Intermultiplet Transitions in Praseodymium Using Neutron Spectroscopy

A. D. Taylor,[1] R. Osborn,[1] K. A. McEwen,[2] W. G. Stirling,[3] Z. A. Bowden,[1] W. G. Williams,[1] E. Balcar,[4] and S. W. Lovesey[1]

[1]*Neutron Division, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, United Kingdom*
[2]*Department of Physics, Birkbeck College, University of London, London, WC1E 7HX, United Kingdom*
[3]*Department of Physics, Keele University, Keele, Staffordshire, ST5 5BG, United Kingdom*
[4]*Atominstitut der Österreichischen Universitäten, A-1020 Vienna, Austria*

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Intermultiplet transitions with energies up to 810 meV in praseodymium metal have been observed by neutron spectroscopy. Both dipolar ($^3H_4 \rightarrow {}^3H_5$) and, for the first time, nondipolar, interterm ($^3H_4 \rightarrow {}^3F_{2,3,4}$) transitions have been identified. The energies of the interterm transitions are significantly reduced by approximately 50 meV from their free-ion values. This gives direct evidence of conduction-electron screening of the (on-site) Coulomb interaction between $4f$ electrons in rare-earth metals.

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Neutron-electron spectroscopy is a valuable technique for the study of the highly correlated wave functions of $4f$ electrons in rare-earth metals and compounds. It has been used extensively to determine the crystal-field potential which lifts the degeneracy of the ground-state (Hund's rule and total angular momentum J) multiplet. Typically the overall splitting is in the range 10 to 20 meV.[1] The crystal-field splittings are much smaller than the intermultiplet splittings (>200 meV for all but Sm and Eu) and J mixing can be neglected. Such experiments give information on the interaction of f electrons with the crystalline electric field, but they are insensitive to the spin-orbit and Coulomb interactions which give rise to the multiplet splittings. The lowest $J \rightarrow J \pm 1$ intermultiplet transitions in Sm^{2+} and Eu^{3+} have been observed with conventional neutron sources.[2] With the advent of pulsed spallation neutron sources, intermultiplet transitions at 130 meV in Sm^{3+} (Ref. 3) and at 260 meV in Pr^{3+} (Ref. 4) have been reported. These energies are hardly changed from the free-ion values since they are dominated by the spin-orbit coupling, which principally depends on the interaction of the $4f$ electrons with the ionic core. In contrast, we anticipate that transitions from the ground-state multiplet to levels derived from different Russell-Saunders terms (i.e., with different values of total orbital and spin angular momenta, L and S) may be sensitive to modifications of the Coulomb interaction between the $4f$ electrons induced by a metallic environment. This Letter reports new measurements on Pr metal with the first observation of transitions from the $^3H_4$ ground state to the $^3F_{2,3,4}$ states and evidence for an enhanced screening of the intra-$4f$ Coulomb potential in a metal.

Comprehensive optical spectroscopy studies on trivalent rare-earth ions in insulating ionic solids reveal that all these interterm or "Coulomb" excitations have energies greater than 500 meV.[5] High-energy neutron spectroscopy opens up this field to optically opaque materials. An important advantage of neutron scattering is that the wave-vector dependence of excitations can be determined. Further, calculations of intermultiplet transition probabilities are more tractable for neutron, as opposed to optical, spectroscopy. A framework for such calculations has recently been developed by Balcar and Lovesey.[6] This theory expresses the single-ion approximation to the neutron-scattering cross section as

$$\frac{d^2\sigma}{d\Omega\, dE_f} = \left(\frac{E_f}{E_i}\right)^{1/2} r_0^2 G(\mathbf{Q};\mu,\nu)\,\delta(\hbar\omega + E_\mu - E_\nu),$$

where E_i and E_f are the incident and scattered neutron energies, $r_0^2 = 0.29$ b, $\hbar\omega = E_i - E_f$, and $\mathbf{Q}$ is the scattering vector. The structure factor $G(\mathbf{Q};\mu,\nu)$ for transitions between states labeled by the quantum numbers μ and ν may be expressed as a sum of products of radial integrals of the type $\langle j_K(Q)\rangle\langle j_{K'}(Q)\rangle$, in which

$$\langle j_K(Q)\rangle = \int_0^\infty dr\, r^2 f^2(r) j_K(Qr) \quad K = 0,2,4,\ldots,$$

where $j_K(x)$ is a spherical Bessel function and $f(r)$ is the normalized radial part of the one-electron wave function. The $\langle j_K(Q)\rangle$ values have been tabulated for all the rare earths by Freeman and Desclaux[7] using relativistic free-ion wave functions.

