

Knight shift is expected to vanish, yet most experiments at these low temperatures have found an anomalous "shift" that is about $\frac{2}{3}$ of its value in the normal state. For example, Androes and Knight¹ found at $T \ll T_c$ a shift = 0.55% and a linewidth = 0.34% H_0 . Equations (8), which were derived by using the numerical quantities that correspond to the experiments of Androes and Knight, agree favorably with their results. This means that in order to measure the true Knight shift for small particles at low temperatures steps must be taken to keep a layer of air (or layer of any paramagnetic molecules) from adsorbing to the particle's surfaces.

The spin-lattice relaxation time also has often shown anomalous behavior below T_c for superconducting particles less than 1μ in size.² If there is

a layer of air on the surfaces of the small particles, most of the superconducting nuclei will be within several hundred Å of an O_2 molecule on the surface. This suggests that the anomalous relaxation that has been observed for the superconducting nuclei is due to the combination of direct relaxation of the nuclei by the surface O_2 and nuclear spin diffusion. Evidence that this effect might be present is the experimental work on nonconducting solids where nuclei are relaxed by paramagnetic impurities several hundred Å away, and the nuclear relaxation times measured are often on the order of those observed in small superconducting particles.³ Thus, in order to eliminate this source of anomalous relaxation in small superconducting particles all O_2 (or other paramagnetic impurities) must be removed from the particle's surfaces.

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¹G. M. Androes and W. D. Knight, Phys. Rev. 121, 779 (1961).

²K. Asayama and Y. Masuda, J. Phys. Soc. Japan 21, 1459 (1966); L. C. Hebel and C. P. Slichter, Phys. Rev. 113, 1504 (1959) have experimental results for larger superconducting particles in agreement with theory.

³N. Bloembergen, Physica 25, 386 (1949).

Paramagnetic Curie Temperatures of the Rare-Earth Monophosphides[†]

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We show how it is possible to understand the sign change of the paramagnetic Curie temperatures in going from the light to heavy rare-earth monophosphides.

The paramagnetic Curie temperatures Θ_p of the rare-earth monophosphides REP have recently been determined by Jones.¹ The striking feature of his results is the change in sign of the temperatures Θ_p in going from the light to heavy rare earths. The paramagnetic Curie temperature derived from the Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange interaction together with the spherical band approximation is proportional²

$$k\Theta_p \propto Z^2(g_J - 1)^2 J(J+1) \Gamma^2 E_F^{-1} \sum_m F(2k_F R_m). \quad (1)$$

In this expression, Z is the number of conduction electrons per atom, g_J is the Landé g factor for the ground state of total angular momentum J , Γ is a diagonal s - f exchange integral, k_F is the Fermi momentum, and E_F is the Fermi energy. R_m is the distance between rare earths, and the function $F(x)$ is

$$F(x) = (x \cos x - \sin x)/x^4.$$

The sum $\sum_m F(X_m)$ is the only term in Eq. (1) that can change sign. For a given structure it is a function only of the number of conduction electrons Z .³ If we assume that Z remains constant, the sum is the same for all rare-earth monophosphides.⁴

Three possible explanations for the sign change of the paramagnetic Curie temperatures suggest themselves. They are (i) the crystal field spuriously contributes to the Θ_p ; (ii) the sum $\sum_m F(X_m)$ varies in such a way as to fit the observed data; and (iii) the RKKY interaction is insufficient. Other terms are present in the indirect-exchange interaction. A plot of the inverse susceptibility of paramagnetic ions subject to crystal fields appears linear over a wide range of temperatures

T ; however, there is a slight curvature for temperatures less than the characteristic crystal-field splitting parameter Δ . If we fit the portion of the inverse susceptibility curve about $T/\Delta = 1$ to a Curie-Weiss law, the parameter Θ_p will not be zero as it should be for paramagnetic ions.⁵ As an illustration of this point, we plotted the inverse susceptibility of paramagnetic cerium ions in sites of cubic symmetry; we found that for a crystal field of the size that exists in cerium monophosphide CeP the paramagnetic Curie temperature Θ_p is of the same order of magnitude as the Θ_p owing to exchange in CeP. Therefore, if we do not recognize the slight curvature due to crystal fields, there will be a spurious contribution to the paramagnetic Curie temperature. As this contribution can be either positive or negative, the crystal field is one possible indirect source for the sign change of the paramagnetic Curie temperatures. As Jones has noted, it is necessary to extend the temperature range of the Knight-shift measurements on some of the rare-earth monophosphides in order to ascertain these crystal-field contributions.

