

Crystal field at the paramagnetic praseodymium ion in the mixed-valence compound CeNi_5

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A splitting of the ground multiplet of Pr^{3+} ions has been observed in the mixed-valence compounds $\text{Ce}_{1-x}\text{Pr}_x\text{Ni}_5$ ($0.1 \leq x \leq 0.9$). This splitting is evidence of a quasisteady crystal electric field. A component of the potential of this field stems from ions in a mixed-valence state in the crystal.

In intermetallic compounds in which cerium ions are in a mixed-valence state, the usual crystal-field effects are not seen in inelastic magnetic scattering of neutrons.¹ It is worthwhile to study such systems by the spectroscopy of impurity paramagnetic ions, whose inelastic-magnetic-neutron-scattering spectrum should contain information on how the host ions in a mixed-valence state affect the crystal electric potential.

For an experimental study of the possibilities of this approach, we have measured the inelastic-magnetic-neutron-scattering spectra of the Pr^{3+} ion in the mixed-valence systems $\text{Ce}_{1-x}\text{Pr}_x\text{Ni}_5$, and also in several isostructural paramagnetic compounds $\text{Pr}(\text{La}, \text{Y})\text{Ni}_5$. The compound CeNi_5 is known² to be a mixed-valence system with a valence $\nu_{\text{Ce}} \approx 3.4$. The valence state of the cerium remains essentially the same when

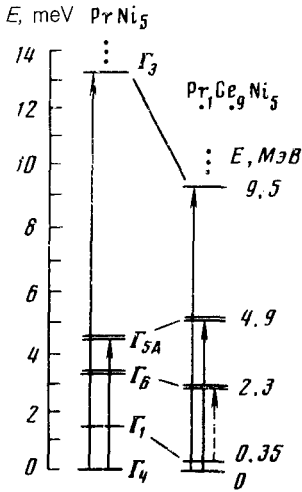


FIG. 1. Splitting of the ground multiplet, 3H_3 , of the Pr^{3+} ion in a crystal electric field of hexagonal symmetry for ${}^4\text{PrNi}_5$ (without the Γ_{5B} level); experimentally determined level energies for $\text{Ce}_{0.9}\text{Pr}_{0.1}\text{Ni}_5$. The arrows mark the transitions observed at a sample temperature $T = 4\text{--}5$ K.

the Ce is replaced by Pr or La (Ref. 3). The parameters of the electric potential of the crystal at the Pr^{3+} ion in PrNi_5 , which is an intermetallic compound with a Van Vleck paramagnetism, are quite well known,⁴ and the splitting pattern makes it possible to observe transitions from the ground state, facilitating measurements with low concentrations of Pr in CeNi_5 at low temperatures.

The present experiments were carried out on the triaxial spectrometer of the I. V. Kurchatov Institute of Atomic Energy, Moscow, by the $Q = \text{const}$ method over the energy-transfer interval $\epsilon = 0\text{--}16$ meV and the sample-temperature interval $T = 4.3\text{--}50$ K. In the spectra of the $\text{Ce}_{1-x}\text{Pr}_x\text{Ni}_5$ ($x \geq 0.1$) we detect peaks corresponding to transitions between levels of the crystal field of the Pr^{3+} ion. These peaks are evidence of the existence of a quasisteady potential of the crystal electric field in this mixed-valence system ("quasisteady" here means over a time scale $\sim 10^{-13}$ s, determined by the energy of the interaction of the ion with thermal neutrons). It can be seen from Fig. 1 that the scheme of Pr^{3+} levels in the mixed-valence system $\text{Ce}_{0.9}\text{Pr}_{0.1}\text{Ni}_5$ is greatly different from that in PrNi_5 . The following factors could, in principle, be responsible for the observed change in structure: 1) changes in the lattice constants as we go from PrNi_5 to $\text{Ce}_{0.9}\text{Pr}_{0.1}\text{Ni}_5$; 2) a change in the electrostatic ion contribution to the crystal electric field when Pr is replaced by Ce; and 3) a change in the electron component of the crystal electric field due to the presence of ions in a mixed-valence state.

For assistance in analyzing these factors, we consider the experimental and theoretical results on the transitions $\Gamma_4 - \Gamma_3$ in Fig. 2. The energy of this transition depends strongly on x and is directly related to only one of the four coefficients of the Hamiltonian of the crystal electric field⁵ ($\hat{\mathcal{H}}_{CF} = \sum_{n,m} B_n^m \hat{O}_n^m$):⁵ $\epsilon_{4-3} = 0.502 \times 10^4 \cdot B_6^6$. Other transitions are related to the coefficients B_n^m in a more complicated way. The effect on the crystal field of a change in the lattice constants and of a replacement of the praseodymium ion by another, isovalent ion (of lanthanum or yttrium) is illustrated by the results of measurements of the energy of $\Gamma_4 - \Gamma_3$ transi-

