Possible Observation of a Compensated Spin State in the Actinide Intermetallic Compounds $U_xTh_{1-x}Pd_3$

D. DAVIDOV, H. LOTEM, D. SHALTIEL, AND M. WEGER
Physics Department, the Hebrew University, Jersualem, Israel

AND

J. H. WERNICK
Bell Telephone Laboratories, Murray Hill, New Jersey 07974

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An EPR measurement of Gd in $U_xTh_{1-x}Pd_3$, $0<x<1$, shows anomalous behavior as a function of temperature. These results, as well as previous anomalous susceptibility measurements of the same compounds, are taken to indicate the existence of a partially compensated spin state on the uranium in $U_xTh_{1-x}Pd_3$. This work indicates the possibility of the existence of the Kondo effect in concentrated spin systems. It shows, also, that the utilization of the EPR technique is a powerful method for investigating the Kondo effect.

RECENTLY, Wernick *et al.*[1] have measured the susceptibility of the actinide intermetallic compounds $U_xTh_{1-x}Pd_3$, $0.005<x<1$. The main features of their results are:

(1) The compound $ThPd_3$ is diamagnetic and shows temperature-independent susceptibility, but the addition of uranium, even in small amounts, gives rise to a strongly temperature-dependent paramagnetic susceptibility.

(2) The data, analyzed in terms of a plot of $1/(\chi-\chi_\infty)$ against T, show a break in the slope at approximately 100°K, for *all* the compounds $U_xTh_{1-x}Pd_3$. For $T>100$°K, the susceptibility is proportional to $1/(T-\theta_1)$ with $\theta_1\simeq 0$, while for $T<100$°K, the susceptibility was found to be proportional to $1/(T+\theta_2)$ with $\theta_2=(45\pm 15)$°K. The effective magnetic moment obtained from the susceptibility at the high-temperature range decreases from 3.35 for the lowest U concentration to 2.55 for the high concentration.

(3) There is no saturation of the magnetic moment up to 80 kG at 4.2°K.

A possible interpretation for the susceptibility data may be given by any one of the following models:

1. Crystal field splitting. For low U concentrations, the effective moment per U atom at the high-temperature region is close to the value of 3.58 expected for the ground state $^3H_4$. Therefore, U is probably dissolved in $ThPd_3$ as U^{+4} with the configuration $5f^2$. Both UPd_3 and $ThPd_3$ have the hexagonal structure DO_{24}. Therefore, the point symmetry of the U^{+4} ion in $U_xTh_{1-x}Pd_3$ is determined by the point group D_{6h}. The $^3H_4$ state, in such a crystal field, is split into three doublets and three singlets. Since the amount of the splitting at the lowest state is unknown, one cannot calculate the exact susceptibility. However, physical considerations indicate that if the splitting between the ground state and any higher sublevel were of the order of magnitude of 100°K, it could account for the sudden break that occurs at 100°K in the susceptibility data.

2. Band structure. The Curie-Weiss behavior for the high-temperature range, and the fact that no saturation of the magnetic moment was achieved, indicates that we are dealing with a very narrow U $5f$ band. A possible model for such a band structure has been proposed by Scott *et al.*[2] for the case of $U_xTh_{1-x}Al_2$, in which the U $5f$ electrons form virtual states at the Fermi surface. According to this model, a significant deviation from the Curie-Weiss law may occur when kT is half of the bandwidth. We may therefore attribute the break at 100°K to this effect.

3. Antiferromagnetically aligned uranium atoms. A susceptibility proportional to $1/(T+\theta)$ is characteristic for antiferromagnets.