Let us now consider the remaining possible explanations for the sign change of the Θ_p . It is conceivable that the number of conduction electrons varies across the rare-earth series in such a way as to account for the change in sign of Θ_p ; also, it is possible that a calculation of the paramagnetic Curie temperature, using more realistic bands, yields a sum like $\sum_m F(X_m)$ but with a more propitious variation. Since the details of the band structure on these compounds are not known we must defer further consideration of these possibilities.

We are left with the possibility that additional terms are present in the indirect exchange between the rare-earth ions in these intermetallic compounds. Kaplan, Kasuya, and Lyons⁶ have considered orbital contributions to the indirect exchange. We have derived an expression for Θ_p based on their interaction and find that in spite of the additional terms present we are unable to explain the observed sign change of Θ_p (see last column in Table I). Jones has found that the band electrons near the Fermi surface have considerable orbital character.⁷ Therefore, to properly describe the indirect exchange it is necessary to include the spin-orbit splitting of the conduction electrons. We have previously derived the Hamiltonian which includes these effects⁸ and have found that new terms are present in the exchange interaction. With these new terms, we are able to explain the observed sign change of the paramagnetic Curie temperatures of the REP compounds.

Using the bilinear scalar-exchange interaction appropriate to indirect exchange via conduction

electrons in spin-orbit coupled states, we find that the paramagnetic Curie temperature is given as⁸

$$k\Theta_p = \frac{1}{3}J(J+1) [(g_J - 1)^2 Q_{0101} + (2 - g_J)^2 Q_{1010} + c_n^2 Q_{2121} + 2(g_J - 1)(2 - g_J) Q_{1001} + 2(g_J - 1) c_n Q_{0121} + 2(2 - g_J) c_n Q_{1021}] \quad (2)$$

The parameters $Q_{p_1 K_1 p_2 K_2}$ are generalizations of the term $\Gamma^2 \sum_m F(2k_F R_m)$ in the RKKY expression Eq. (1); they represent the contributions to Θ_p from portions of the pair interactions described by orbital and spin operators of ranks p and K . The coefficient c_n is proportional to the ratio of the reduced matrix element

$$(J || \sum_i^n [O^{[2]}(\vec{L}_i) \times \vec{S}_i^{[1]}]^{[1]} || J)$$

and that for the total angular momentum ($J || \vec{J}^{[1]} || J$); n is the number of $4f$ electrons. The last three terms of Eq. (2) appear only when the spin-orbit splitting of the conduction electrons is considered.

We have fitted the paramagnetic Curie temperatures given by Jones¹ to Eq. (2) and find the best three-parameter fit⁹ by using the parameters $Q_{0101} = -2.58 \times 10^{-3}$ eV, $Q_{1001} = 2.12 \times 10^{-3}$ eV, and $Q_{1021} = 24.7 \times 10^{-3}$ eV; see Table I. These were de-

TABLE I. The paramagnetic Curie temperatures Θ_p ($^{\circ}$ K) of the rare-earth monophosphides REP. The experimental data are given by Jones; see Ref. 1. The best three-parameter fit is obtained by using Eq. (2) and the parameters $Q_{0101} = -2.58 \times 10^{-3}$ eV, $Q_{1001} = 2.12 \times 10^{-3}$ eV, and $Q_{1021} = 24.7 \times 10^{-3}$ eV. The parameters in the conventional anisotropic s - f exchange interaction (see Refs. 6 and 8) that were used to find the fit in the last column are $Q_{0101} = -2.58 \times 10^{-3}$ eV, $Q_{1010} = -6.71 \times 10^{-3}$ eV, and $Q_{2121} = 320 \times 10^{-3}$ eV.

Element	Experiment	Best three-parameter fit	Fit using conventional parameters
Ce	3.6 ± 1.0	11.8	26.5
Pr	21.5 ± 1.2	15.5	7.75
Nd	8.9 ± 0.2	9.05	-12.6
Sm	•••	-11.05	1.54
Gd	-22.4 ± 1.2	-22.4	-22.4
Tb	-15.6 ± 2.8	-16.4	-9.62
Dy	-10.5 ± 1.6	-10.5	-10.5
Ho	-22.3 ± 5.9	-11.2	-17.6
Er	-14.9 ± 2.5	-14.9	-14.9
Tm	•••	-15.0	-2.14
Yb	-11 ± 8^a	-7.97	5.45

