5$ (○) measured on the IN4 time-of-flight spectrometer at the Institut Laue-Langevin, Grenoble, for $Q = 1.5$ Å. (b) Same for $Q = 7.0$ Å. (c) Q-dependence of the magnetic INS intensity of Pr$_2$Co$_{12}$Fe$_5$ (■, after phonon subtraction) extracted at a constant energy transfer value of 18 meV, compared with the square form factor of the Pr^{3+} ion (——). (d) Q-dependence of the phonon INS intensity of Y$_2$Co$_{12}$Fe$_5$ (■) extracted at a constant energy transfer value of 18 meV, and fit (——) to a Q^2 dependence of the phononic cross section.

the third is the CF potential. It is worth recalling that the exchange field **H**$_{ex}$ is proportional to the transition-metal sublattice magnetization **M**$_T$ [1]. We refer to [6] for a detailed explanation of the theoretical model used to describe the ordered phase of these compounds, limiting the discussion to the main results. The eigenstates of equation (1) are determined to a large extent by the exchange term, and in the single-ion description they can be labelled by quantum numbers as $|J, M\rangle$ if the quantization axis is chosen along the direction of H_{ex}. Preliminary studies apparently indicate that the anomalous crystallographic sites found in the end-members Pr$_2$Co$_{17}$ and Pr$_2$Fe$_{17}$ [7] are instead not present with appreciable concentration in the mixed Co–Fe compositions; therefore, it is a good approximation to consider all the RE positions as magnetically equivalent, due to the random distribution of transition-metal ions in the lattice. Only one intramultiplet transition ($|J, -J\rangle \rightarrow |J, -J + 1\rangle$) is then allowed by the INS selection rule $\Delta M = 0, \pm 1$ from the ground state. INS data were collected at 1.5 K, so that only the ground state is populated, and with an incident energy of 38 meV. The results are displayed in figure 1. The data of the Y-based compound were used as a measure of the pure

phonon scattering; the fact that the energy spectra of the two compounds at large momentum transfer $Q = 7$ Å (where the magnetic signal is expected to be negligible) are exactly the same for the two compounds (figure 1(b)) is a proof that the phononic scattering is well accounted for. A large peak centred at 18 meV is detected, likely an optical phononic mode. At small Q, the same peak at 18 meV is present in both compound, but its intensity is much higher for the Pr-based compound (figure 1(a)), meaning that it also has a magnetic contribution. This is also witnessed by studying the Q dependence of the INS signal around 18 meV: the magnetic contribution (obtained by subtracting the Y spectra from the Pr ones) follows the shape derived from the tabulated form factor for Pr^{3+} ions [8] (figure 1(c)), while for the nonmagnetic Y$_2$Co$_{12}$Fe$_5$ the 18 meV peak follows the Q^2 dependence typical of phonons (figure 1(d)).

3. Discussion

To put these findings in context, we have applied a mean-field model [9] to find the value of the exchange field. Assuming that the crystal-field parameters of Pr$_2$Co$_{12}$Fe$_5$ lie somewhere
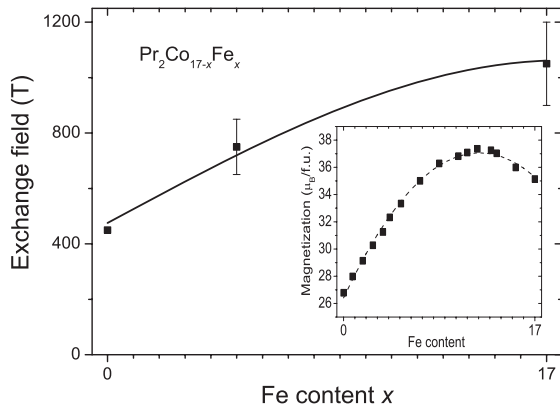
Figure 2. Experimental (■) and calculated (——) values of the exchange field H_{ex} for the $Pr_2Co_{17-x}Fe_x$ family as a function of the Fe content x. Inset: saturation magnetization of $Y_2Co_{17-x}Fe_x$ [2].

Table 1. Measured 3d–4f exchange field for several intermetallic compounds.

Compound	H_{ex} (T)	Reference
Pr_2Co_{17}	450	[10]
Nd_2Co_{17}	320	[11]
Sm_2Co_{17}	270	[5]
Dy_2Co_{17}	110	[11]
Pr_2Fe_{17}	1050	[9]
$Nd_2Fe_{14}B$	520	[12]
Sm_2Fe_{17}	380	[13]
Gd_2Fe_{17}	285	[14]
$Pr_2Co_{12}Fe_5$	750	This paper

between those of Pr_2Co_{17} and those of Pr_2Fe_{17} [9, 10], a gap of 18 meV can be reproduced with $H_{ex} = 750 \pm 100$ T. This lies well in the middle of the values obtained for Pr_2Co_{17} and Pr_2Fe_{17}. Recalling that the exchange field experienced by the RE ions is proportional to $n_{RT}\mathbf{M}_T$ (where n_{RT} is the molecular field coefficient [1]), we can analyse its dependence on the Fe composition x, with the common assumption that $\mathbf{M}_T$ is well approximated by the saturation magnetization of the blank compound $Y_2Co_{17-x}Fe_x$ [2]. We conclude that the experimental values of H_{ex} can be reproduced (figure 2) if we assume that n_{RT} increases linearly from Pr_2Co_{17} to Pr_2Fe_{17}. For the same reason, comparing values of the intersublattice exchange field for various 3d–4f intermetallic compounds from several sources [5, 9–14] (table 1) we note that, for the same rare-earth ion, H_{ex} is always larger for Fe-based than Co-based compounds. Moreover, in a given family of compounds, H_{ex} monotonically increases moving from heavy to light rare earths. This trend can be ascribed to the different spatial extent of the 4f electronic wavefunctions, and this also confirms the qualitative analysis of the microscopic exchange constants n_{RT} determined by measurements of the Curie temperature T_C in [15].

4. Conclusions

The fundamental magnetic interactions of $Pr_2Co_{12}Fe_5$ have been studied by INS. The resulting exchange-field value is

consistent with qualitative trends derived for other similar intermetallic compounds. The gap between the two lowest electronic levels of Pr^{3+} in $Pr_2Co_{12}Fe_5$ amounts to 18 meV; this is exactly the same energy as the most intense phononic mode detected in both $Pr_2Co_{12}Fe_5$ and $Y_2Co_{12}Fe_5$. If the energy separations between electronic states are comparable with the energies of thermal and zero-point motion of the lattice, a strong magnon–phonon coupling of the two subsystems may give rise to complex thermodynamic phenomena, structural changes or magnetostriction anomalies [16], also with the formation of a bound state such as in $CeAl_2$ [17] or NpO_2 [18, 19]. This might well be the physical phenomenon which, coexisting with the SRT, gives rise to the anomalous volume magnetostriction reported for $Pr_2Co_{12}Fe_5$; experimentally, this anomaly is not present for other compositions in the $Pr_2Co_{17-x}Fe_x$ series, a straightforward explanation being that the energy gap of the magnetic excitation changes rapidly with x, therefore not coinciding with the phonon energy anymore. However, the present studies do not allow to check if the symmetry requirements of the electronic wavefunctions and of the phononic modes are satisfied [16], nor to estimate the magnon–phonon coupling strength. We are therefore planning to perform more detailed INS experiments to study these details, as soon as a large single crystal sample becomes available.

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