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DIRECT MEASUREMENT OF CRYSTAL-FIELD SPLITTINGS IN PrN*

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ABSTRACT

Inelastic neutron scattering has been employed to measure the crystal-field splittings of the $^3H_4$ ground multiplet corresponding to the Pr^{3+} ion in PrN. An analysis of the resulting data places the Γ_4 crystal-field level at 27.0±1.0 meV, the Γ_3 at 46.3±1.0 meV, and the Γ_5 at 91.±2. meV, above the ground Γ_1. These results can be quantitatively accounted for by a point-charge model with a charge of -3, which sharply contrasts with previous work of others that established the crystal-field levels in other PrX compounds (X=P,As, Sb,Bi,S,Se,Te) could be accounted for by point charges of -2. This difference between PrN and the other PrX compounds strongly implies some major difference in their electronic structures, which may indicate their being, respectively, semiconducting and metallic.

INTRODUCTION

The compound PrN belongs to the large class of NaCl-structured rare-earth monopnictides (N,P,As,Sb,Bi) and monochalcogenides (S,Se, Te). Generally, this class contains a diversity of different magnetic behaviors due to the presence of the rare-earths' 4f electrons, with some compounds being ferromagnetic, others ferrimagnetic, while others are antiferromagnetic. But as is the case for the Pr compounds, not all the compounds are found to undergo magnetic ordering, presumably due to crystal-field effects separating off a nonmagnetic ground level. Be it as it may, irregardless of whether a given compound undergoes magnetic ordering or not, its magnetic properties are profoundly affected by crystal-field effects. Thus, some quantitative information regarding the crystal-field effects in these compounds is important for understanding their magnetic properties.

Since the vast majority of the compounds in the above class have a basically metallic behavior, the standard photon spectroscopy methods, which have been useful for crystal-field studies in insulators, are of little value for the rare-earth compounds. Thus, most previous attempts at extracting crystal-field information for these compounds has been concerned with model analyses of "broad-band-spectral" data, such as specific-heat and/or susceptibility data. A markedly promising exception to the broad-band methods has been the application of neutron spectroscopy. For example, such techniques have been applied to all the PrX compounds except X=N by Turberfield *et al.*[1] (TPBB) and to TmSb by Birgeneau *et al.*[2]

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For the considered rare-earth compounds, the rare-earth site-symmetry is O_h. Thus, following the notation of Lea *et al.*[3] (LLW), the crystal-field Hamiltonian may be written

$$H = W\{[x/F(4)]O_4 + [(1-|x|)/F(6)]O_6\} \quad , \qquad (1)$$

with W being an overall splitting factor and x related to the ratio of fourth-and sixth-order terms. From LLW it is seen the ninefold-degenerate $^3H_4$, the ground J-multiplet of Pr^{3+}, will split into two triplets Γ_5 and Γ_4, one doublet Γ_3, and one singlet Γ_1. The energetic ordering of these Γ_i depends on the x value representative of the considered solid; however, a simple point-charge model indicates for PrN they would order, with increasing energy, in the sequence Γ_1 Γ_4, Γ_3, and Γ_5. Indeed, this is the ordering found by TPBB on the Pr compounds they investigated, and it is the order reasonably expected for PrN. At the same time, bulk magnetic data does indicate Γ_1 is the ground level for PrN, but a disagreement exists concerning the W and x values which best reproduce PrN's susceptibility and specific heat data. For example, the work of Junod *et al.*[4] gives x = -0.8 and W = 0.62 meV, while Stutius[5] estimates x = -1.0 and W = 1.76 meV. Thus, application of neutron spectroscopy to PrN should provide information concerning which values of x and W are more realistic.

The cross-section for scattering neutrons from a single J-multiplet follows the proportionality[6]

$$(\partial^2\sigma/\partial\Omega\partial\omega) \sim (k_f/k_i)F^2(\vec{Q}) \sum_{nm} \rho_n |\langle n|\vec{J}_\perp|m\rangle|^2 \delta(\varepsilon_{nm} - \hbar\omega) \quad , \qquad (2)$$

which is valid for small momentum transfers. The states $|n\rangle$ and $|m\rangle$ are crystal-field levels having an energy difference ε_{nm}, with the delta-function indicating the scattering neutron will undergo a gain or loss, $\hbar\omega$, in its kinetic energy depending on the sign of ε_{nm}. Also, $\vec{J}_\perp$ is the component of $\vec{J}$ $\perp$ to the scattering vector $\vec{Q}$, F is the form factor, and k_i and k_f are the momentums of the incident and scattered neutrons. It is important to note, to first order, the relative scattering intensities for the allowed $\hbar\omega$ are proportional to $\rho_n|\langle n|\vec{J}_\perp|m\rangle|^2$, with ρ_n being a Boltzmann population factor. This proportionality provides a valuable tool for interpreting the neutron data, since any resulting interpretation must provide consistency with any observed changes of intensity with temperature and allowed $\hbar\omega$. In this aspect, the recent documentation of the $|\langle n|\vec{J}_\perp|m\rangle|^2$ for the LLW Hamiltonian provided by Birgeneau[7] is a valuable tool in the preliminary analysis of neutron crystal-field data.