4. Compensated spin state. The negative exchange interaction between the spin part of the U magnetic moment and the conduction electrons will result in the formation of a partially or wholly compensated spin state below some critical temperature.[3] The susceptibility of samples which exhibit this effect (Kondo effect) has not yet been completely solved. For very dilute alloys, Anderson[4] has suggested a $T^{-1/2}$ dependence of the susceptibility on temperature. Other authors[5] indicate $1/(T+\theta)$ behavior. Recently, Edelstein[6] has reported on the susceptibility of the concentrated Ce_xLa_{1-x} alloys. His results indicate no saturation of the magnetic moment and $T^{-1/2}$ dependence of the susceptibility. Edelstein explained this behavior by the existence of a Kondo effect in Ce_xLa_{1-x} according to the Anderson theory. However, the $T^{-1/2}$ dependence was predicted for very dilute alloys, and a concentrated spin system may show a different dependence. This point has not yet been investigated

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[5] C. M. Hurd, Phys. Rev. Letters **18**, 1127 (1967); K. Kume, J. Phys. Soc. Japan **22**, 1167 (1967); G. Knapp, J. Appl. Phys. **38**, 1268 (1967); A. J. Heeger, L. B. Welsh, M. A. Jensen, and G. Gladstone, Phys. Rev. **172**, 302 (1968).

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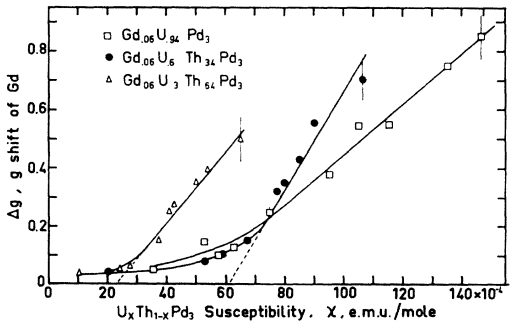

FIG. 1. Gd g shift as a function of the susceptibility of $U_xTh_{1-x}Pd_3$ ($x=0.94$, 0.6, 0.3) with the temperature as the explicit parameter.

theoretically. The susceptibility data of $U_xTh_{1-x}Pd_3$ reveal a $1/(T+\theta)$ dependence for $1.2<T<100°K$; for the smaller temperature range $20<T<100°K$, the susceptibility data also show a $T^{-1/2}$ dependence.

To decide which is the correct model, we have measured the electron paramagnetic resonance (EPR) of Gd in $Gd_{0.06}U_xTh_{0.94-x}Pd_3$. The measurements were conducted as a function of temperature from 4 to 300°K at 0.8-cm wavelength. The alloys were prepared by arc melting in an argon atmosphere and were examined by x-ray technique. The samples were ground to powder form in an argon atmosphere using an automatic grinder.

Figure 1 describes the variation of the g shift, Δg, as a function of the susceptibility χ of the various $U_xTh_{1-x}Pd_3$. It indicates that *there is no linearity between Δg and χ when the temperature is varied.*[7] However, at constant temperature, the g shift is approximately linear as a function of χ, when the uranium concentration is varied, the slope being dependent on temperature. The linearity between Δg and χ for the constant temperature $T=20°K$, as well as the proportionality between Δg and the U concentration, is shown in Fig. 2.

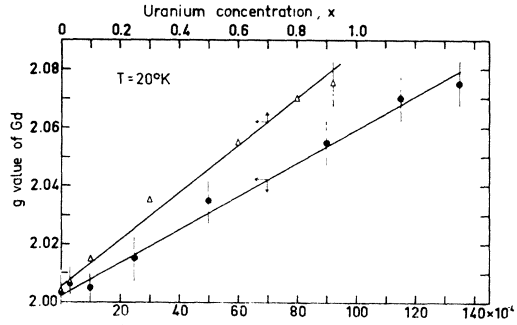

FIG. 2. Gd g value as a function of susceptibility and uranium concentration at the constant temperature of 20°K. The susceptibility of $U_xTh_{1-x}Pd_3$ was varied by changing the U concentration.

The g shift of Gd in $ThPd_3$ was found to be small and positive with a value of $\Delta g=0.005\pm0.005$. The value $\Delta g_0=+0.005$ is supported also by the variation of the linewidth of $ThPd_3$ with temperature, as will be explained later.

