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INTERMULTIPLY TRANSITIONS IN RARE-EARTH METALS

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ABSTRACT

We report here on direct observations of intermultiplet (IM) transitions in the rare-earth metals, Pr, Nd and Tb, made using the chopper spectrometers at the Intense Pulsed Neutron Source of Argonne National Laboratory. Despite hydrogen contamination of the polycrystalline samples, we have observed inelastic peaks at small Q arising from IM transitions in Pr (~260 meV), Nd (~242 meV) and Tb (~256 meV) although the latter has not yet been observed unambiguously. Future work will investigate the energy level structure and dynamical properties of rare-earth ions in stoichiometric metallic systems.

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1. Introduction

Inelastic scattering measurements at conventional research reactors are normally limited by the (Maxwellian) reactor spectrum to energy transfers of less than about 200 meV. "Hot" sources may extend this range somewhat, but only in exceptional cases can detailed dynamical information be obtained at higher energies. The high instantaneous fluxes of epithermal and "fast" neutrons from the newly-developed spallation neutron sources should allow a wide range of inelastic experiments with large energy transfers extending up to at least 500 meV. An interesting and obvious application of inelastic instruments on these sources is the study of high energy magnetic excitations (spin-waves, crystal field excitations, etc.), although these experiments are notoriously difficult, due to the simultaneous requirements of large energy transfer $\hbar\omega$ and small momentum transfer, Q .

Over many years, attention has been devoted to neutron scattering investigations of the magnetic excitations in rare-earth (R.E.) systems [1]; the energies of these

excitations within the spin-orbit-coupled ground state of the R.E. ion are in the 1 to 20 meV range. However, the energy separation between multiplets of different total angular momentum J is typically one or two orders of magnitude greater and photon spectroscopy techniques have dominated studies of the higher multiplet states for dilute R.E. ions in insulating salts [2]. This paper is a preliminary report of neutron scattering observations of intermultiplet transitions (IMT) in the R.E. metals Pr, Nd, and Tb, made using the IPNS chopper spectrometers.

2. Experimental details

The polycrystalline samples of Pr (236 gm) and Nd (238 gm), of nominal 99.9% purity [obtained from Rare Earth Products, England], were in the form of discs of thickness 0.8 cm and diameter 2.3 cm, stacked to cover the beam area of 9.6 by 4.5 cm²; the Tb sample (193 gm) was a plate of thickness 0.8 cm. The samples were enclosed in a thin Al sample cell. The experiments reported here were made on the LRMECS chopper spectrometer [3], operated with an incident energy of 500 meV

which yields an energy resolution varying from approximately 40 to 30 meV over a range of energy transfer from 0 to 250 meV. The samples were cooled to 15 K in a Displex refrigerator to minimise multiple phonon scattering. All data have been corrected for scattering from the empty sample cell and cryostat, and data at different scattering angles were normalized using a Vanadium "standard".

3. Results

3.1 Praseodymium

Some representative energy spectra for Pr are presented in Fig. 1. Surprisingly, for these nominally "pure" samples, the inelastic spectra were dominated by local-mode scattering from hydrogen impurities, as is seen in the lower frame where fundamental (H1, 117 meV) and 1st and 2nd harmonic (H2, 227 and H3, 335 meV) peaks are clearly visible. The identification with H-mode scattering was made on the basis of the energies and structure factors of the observed peaks (see below). At the smallest

wavevectors (Fig. 1, upper frame), the spectrum in the vicinity of the H2 peak develops a high-frequency component which, as Q decreases, increases in intensity, following the Pr^{3+} form factor, while the H-peak decreases. We identify this low Q peak at about 260 meV with the $^3\text{H}_4 \rightarrow ^3\text{H}_5$ intermultiplet transition.

An average over all the low angle detector banks (Fig. 2, upper frame) provides a graphic demonstration of this double peak structure. The lower frame of Fig. 2 when compared with Fig. 1 shows that the relative intensities of the 3 H peaks vary with Q as expected theoretically for a localized Einstein oscillator [4], i.e.

$$S_n(Q, \omega) \propto \frac{1}{n!} \left(\frac{Q^2}{\omega_0} \right)^n \exp(-DQ^2) \quad (1)$$

where ω_0 is the oscillator frequency and D the Debye-Waller factor; $n = 0, 1, 2$ refer to elastic, fundamental, 1st harmonic etc.

Fig. 3 presents the observed Q dependences of the integrated intensities and mean frequencies of the three peaks. The observations accurately follow the behavior expected theoretically. In the region of 220 to 260

meV, it is evident from the center frames of Fig. 3 that we are observing the sum of H (local-mode) scattering and magnetic (IMT) scattering. The extra intensity and rapidly decreasing mean frequency at small Q are direct evidence of the observation of the 260 meV IMT. In a previous experiment on PrAl_2 using the HRMECS spectrometer, Loewenhaupt [5] has reported a barely-resolved line at about 260 meV. His interpretation of this as the Pr IMT supports the present observations.

3.2 Neodymium

The Nd sample was apparently much less contaminated by hydrogen as at no scattering angle was a clear 3 peak inelastic spectrum observed. A peak at about 240 meV which decreased smoothly with increasing Q, following the Nd^{3+} form factor, is identified as arising from the $^4I_{9/2} + ^4I_{11/2}$ IMT. At larger wavevectors, weak inelastic scattering was observed, suggesting a low level of H impurities.

3.3 Terbium

This sample was the least pure of the three studied, with a (measured) hydrogen content of 0.9 atomic percent. As for the Pr sample, a strong 3 peak inelastic spectrum was observed, albeit at different energies (132, 256, and 370 meV). Nevertheless, the 256 meV peak intensity at first decreases with increasing Q, before increasing strongly. It thus seems reasonable to assume that at small Q both the H₂ and the ${}^7F_6 + {}^7F_5$ IMT peaks contribute to the observed intensity.

4. Conclusion

Despite strong inelastic scattering from hydrogen impurities, intermultiplet transition peaks have been identified in the rare-earth metals Pr (~260 meV), Nd (~242 meV) and Tb (~256 meV). These values are in good agreement with results for dilute solid solutions in insulators [2]. Although the present results are inadequate to judge the effects, if any, of the conduction electrons, we plan future linewidth measurements on higher purity samples to study this interesting problem. A

more complete description of this work will be published elsewhere.

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FIGURE CAPTIONS

Fig. 1. Representative time-of-flight spectra of Pr at 15 K. For each spectrum the scattering angle and wavevector, calculated for an energy transfer of 250 meV, are given. The lines are (multiple) Gaussian fits to the data.

Fig. 2. Upper: Average over 21 low angle detector banks (Pr). The arrows indicate the energies of the H local mode and (magnetic) IMT. Lower: Spectrum at an intermediate angle where all 3 hydrogen peaks are well-developed (Pr).

Fig. 3. Integrated intensities and mean frequencies of the 3 hydrogen inelastic peaks observed for the Pr sample. The center frames (H2) correspond to the superposition of H2 and IMT scattering. The dashed lines are guides to the eye. Note the wide range of wavevector.

FIG. 1

FIG. 2

FIG. 3