CONDUCTION-ELECTRON POLARIZATION AT INEQUIVALENT Pt SITES IN RARE-EARTH-PLATINUM ALLOYS

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(Received 6 October 1967)

The conduction electron polarization in rare-earth (RE) metals and alloys has been investigated by various techniques.[1-3] In particular, one can test the applicability of the Ruderman-Kittel-Kasuya-Yosida (RKKY) theory[4] to explain the observed polarizations, although sometimes the simpler but less realistic uniform-polarization model is used.[5] We report here the deductions made from the study of the ^{195}Pt Knight shifts in the intermetallic compounds $R\text{Pt}_2$ and $R\text{Pt}_5$ ($R \equiv$ La, Ce, Pr, and Nd) in the temperature range 80-400°K.

Of special interest is the observation of two different polarizations at the inequivalent Pt sites in the $R\text{Pt}_5$ compounds. These have the hexagonal Laves structure (CaCu_5 type) with two sets of inequivalent Pt atoms arranged in alternate planes normal to the c axis. Those in planes containing the RE atoms are designated as Pt_I and the others as Pt_II. Their relative numbers are in the ratio 2:3 and this has made it possible to identify the two ^{195}Pt resonances separately. The $R\text{Pt}_2$ compounds have the cubic Laves structure (MgCu_2 type) with all the Pt atoms equivalent.

The ^{195}Pt Knight shifts (k) in all except the La compounds showed strong temperature dependence. The magnetic susceptibilities (χ_M) of the paramagnetic compounds showed Curie-Weiss behavior with the RE moments close to the free-ion values. The paramagnetic Curie temperatures (θ_P) were positive in the $R\text{Pt}_2$ and negative in the $R\text{Pt}_5$ compounds. The plots of k versus χ_M, with temperature the implicit variable, were straight lines (Fig. 1) intersecting the k axis at values close to k_0, the Knight shifts in the nonmagnetic La compounds. It is to be noted that in the $R\text{Pt}_5$ compounds, the plots of k versus χ_M for the two Pt sites converge at two different k_0 values corresponding to the unenhanced Knight shifts in LaPt_5 and have unequal slopes. The epr of Gd^{3+} in GdPt_2 yielded a broad line with a g value of 1.873 ± 0.007 (obtained at 300°K after applying demagnetization and line-shape corrections), which in the conventional sense corresponds to a negative g shift when compared with the g

value of a free Gd^{3+} ion. Shaltiel et al.[6] observed a g shift of +0.01 for the epr of Gd impurities in LaPt_2, while a g shift of +0.02 is obtained[7] for the epr of 5 mole % Gd substituted for the

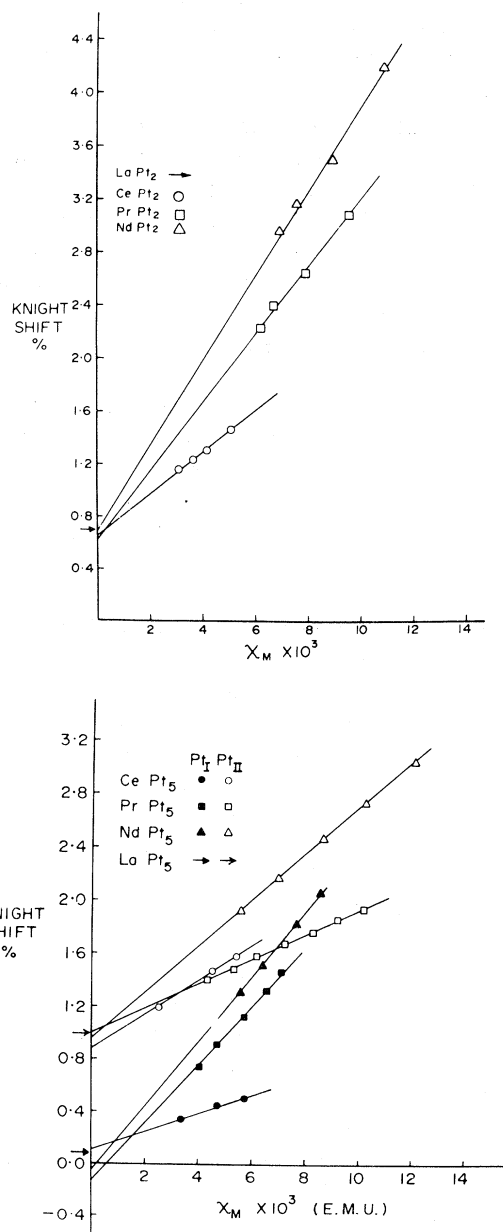
FIG. 1. Plots of ^{195}Pt Knight shift versus susceptibility for the $R\text{Pt}_2$ and $R\text{Pt}_5$ intermetallic compounds.