Since Δg_0 is given by[8] $\Delta g_0=J_{4f}\chi_e/g_e\beta^2N_0$, we found J_{4f}, the exchange interaction between the Gd ion and the conduction electrons, to be positive.

Figures 1 and 2 indicate that the U ions affect the Gd g shift appreciably. Since the average distance between Gd ion and U ion is much greater than the effective range of the U $5f$ wave function,[9] we can neglect the direct interaction between Gd and U ions and consider only the indirect interaction via the conduction electrons. The exchange interaction $J_{5f}(\mathbf{S}_{5f}\cdot\mathbf{s})$ between the spin part of the U moment and the conduction electrons polarizes the conduction electrons. This polarization creates an additional Gd g shift due to its interaction with the Gd ion. This additional shift is always positive (Fig. 1).

The results of the EPR experiment eliminate the first two of the four models proposed above to explain the anomalous behavior of the susceptibility. In our experiments we observe a marked deviation from linearity of the g shift versus the susceptibility (Fig. 2). However, the following indicates that the first two models require that the g shift be a linear function of the susceptibility when the temperature is an explicit parameter.

The effective interaction between the U and the Gd spins produces a Gd g shift which is proportional to the spin part of the U magnetic moment $\langle S_z\rangle$.[10] For a band model, the orbital part of the susceptibility was found theoretically by Kubo and Obata,[11] and experimentally by Gossard *et al.*,[10] to be small and temperature-independent. Therefore, the variation of a band susceptibility with temperature is due to the variation of the spin of the $5f$ electrons with temperature. Therefore, for the band model, one expects a linearity between the g shift and the susceptibility.

In the crystal-field-splitting model, the U ions are localized and, therefore, the relation $\langle S_z\rangle=(g_J-1)\langle J\rangle$ holds; g_J is the Landé g factor for the $^3H_4$ state and $\langle J\rangle$ is the expectation value of the total angular momentum of the U atom. Although $\langle J\rangle$ depends on the crystal-field splittings, it is always proportional to the total U susceptibility. Thus the linearity between the g shift

[7] Shaltiel *et al.* have measured the EPR of Gd in $Gd_{0.08}U_{0.92}Pd_3$: D. Shaltiel, J. H. Wernick, H. J. Williams, and M. Peter, Phys. Rev. **135**, 1346 (1964). They found the Gd g shift to be linear with the susceptibility of UPd_3. However, our results disagree slightly with their results for temperature of 90°K and above.

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[9] The effective range of the $5f$ wave functions was calculated by A. J. Freeman and R. E. Watson, in *Magnetism*, edited by G. Rado and H. Suhl (Academic Press Inc., New York, 1966), Vol. BI.

[10] A. C. Gossard, V. Jaccarino, and J. H. Wernick, Phys. Rev. **128**, 1038 (1962).

[11] R. Kubo and Y. Obata, J. Phys. Soc. Japan **11**, 547 (1956).

and the susceptibility should also exist for the crystal field model.

As for the antiferromagnetic model, it is excluded too, since, for an antiferromagnet, θ increases with the concentration of magnetic atoms, while here a change of two orders in the concentration of uranium atoms changes θ by only a factor of 2; also, for an antiferromagnet, the susceptibility follows the $C/(T+\theta)$ law only for $T>\theta$, while for $T<\theta$, the susceptibility decreases with decreasing temperature. Here, this behavior is observed to temperatures at least 20 times lower than θ.

Hence, these three models are excluded. Our results can be expressed using the compensated state model, as follows: The negative exchange interaction between the localized $5f$ electrons and the conduction electrons, J_{5f}, creates a quasibound state or a partially compensated spin state on the U atom. Since this compensated spin state may have a relatively long range,[12] it may affect the Gd atoms and create a g shift. An increase in temperature destroys this bound state, resulting in the rapid decrease of the spin density around the U ion, and hence in the decrease of the shift faster than the U susceptibility (Fig. 2).

