Interaction of Pr^{3+} ions with the crystal electric field and with conduction electrons in a $CeAl_3$ Kondo system

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Experiments on the inelastic scattering of neutrons by the Kondo lattice $Ce_{0.97}Pr_{0.03}Al_3$ reveal a clearly defined peak corresponding to magnetic scattering by praseodymium ions. The results agree with the interpretation that some of the conduction electrons responsible for the anomalous properties of $CeAl_3$ "stick to" cerium ions.

Several anomalous physical properties distinguish $CeAl_3$ from other compounds of the $REMAl_3$ type (REM = Ce, Pr, or Nd). In particular, the electron coefficient in the specific heat is huge: $\gamma \cong 1600$ mJ/(mole·K^2) (Ref. 1), in comparison with $\gamma(LaAl_3) \cong \gamma(PrAl_3) \cong 5$ mJ/(mole·K^2). As yet we do not have a complete explanation of these anomalies, but recent experiments[2,3] suggest that $CeAl_3$ is a concentrated Kondo system (a Kondo lattice).

Measurements of the inelastic scattering of neutrons have revealed a qualitative distinction between $PrAl_3$ (Ref. 4) and $CeAl_3$ (Ref. 5): The widths of the peaks corresponding to transitions between levels of the Pr^{3+} ion, split by the crystal electric field, in $PrAl_3$ are much smaller (5–15 K) than in $CeAl_3$, where they are comparable to the energy of transitions between levels of the Ce^{3+} ion split by the crystal field (50 K). The width of the peak in the spectrum of the inelastic neutron scattering correspond-

ing to the magnetic dipole transition between levels of an ion of a rare-earth metal split by the crystal electric field in a paramagnet is determined primarily by the relaxation interaction of f electrons with conduction electrons and is substantially smaller than 50 K. A parameter characterizing the peak width in the limit[6] $T \to 0$ is the product $[N(0)J_{s\text{-}f}]^2$, where $N(0)$ is the s-electron state density at the Fermi surface, and $J_{s\text{-}f}$ is the constant of the exchange interaction between s and f electrons. The blurring of the peaks in $CeAl_3$ suggests an additional mechanism for the interaction of the cerium ions with their surroundings—a mechanism which competes with the crystal electric field.

In order to reach an understanding of the unusual properties of $CeAl_3$, in particular, the huge value of γ, which is ordinarily attributed to a high state density at the Fermi surface, it would be interesting to study the effect of this factor on the spectrum of inelastic neutron scattering by ions of another rare-earth metal, introduced into the cerium sublattice as ions of a substantial impurity which do not interact with each other. These ions, which demonstrate the ordinary relaxation mechanism for broadening in compounds that are isostructural with $CeAl_3$, could serve as a "tag" on the structural features in the electron spectrum in $CeAl_3$. As these tags it is convenient to choose praseodymium ions, and a concentrated system of $PrAl_3$ and the impurity system $La(Pr)Al_3$ ($LaAl_3$ is a diamagnetic matrix) could be used as "reference points," since they do not exhibit anomalies in their electron properties.