These intermultiplet cross sections differ from the intramultiplet cross sections in both their magnitude and Q dependence (see Fig. 1). First, for Q less than 9 $Å^{-1}$, the intermultiplet cross sections are smaller by at least an order of magnitude. Second, the Q dependence of $G(\mathbf{Q};\mu,\nu)$ is quite different from that of the magnetic form factor. The structure factors of dipolar transitions fall more sharply from their value at $Q=0$, while those of the nondipolar transitions, which have zero intensity at $Q=0$ (by definition), exhibit maxima at finite wave vectors in the range $Q=5$–15 $Å^{-1}$. The measured Q

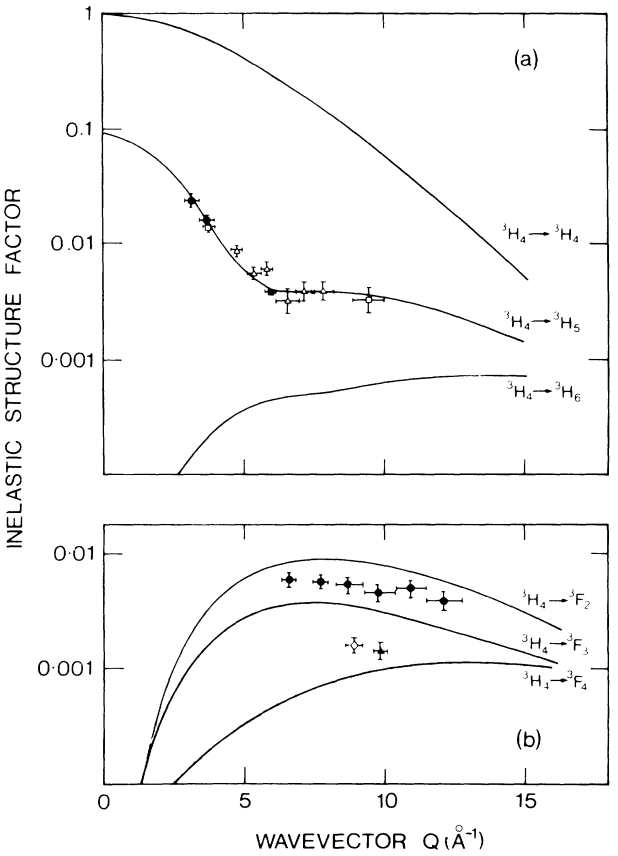

FIG. 1. Neutron inelastic structure factors for intermultiplet transitions in praseodymium. The lines represent the calculated intensities (Ref. 6) of the $^3H_4 \rightarrow {}^3H_4$, $^3H_5$, $^3H_6$, $^3F_2$, $^3F_3$, $^3F_4$, and $^1G_4$ transitions. The structure factors are normalized to the $^3H_4 \rightarrow {}^3H_4$ intensity at $Q=0$, which has a cross section of 620 mb/sr. (a) The intensity of the 260-meV transition measured with incident energies of 370 meV (filled square); 515 meV (open triangles); 830 meV (open squares); and 1300 meV (filled circles). (b) The intensity of the transitions at 578 meV, $^3H_4 \rightarrow {}^3F_2$ (filled circles); 747 meV, $^3H_4 \rightarrow {}^3F_3$ (open diamond); and 809 meV, $^3H_4 \rightarrow {}^3F_4$ (filled triangle) measured with an incident energy of 1300 meV. While the Q dependence of the 578-meV transition could be studied in detail, the 747- and 809-meV transitions could only be resolved individually at low scattering angles.