^aThe paramagnetic Curie temperature of YbP as given in Table V of Ref. 1 is incorrect. The value given in the text on p. 465 should be used; E. D. Jones (private communication).

terminated by fitting Eq. (2) to the Curie temperatures of gadolinium, dysprosium, and erbium monophosphide.⁵ With the exception of cerium and holmium, the temperatures Θ_p predicted by Eq. (2) for the other REP are in good agreement with those of Jones. Cerium is a special case,¹⁰ and we should not expect an accurate prediction by using Eq. (2). The reasons for the poor fit to holmium are not clear. We include in Table I the values of Θ_p predicted for samarium¹¹ and thulium monophosphide; these could not be determined from the data on the phosphorous nuclear magnetic resonance Knight shifts. For the conventional anisotropic exchange interaction,⁶ only the first three terms in Eq. (2) enter, and we are unable to find a satisfactory fit to the data¹² (see last column in Table I). To compare the magnitudes represented by the parameters $Q_{p_1 K_1 p_2 K_2}$ we relate them to sums over the pair-interaction constants

$$Q^{[0]}(p_1 p_2 p; K_1 K_2 p; R_{AB}),^8$$

$$\sum_{R_{AB}} Q^{[0]}(000; 110; R_{AB}) \\ = (1/\sqrt{3}) Q_{0101} = -1.49 \times 10^{-3} \text{ eV}, \quad (3a)$$

$$\sum_{R_{AB}} Q^{[0]}(101, 011; R_{AB}) \\ = (1/3\sqrt{3}) Q_{1001} = 0.407 \times 10^{-3} \text{ eV}, \quad (3b)$$

and

$$\sum_{R_{AB}} Q^{[0]}(121, 011; R_{AB}) \\ = (1/3\sqrt{3}) Q_{1021} = 4.75 \times 10^{-3} \text{ eV}. \quad (3c)$$

The conduction electrons, in addition to the 4f, are orbitally degenerate; therefore, it is reasonable for the sums representing interactions with orbital contributions (nonzero p), Eqs. (3b) and (3c), to be of the same order of magnitude as the one for spin only, Eq. (3a).

We conclude that when we consider the spin-orbit coupling of both the 4f and conduction electrons we are able to account for a change in sign of the paramagnetic Curie temperatures as we go from the light to heavy rare-earth monophosphides. To obtain a better fit and more realistic values for the parameters $Q_{p_1 K_1 p_2 K_2}$, it is necessary to allow for the variation of these parameters with the number of 4f electrons and to consider the crystal-field contributions to the Θ_p . Some causes for the variation are the lanthanide contraction of the 4f shell with the attendant changes in the magnitudes of the s - f exchange integrals and the dependence of the sums

$$\sum_{R_{AB}} Q^{[0]}(p_1 p_2 p; K_1 K_2 p; R_{AB})$$

on the number of conduction electrons per rare-earth ion.

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²P. G. de Gennes, J. Phys. Radium **23**, 510 (1962); also see Ref. 1.

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⁴M. I. Darby and K. N. R. Taylor [Phys. Letters **14**, 179 (1965)] have attributed variations of the sum $\sum_m F(2k_F R_m)$ to the dependence of the Fermi momentum on the lattice constant of a compound $k_F \propto a_0^{-1}$. However, Jones (Ref. 1) has pointed out that the product of the Fermi momentum and the lattice constant ($k_F a_0$) forms an invariant; therefore, the sum is invariant if we assume that the number of conduction electrons per rare-earth ion remains constant.

⁵We should like to thank Dr. W. P. Wolf for several

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⁸P. M. Levy, Solid State Commun. **7**, 1813 (1969); J. Appl. Phys. **41**, 902 (1970).

⁹With three parameters we are able to reproduce the observed sign change; if we include the remaining parameters, the fit is further improved.

¹⁰This is true for cerium metal and alloys. For a treatment of the indirect-exchange interaction appropriate to cerium, see B. Coqblin and J. R. Schrieffer, Phys. Rev. **185**, 847 (1969).

¹¹The value of Θ_p for samarium is approximate because it is predicted on the basis of a pure $J = \frac{5}{2}$ ground state.

¹²The parameter $Q_{2121} = 320 \times 10^{-3}$ eV for the conventional fit is much too big in comparison to the parameter in the RKKY theory $Q_{0101} = -2.58 \times 10^{-3}$ eV. On the basis of the conventional anisotropic Hamiltonian (see Ref. 6), the parameter Q_{2121} should be much less than Q_{0101} .