RESULTS AND DISCUSSION

Our experiments used the Oak Ridge magnetically-pulsed time-of-flight spectrometer,[8] which is capable of producing pulsed monochromatic neutron beams over a wide energy range. For example, in our study of PrN we have utilized beams of energies 13.1, 36.7, 69.8, and 91.6 meV. Then, by using cross-correlation applied between the pulsing signal and the time distribution of neutrons arriving at a given

detector, the desired data relating scattered neutron counts vs. time-of-flight channel (or energy) is readily obtained.

The PrN samples consisted of about 3 cc. of powder, and were kindly furnished by D. E. LaValle.[9] Results obtained at helium temperature when using 36.7 meV incident neutrons are shown in Fig. 1. This figure is a plot of scattered neutron counts vs. energy of the time-of-flight channel. The energies plotted in this and later figures correspond to the average times of the time channels, with a positive (negative) energy representing a neutron gaining (losing) that energy. Also, due to the (k_f/k_i) factor of Eq. (2) and the channels' energy-widths being proportional to $(k_f/k_i)^3$, the results of Fig. 1 represent raw data after multiplication by a factor $(k_i/k_f)^4$ and being averaged over the resolution width of the spectrometer. Results obtained at room temperature, using an incident neutron energy of 13.1 meV, are displayed in Fig. 2; here raw data is plotted without any $(k_i/k_f)^4$ or resolution corrections.

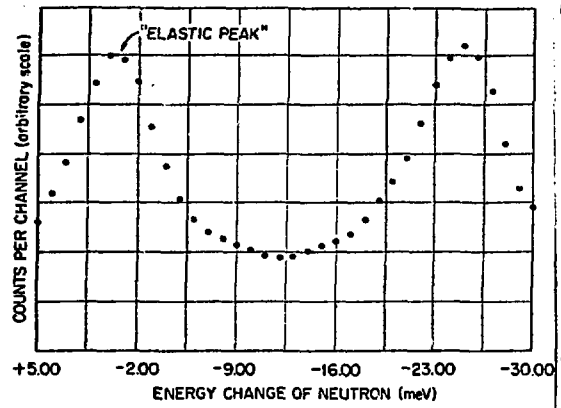

Fig. 1. Data for PrN at helium temperature.

The helium temperature results of Fig. 1 are easily and directly analyzed, since only excitation transitions from the ground Γ_1 will be possible. Also, because the only allowed transition with Γ_1 involves Γ_4, the energy loss peak in the vicinity of 26 meV corresponds to this transition. However, the $\Gamma_1 \rightarrow \Gamma_4$ transition energy will be slightly greater than the energy of the peak maximum due to the $F^2(\vec{Q})$ factor in Eq. (2). Of course, for higher temperatures, transitions involving both neutron energy loss and gain are possible and will have intensities as dictated by the products $\rho_n|\langle n|\vec{J}_\perp|m\rangle|^2$ of Eq. (2). Two such energy gain transitions are contained in the data of Fig. 2, with its peak maximum corresponding to the $\Gamma_4 \rightarrow \Gamma_1$ transition. At the same time, there appears to be a shoulder on the right of the major peak in Fig. 2. Since the LLW results show the ratio $(\Gamma_4 \rightarrow \Gamma_1)/(\Gamma_3 \rightarrow \Gamma_4)$ is independent of x and equal to 7/5, it is entirely reasonable to assign this shoulder to de-excitation from the Γ_3 to Γ_4.

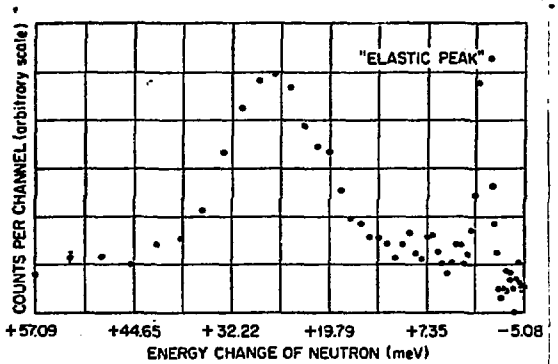

Fig. 2. Data for PrN at room temperature.