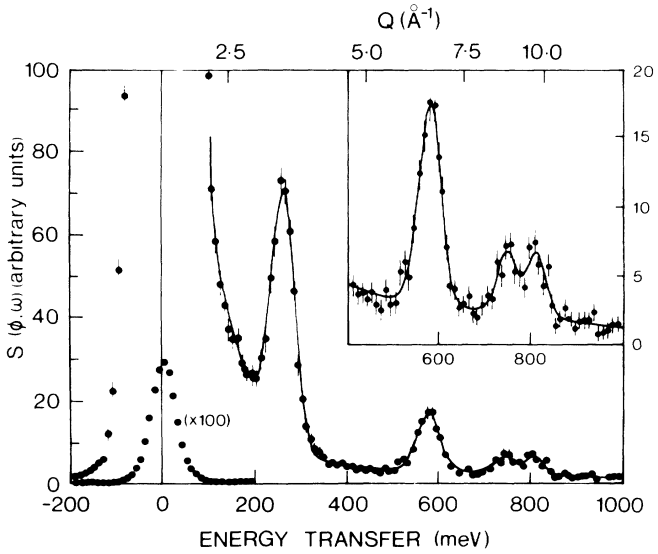

FIG. 2. Neutron-scattering cross section of praseodymium at 17 K, measured at an angle of 5° with an incident neutron energy of 1300 meV. The change in scattering vector across the spectrum is shown at the top of the diagram. The instrumental resolution varies from 60 to 25 meV as the energy transfer increases from 0 to 1000 meV. The data have been fitted by four Gaussians and a tail of low-energy scattering. Inset: the results above 400 meV on an expanded scale.

dependence has been a crucial factor in assigning the transitions that we have observed.

It is well known that the combined requirements of high energy transfer and low momentum transfer are difficult to achieve in neutron spectroscopy without the use of excessively high incident energies coupled with very small scattering angles. Indeed, it has sometimes been suggested that such kinematic constraints would effectively limit all magnetic scattering experiments to energy transfers below about 400 meV. Fortunately, the calculated structure factors shown in Fig. 1 lead to less stringent kinematic requirements because of the strength of the $\langle j_K(Q) \rangle$ terms when K is greater than zero. Recent experiments[3] on the $J \rightarrow J+1$ transition in $SmPd_3$ are in accord with theory.[6]

Praseodymium has the lowest "Coulomb" or interterm splitting ($^3H \rightarrow {}^3F$) of the rare-earth ions[5] and is therefore an appropriate first candidate for exploration of the Coulomb potential in a metal. The sample consisted of ~100 g of high-purity praseodymium metal[8] supplied by the Materials Preparation Center, Ames Laboratory, Iowa. It was mounted in a thin-walled aluminum can and cooled in a closed-cycle refrigerator to 17 K in order to reduce multiple phonon scattering. The measurements were performed on the high-energy transfer spectrometer (HET)[9] at the Rutherford Appleton Laboratory's pulsed spallation neutron source, ISIS. HET is a direct geometry chopper spectrometer capable of high resolution (~1% for E_i) and low momentum transfer equipped with a bank of detectors at 4 m from the sample position (scattering angle 3°-7°). A lower-resolution bank at 2 m (scattering angle 10°-30°) allows measurements at higher Q. The momentum transfer may also be varied by the selection of different incident energies. In our measurements, incident energies of 370, 515, 830, and 1300 meV were used, and the different runs were normalized to each other by using the scattering from a vanadium standard.

Figure 2 shows the scattering intensity measured with $E_i = 1300$ meV at a scattering angle of 5°. There are four inelastic peaks with energies at 261, 578, 747, and

TABLE I. The experimental and calculated energies (meV) of intermultiplet transitions from the $^3H_4$ ground-state multiplet of the Pr^{3+} ion. Free ion (Ref. 10); Pr doped in anhydrous $LaCl_3$ (Ref. 5); Pr metal (this work); calculation using the following parameters: $F^{(2)}=8102$ meV, $F^{(4)}=6200$ meV, $F^{(6)}=4060$ meV, $\zeta_{4f}=92.2$ meV.