However, from the linear dependence of Δg versus the susceptibility at constant temperature (Fig. 1), we obtain the result that the ratio of the spin susceptibility to the total susceptibility at constant temperature remains constant. (The susceptibility at constant temperature is varied by varying the uranium concentration.) This indicates that the spin density around the U atoms at constant temperature is proportional to the uranium susceptibility. The situation may also be described by the following phenomenological equations: Let us assume that the susceptibility χ of the compounds $U_xTh_{1-x}Pd_3$ may be written

$$\chi(T)=\chi_{\text{c.e.}}(T)+\chi_{5f}(T),$$

where $\chi_{\text{c.e.}}(T)$ is the spin susceptibility of the conduction electrons and $\chi_{5f}(T)$ is the susceptibility of the localized $5f$ electrons. At 0°K, for a fully compensated spin state, these susceptibilities might satisfy the relation $\chi_{\text{c.e.}}(0)=\chi_{5f}(0)$, according to the Kondo theory. Let us assume that the Gd g shift Δg is proportional to $\chi_{\text{c.e.}}(T)$. Then for low temperatures, the initial slope of χ versus Δg can be written approximately as

$$\left(\frac{d\chi}{d\Delta g}\right)_{T=0}=\frac{\chi_{\text{c.e.}}(0)}{\Delta g(0)}\left[1+\left(\frac{d\chi_{5f}/dT}{d\chi_{\text{c.e.}}/dT}\right)_{T=0}\right].$$

Extrapolating this initial slope to $\Delta g=0$, we get

$$\chi_{\text{extrap}}=\chi_{5f}(0)\left[1-\frac{\chi_{\text{c.e.}}(0)}{\chi_{5f}(0)}\left(\frac{d\chi_{5f}/dT}{d\chi_{\text{c.e.}}/dT}\right)_{T=0}\right].$$

χ_{extrap} is found experimentally to be approximately $0.4\chi(0)$; thus, if $\chi_{\text{c.e.}}(0)=\chi_{5f}(0)$, this is consistent with a temperature dependence of $\chi_{\text{c.e.}}$ which is five times larger than that of χ_{5f}. Since it is not known to what accuracy the equality between $\chi_{5f}(0)$ and $\chi_{\text{c.e.}}(0)$ holds, this estimate of the relative temperature dependence must be regarded with caution.

Finally, the linewidth for the various compounds was found to vary linearly with temperature for $T>20$°K. Its slope in this temperature region is almost constant for all the compounds, and equals approximately 1 G/deg. For constant temperature, the linewidth was found to increase with U concentration. This behavior may be explained by assuming the presence of two relaxation processes,

$$1/T_1=(1/T_1)_s+(1/T_1)_{5f},$$

where $(1/T_1)_s$ is the ordinary Koringa mechanism, and $(1/T_1)_{5f}$ is a relaxation due to interaction with $5f$ electrons.

The linewidth DH_1, due to the Koringa mechanism alone [$\gamma DH_1=(1/T)_s$], is given by

$$DH_1=(\pi/g\beta)(\Delta g_0)^2kT. \quad (1)$$

This calculated linewidth is essentially the observed linewidth of Gd in $ThPd_3$. Substituting the proper values for $ThPd_3$, in Eq. (1), gives $\Delta g_0=0.006$. This value is close to the observed one.

Since the slope of the linewidth versus temperature is almost the same for all the compounds $U_xTh_{1-x}Pd_3$, the relaxation process $(1/T_1)_{5f}$ should be temperature-independent. Such a mechanism can be a spin-flip process.[13] The variation of the linewidth with temperature and concentration indicates that there is no bottleneck or dynamic effects in $ThPd_3$. A more detailed work will be published.

In conclusion, it should be stressed that the compensated spin model might account for the anomalies in both the EPR and susceptibility measurements. Other models cannot explain both phenomena, and are therefore eliminated. These experiments strongly support the possibility of the existence of a uranium spin-compensated state in an actinide intermetallic compound.

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