In order to test the above peak and shoulder assignment, we have written a computer program based on the theoretical model described by Eqs. (1) and (2). The procedures used were similar to, but not identical to, the ones described by TPBB, and basically involve varying parameters to obtain a "best fit". The parameters used are W and x of Eq. (1), and a level width to introduce an assumed gaussian smearing of the Γ_i levels. For a given set of these parameters the program calculates the cross-section of Eq. (2) as a function of $\hbar\omega$, and then convolutes the cross-section results with the measured instrumental resolution which varies with $\hbar\omega$. These results are then integrated over the energy-widths for each of the considered channels. The final result of this process is relative values of theoretical counts per channel, and these can be compared with experimental counts after subtraction of a parametric background value which is assumed constant for each considered channel. The results of using the program to obtain the best rms deviation to some of the data of Fig. 2 is shown in Fig. 3(a). The rms deviation between the calculated and experimental points of Fig. 3(a) is less than the statistical counting error which is indicated in Fig. 2. Also, the fit illustrated by Fig. 3(a) leads to the energies quoted for the Γ_4 and Γ_3 levels in Fig. 3(b), which should be considered to have experimental errors of, roughly, ± 1.0 meV.

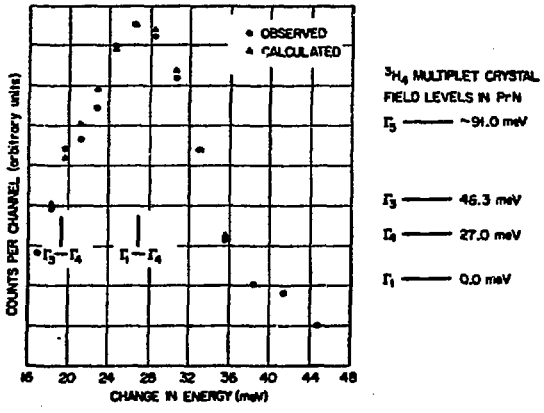

Fig. 3. (a). Comparison of PrN data at room temperature with calculated results. (b). The energy-level diagram for PrN following from our analysis.

The data of Figs. 1 and 2 is insufficient to place the remaining Γ_5 of the $^3H_4$ multiplet, which can have transitions with the Γ_3 and Γ_4. In order to place the Γ_5 we have used data which were obtained at room temperature using incident neutron results of 69.8 and 91.6 meV. The only pertinent information these data contain, not already contained in Figs. 1 or 2, are a weak peak corresponding to neutrons losing ≈ 45 meV with use of the 69.8 meV beam and a strong shoulder-type indication of energy loss at ≈ 65 meV with the 91.6 beam. These results are entirely consistent with placing the Γ_5 at 91±2 meV, which would give a $\Gamma_3 \rightarrow \Gamma_5$ transition at ≈ 45 meV and a $\Gamma_4 \rightarrow \Gamma_5$ at ≈ 65 meV. Also, although we have not attempted detailed intensity calculations involving the Γ_5, qualitative intensity considerations are consistent with out assignment.

The energy values of Fig. 3(b) may be generated, within the quoted error limits, by use of LLW parameters x = -0.97 and W = 1.68 meV. These direct neutron spectroscopy values are quite close to the values estimated by Stutius[5] of x = -1.0 and W = 1.76 meV from

specific heat data; thus we conclude the values x = -0.8 and W = 0.62 estimated by Junod *et al.*[4] do not realistically reflect the actual crystal-field of PrN. At the same time, our value of 27.0 ± 1.0 meV for the Γ_4 is entirely consistent with the value 27.2 meV tabularly quoted by Bucher *et al.*[10] as having been obtained by neutron spectroscopy. Although no details of their data have been reported, it is our impression Bucher *et al.* were only able to detect the Γ_4 level.

The W and x values we have obtained for PrN are surprisingly close to the values x = -0.96 and W = 1.69 meV, which would be predicted by a nearest-neighbor point-charge model with charges of -3. To obtain this result we have used the nonrelativistic Hartree-Fock radial integrals $\langle r^n \rangle$ tabulated by Freeman and Watson[11] for Pr^{3+}. Although relativistic effects can be very significant in the $\langle r^n \rangle$ integrals, we have used the Freeman and Watson values in order to easily compare our result with the point-charge analysis of TPBB on the other Pr compounds since they used the same $\langle r^n \rangle$ values. That is, the main point we want to make here is not that our PrN results have an apparent agreement with a point-charge model, which they would not if relativistic $\langle r^n \rangle$ were used, but that the PrN results do not follow the same trend as found for the other PrX compounds. This is immediately seen from the fact that TPBB found that the same point-charge model we have used to obtain a charge of -3 for PrN requires a charge of -2 for PrX (x=P,As,Sb,Bi,S,Se,Te). Thus, we conclude that this difference in model charge value implies some major difference between the overall electronic structure of PrN and that of the other PrX compounds. We suggest this difference is that PrN is indeed an intrinsic semiconductor as has been implied by the work, e.g., of Sclar,[12] while the other PrX compounds are intrinsically metallic.

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