Samples of $Ce_{0.97}Pr_{0.03}Al_3$, $La_{0.97}Pr_{0.03}Al_3$, $LaAl_3$, $PrAl_3$, and $CeAl_3$ were melted in an arc furnace and then subjected to an annealing which rendered the samples homogeneous within 3–5%. The spectra of the inelastic neutron scattering were measured on the triaxial crystal spectrometer of the Institute of the Physics of Metals, Ural Scientific Center, Academy of Sciences of the USSR, by the "constant-Q" method with a fixed initial neutron energy, $E_0 = 22.1$ meV ($\Delta E_0 = 1.6$ meV) and by the method of the "release" of the energy of these neutrons upon scattering. The measurements taken at $T = 5$ K and $T = 80$ K from $LaAl_3$ and $CeAl_3$ compounds revealed no deviation from a monotonic behavior in the spectrum of the inelastic neutron scattering over the energy-transfer range $0 < \epsilon < 5$ meV. The spectrum of the compound $PrAl_3$ has a clearly defined peak, with greatest intensity at $T = 5$ K and a maximum near $\epsilon = 4.5$ meV. According to the results of Ref. 4, this peak corresponds to the transition $\Gamma_1 - \Gamma_6$ (Γ_1 is the ground state of the Pr^{3+} ion in the $PrAl_3$ crystal field). In addition, the $La_{0.97}Pr_{0.03}Al_3$ and $Ce_{0.97}Pr_{0.03}Al_3$ spectra each contain a single peak (Fig. 1, a and b), with maxima at $\epsilon_1 = 3.3 \pm 0.1$ meV and $\epsilon_2 = 4.3 \pm 0.1$ meV, respectively. The widths of the two peaks are roughly equal (~ 1.5 meV) and are determined by the resolution function of the instrument. In other words, their intrinsic width is [1] < 0.3 meV.

Let us examine the interaction of the Pr^{3+} ion with the crystal electric field in these compounds. The parameters of the hexagonal lattice for these compounds lie in the interval of values corresponding to $LaAl_3$ and $PrAl_3$. For $Ce_{0.97}Pr_{0.03}Al_3$, the lattice constants a and c are approximately equal to the corresponding values of the isostructural $Pr_xLa_{1-x}Al_3$ compound with[4] $x = 0.80$ (Fig. 2a). The inelastic neutron scattering spectra of the systems $Pr_xLa_{1-x}Al_3$ at liquid-helium temperatures[4] reveal only a single transition, $\Gamma_1 - \Gamma_6$, so that the peaks in Figs. 1a and 1b probably correspond to this transition. In Fig. 2b the experimental values of ϵ_0, ϵ_1, and ϵ_2 (ordered in accordance with the values of the lattice constants of the samples) are compared with

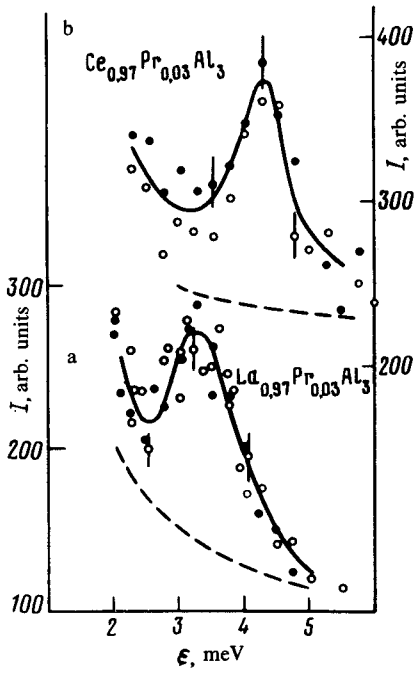

FIG. 1. Spectra of the inelastic neutron scattering by $La_{0.97}Pr_{0.03}Al_3$ (a) and $Ce_{0.97}Pr_{0.03}Al_3$ (b) samples at sample temperatures of 5 K (open circles) and 12 K (filled circles). The neutron momentum transferred is $Q = 1.4$ Å^{-1}. The dashed curves show the scattering due to $LaAl_3$ (a) and $CeAl_3$ (b).

the concentration dependence of $\epsilon_{\Gamma_1-\Gamma_6}$ for the $Pr_xLa_{1-x}Al_3$ systems (solid line). We see that ϵ_1 agrees with extrapolated values for $x = 0.03$, while ϵ_2 agrees with the values of $\epsilon_{\Gamma_1-\Gamma_6}$ for the compound $Pr_{0.8}La_{0.2}Al_3$.