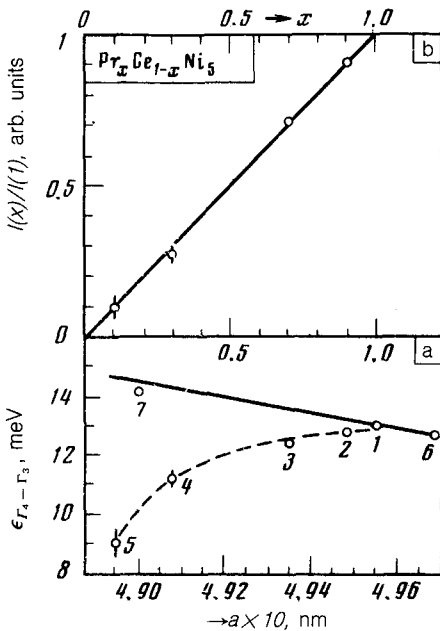


FIG. 2. a—the energy (ϵ_{4-3}); b—the intensity at $T = 4.3$ K [$I(x)$] of the peak in the inelastic magnetic scattering of neutrons corresponding to the transition $\Gamma_4 - \Gamma_3$ versus the praseodymium concentration (x) in $\text{Ce}_{1-x}\text{Pr}_x\text{Ni}_5$ (upper scale). 1) PrNi_5 , $\text{Pr}_y(\text{La}_{0.56}\text{Y}_{0.44})_{1-y}\text{Ni}_5$ ($y = 0.75$; 0.50); 2–5) $x = 0.9$, 0.7, 0.3, and 0.1, respectively; 6, 7) $\text{Pr}_{0.8}\text{La}_{0.2}\text{Ni}_5$ and $\text{Pr}_{0.2}\text{Y}_{0.8}\text{Ni}_5$ samples. The lower scale shows the lattice constant a , which is the strongest function of the sample composition. The solid line is the theoretical behavior of ϵ_{4-3} as a function of the lattice constant according to the model of effective point charges.

tions (points 1, 6, and 7 in Fig. 2a) in $\text{Pr}_y(\text{La}, \text{Y})_{1-y}\text{Ni}_5$ samples. For the compounds $\text{Pr}_y(\text{La}_{0.56}\text{Y}_{0.44})_{1-y}\text{Ni}_5$, which are lattice-matched with PrNi_5 (the difference in lattice constants satisfy $\Delta a, \Delta c \leq \pm 3 \times 10^{-4}$ nm, for $y = 1, 0.50$, and 0.25), we observe an agreement of the $\Gamma_4 - \Gamma_3$ transition energies (and also the $\Gamma - \Gamma_{5A}$ transition energies) with the results for PrNi_5 , within the experimental error (± 0.1 meV). With increasing lattice constant a ($\text{Pr}_{0.8}\text{La}_{0.2}\text{Ni}_5$), we observe a decrease in ϵ_{4-3} , while upon a decrease in a ($\text{Pr}_{0.2}\text{Y}_{0.8}\text{Ni}_5$), we observe an increase in ϵ_{4-3} . Interestingly, the experimental results on ϵ_{4-3} as a function of the lattice constants agree fairly well with the theoretical behavior of B_6^6 as a function of a and c/a according to the model of effective point charges (the solid line in Fig. 2a).

We can draw two conclusions from these results: 1) The behavior of ϵ_{4-3} as a function of the lattice constants (points 6, 1, 7; Fig. 2a) is opposite that which is observed in several $\text{Ce}_{1-x}\text{Pr}_x\text{Ni}_5$ compounds (points 2–5); 2) a decrease in the Pr concentration in PrNi_5 during an isovalent substitution causes no substantial changes in the splitting pattern, at least for the Γ_3 and Γ_{5A} levels. This conclusion agrees with the results of Refs. 5 and 6, where it was noted that the ion-dependent component of the electric potential of the crystal in metals is fairly well localized; i.e., it is determined primarily by the nearest neighborhood (18 nickel ions for Pr in PrNi_5). Consequently, the change in the level scheme found for the impurity ion is due to the presence in the crystal lattice of ions in a mixed-valence state, which strongly affect the electric potential of the crystal. Figure 2b shows the integral intensity of the peak of the $\Gamma_4 - \Gamma_3$ transition as a function of the Pr concentration x . We see that the behavior is nearly linear; i.e., all of the praseodymium ions of the samples contribute to the observed peak. This result is evidence in favor of a uniform effect of the mixed-valence

cerium ions on the crystal electric field in $(\text{Pr})\text{CeNi}_5$. A hybridization of the f -electrons with band electrons may have important manifestations in specifically the sixth-order terms of the Hamiltonian of the crystal electric field.⁶ Furthermore, it follows from the symmetry of the crystal lattice that the ions of the rare-earth metal which are closest to the Pr (these would be cerium ions for the most part at small values of x) do not contribute to B_6^6 . Consequently, the changes in ϵ_{4-3} are determined primarily by the electron component, rather than by the ion component. The delocalization of the f -electrons can apparently explain the absence of crystal-field effects on the cerium ion in the mixed-valence system CeNi_5 , despite the existence of a "stationary" crystal electric field. It should be noted that the widths of the neutron peaks, $\Gamma_{\text{exp}} \simeq 2$ meV, for the $\text{Ce}_{1-x}\text{Pr}_x\text{Ni}_5$ samples (except that with $x = 0.1$) are greater than the instrumental resolution and larger than the corresponding widths for $\text{Pr}_c(\text{La}, \text{Y})_{1-c}\text{Ni}_5$ samples ($\Gamma_{\text{exp}} \simeq 1.6-1.7$ meV). This circumstance indicates that there are some inhomogeneities in the potential, which are small in comparison with the change in the average value over the sample.

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