	Free-ion	(La, Pr)Cl_3	Pr metal	Calculation
$^3H_5$	266.8	262.5	261	259.3
$^3H_6$	544.1	533.9	···	529.3
$^3F_2$	619.5	600.9	578	577.3
$^3F_3$	795.4	772.7	747	751.4
$^3F_4$	849.9	828.4	809	808.7
$^1G_4$	1230.0	1202.3	···	1173.5

809 meV. Their energies are compared with the transition energies of both free Pr^{3+} ions and Pr^{3+} in $LaCl_3$ (Refs. 5 and 10) in Table I. The lowest transition is evidently the $^3H_4\rightarrow{}^3H_5$ at an energy only slightly reduced from the free-ion value. This result confirms the previous observation[4] carried out using the LRMECS spectrometer at the Intense Pulsed Neutron Source (IPNS), Argonne National Laboratory. The Q dependence of the peak intensity was followed by our varying the incident energy and measuring at different scattering angles. These experimental points were normalized to the measured scattering within the $^3H_4$ ground-state multiplet, and are shown in Fig. 1(a); they are seen to be in good agreement with the calculated structure factor. In assigning the remaining levels, we compared their intensities with those calculated for the nondipolar $^3H_4\rightarrow{}^3H_6$ and $^3H_4\rightarrow{}^3F_{2,3,4}$ transitions; see Fig. 1(b). In these cases, we found that the measured peak intensities (which are up to 3 orders of magnitude less in intensity than the intramultiplet scattering) were up to a factor of 2 lower than calculated. Nevertheless, we may conclude that the peak at 578 meV arises predominantly from the $^3H_4\rightarrow{}^3F_2$ transition, since the calculated $^3H_4\rightarrow{}^3H_6$ intensity is an order of magnitude weaker. The relative peak intensities observed at 747 and 809 meV differ significantly from those calculated with use of pure $^3F_3$ and $^3F_4$ wave functions. However, by including the admixture of $^1G_4$ and $^3H_4$ character into the $^3F_4$ wave function (as discussed below), we calculate that these two transitions have similar intensity [see Fig. 1(b)].

With these assignments, it is evident that the "Coulomb" transitions are all reduced to energy by $\sim$50 meV from the free-ion values. To interpret this result, we have adjusted the four parameters which determine the matrix elements of the Coulomb and spin-orbit Hamiltonian. The three Slater integrals, $F^{(2)}$, $F^{(4)}$, and $F^{(6)}$, which characterize the strength of the Coulomb potential, and the spin-orbit parameter, ζ_{4f}, mix $^{2S+1}L_J$ basis states of equal J. The $^3H_4\rightarrow{}^3H_5$ transition is almost exclusively given by ζ_{4f} which was fixed to the value 92.2 meV deduced by optical spectroscopy.[10] The shifts of the other energy levels are determined by the Slater integrals and are well reproduced by a reduction of $F^{(2)}$ by 10.0% from its free-ion value [4.4% from its value in (La,Pr)Cl_3] keeping $F^{(4)}$ and $F^{(6)}$ fixed. We propose that the extra shift in going to the metallic system arises from a more efficient screening of the Coulomb interaction by the conduction electrons.

Additional measurements with an incident neutron energy of 1630 meV were made to search for the $^3H_4\rightarrow{}^1G_4$ transition expected around 1170 meV, but no significant intensity above the background was observed. However, an examination of the wave functions obtained from the above analysis shows that the $^3F_4$ and $^1G_4$ terms are strongly mixed:

$$^3F_4\rightarrow 0.805\,^3F_4-0.580\,^1G_4-0.125\,^3H_4,$$

$$^1G_4\rightarrow 0.797\,^1G_4+0.592\,^3F_4+0.117\,^3H_4.$$

This admixture (particularly the $^3H_4$ component) increases the intensity of the 809-meV transition at the expense of the 1170-meV transition as compared with the calculations which were derived from pure $^{2S+1}L_J$ states.

The reason for the discrepancy in the measured and calculated intensities of the "Coulomb" transitions shown in Fig. 1(b) remains puzzling. The calculated intensities sum over all the $2J+1$ levels of the $^3H_4$ multiplet, whereas, at 17 K, transitions from only the lowest crystal-field levels are significant. Additional scans at room temperature were made in order to thermally populate the whole multiplet, but only a small change in the intensities of the transitions was observed. These experiments have probed previously inaccessible regions of high energy and momentum transfer. It is possible that they are revealing the breakdown of the description of $4f$-electron states by simple atomic wave functions.

These measurements of intermultiplet transitions demonstrate the ability of neutron inelastic spectroscopy to investigate the magnetic response of localized systems at energies up to 1 eV. We have studied the wave-vector dependence of the intensities of both dipolar and, for the first time, nondipolar transitions in Pr metal. The observed shifts in the energies of the Coulomb transitions result from an increased screening of the conduction electrons in a metallic environment.

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