The agreement of the crystal-field effects for Pr^{3+} in $Ce_{0.97}Pr_{0.03}Al_3$ and in the structural analog $Pr_{0.8}La_{0.2}Al_3$ and also the small intrinsic widths of the inelastic neutron scattering peaks in both $La_{0.97}Pr_{0.03}Al_3$ and $Ce_{0.97}Pr_{0.03}Al_3$ seem to imply

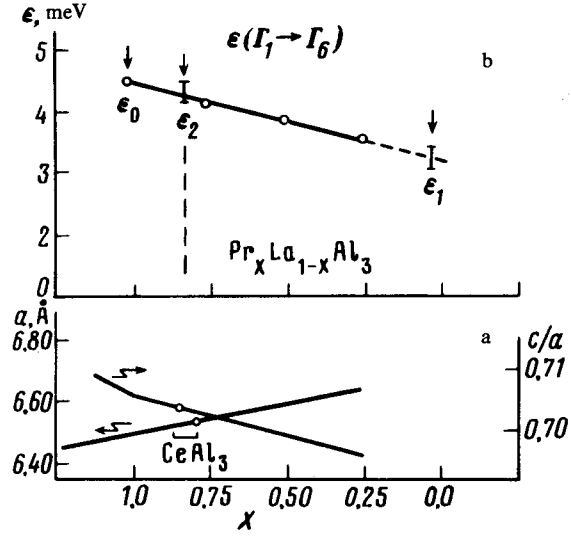

FIG. 2. Concentration dependence of the lattice constants (a) and of the energy of the Γ_1–Γ_6 transition (b) in the compounds[4] $Pr_xLa_{1-x}Al_3$. The lines are fits of the experimental points. The arrows show the values of $\epsilon_{\Gamma_1-\Gamma_6}$ for $PrAl_3$ (ϵ_0), $La_{0.97}Pr_{0.03}Al_3$ (ϵ_1), and $Ce_{0.97}Pr_{0.03}Al_3$ (ϵ_2) found in the present study.

that there are no important differences in electron structure between Ce(Pr)Al_3 and La(Pr)Al_3. This conclusion, however, is contradicted by data on the specific heat and the magnetic susceptibility of $CeAl_3$. According to the models of Refs. 6 and 7, the anomalous value of γ and thus $N(0)$ should be expressed as a pronounced broadening ($\gtrsim 10$ meV) of the peak corresponding to the $\Gamma_1 - \Gamma_6$ transition and a significant shift (~ 1 meV) of this peak toward the elastic line in measurements of the inelastic neutron scattering by praseodymium impurity ions in $CeAl_3$. In other words, this peak in $Pr_xCe_{1-x}Al_3$ should essentially disappear.

This contradiction between the expected and actual results can be resolved by assuming that the praseodymium ions do not interact with the electrons which are responsible for the anomalous state density at the Fermi surface in $CeAl_3$. This assumption agrees with the suggestion that a narrow resonance forms at ϵ_F in Kondo lattices at $T < T_K$ (T_K is the Kondo temperature), because some of the conduction electrons "stick to scattering centers" (cerium ions).[8] These "heavy" fermions with $m^* \gg m_e$ determine the anomalous thermodynamic, kinetic, and magnetic properties of a Kondo lattice, but since they are "stuck" near the cerium ions they do not interact with the praseodymium impurity ions and thus contribute to neither the crystal potential nor the relaxation broadening of the peaks in the spectrum of inelastic neutron scattering by praseodymium ions. Furthermore, if these arguments are correct, then the decrease in the concentration of ordinary "light" conduction electrons caused by the sticking could, in principle, cause a contraction of the peak in the inelastic scattering of neutrons by Pr^{3+} ions in Ce(Pr)Al_3 in comparison with La(Pr)Al_3 at $T < T_K$ (T_K for $CeAl_3$ is [2] 5–7 K).

An experimental study of this question, however, will require a substantial improvement in the resolution of the spectrometer.

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[1)]An estimate of the relaxation width of the transition[7] $\Gamma_1 - \Gamma_6$ yields $\sim 30\ \mu$eV at liquid-helium temperatures.

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