La site in $LaPt_5$.

Although the RKKY theory in its original form involves certain assumptions which are not justified when applied to real metals,[8] it is frequently employed due to its simplicity. In this approximation, if the wave-vector–dependent exchange integral $J(q)$ between the local moment and a $4f$ conduction electron is assumed to be constant and equal to $J(0)$, the Knight shift is given by de Gennes[9] as

$$k = k_0 \left[1 - \frac{6\pi Z(g_J - 1)J(0)\chi_M}{Ng_J\beta^2} \sum_j F(2k_F R_j) \right], \quad (1)$$

where Z is the average number of conduction electrons per atom. The function $F(x) = (x\cos x - \sin x)x^{-4}$ and R_j is the distance of the jth RE atom from the resonant nucleus. The g shift Δg and the paramagnetic Curie temperature θ_P are given by the following expressions:

$$\Delta g = (3Z/2E_F)J(0), \quad (2)$$

$$k_B\theta_P = -3\pi^2 Z^2 J(0)^2(g_J - 1)^2 J(J+1)E_F^{-1}$$
$$\times \sum_m F(2k_F R_m), \quad (3)$$

where R_m are RE-RE distances.

The near-zero Knight shift for Pt_I in $LaPt_5$ evidently shows the presence of a small fraction (~ 0.1) of a hole in the $5d$ sub-band associated with this site, the negative shift arising from it compensating the positive shift due to the s electrons. There is a slight temperature dependence of the susceptibility and $^{195}Pt_I$ Knight shift in $LaPt_5$ due to this $5d$ hole. The temperature-independent positive shift at the $^{195}Pt_{II}$ site indicates that the $5d$ sub-band associated with this site is filled. The choice of a proper value of Z for the RE and Pt sites in the RPt_5 compounds is a somewhat difficult problem, as is the question of the overlap between the $4f$(RE) and $5d$(Pt) wave functions. It has been observed[6,7] that in metals and alloys with nearly filled d bands the g shift of Gd impurities gradually moves from a negative to a positive value as the d band gets filled. This effect has been particularly seen[7] in the alloy systems YNi_xCu_{5-x} and $LaNi_xCu_{5-x}$ which are isostructural with $LaPt_5$. These results have been interpreted[7] to indicate that f-d interactions are negative and f-s interactions are positive. The positive g shift[6,7] for Gd impurities in $LaPt_2$ and $LaPt_5$ indicate that the $4f$-$5d$ interactions play a minor role in comparison to the $4f$-$6s$ interactions. For the RPt_5 compounds, we therefore choose

$$Z = (Z_{RE} + 2Z_{Pt_I} + 3Z_{Pt_{II}})/6,$$

where

$$Z_{RE} = 3, \quad Z_{Pt_I} = 0.1, \quad Z_{Pt_{II}} = 0;$$

and $k_0 = 1\%$ for both the sites. Since the ^{195}Pt Knight shift in $LaPt_2$ indicates that the $5d$ band is filled, we choose for the RPt_2 compounds $Z = (Z_{RE} = 2Z_{Pt})/3$, where $Z_{RE} = 3$, $Z_{Pt} = 0$; and $k_0 = 0.7\%$. These values of k_0 are consistent with those obtained from the purely s-electron hyperfine interaction in platinum and its alloys.[10] The summations in Eqs. (1) and (3) have been made with a CDC-3600 computer to include the contributions from all RE atoms within a sphere of radius 50 Å. It was found that their signs did not change for reasonable variations in the choice of Z.

The values of $J(0)$ that result from using Eqs. (1)-(3) are shown in Table I. The two values of $J(0)$ quoted for the two Pt sites in the RPt_5 alloys are two determinations of what should be a single value of $J(0)$ for the f-s interaction. The sign and magnitude of $J(0)$ from epr measurements on $GdPt_2$ and that of earlier workers[6] on Gd impurities in $LaPt_2$ and $LaPt_5$ are included. It has been shown[7] that there is a strong dependence of the g shift on the concentration of Gd in some alloys like $Gd_xLa_{1-x}Ni_5$. The sign of $J(0)$ in both the systems, as obtained from nmr data, is positive in agreement with the g-shift results of the earlier workers.[6,7] The positive signs of $J(0)$ seem to indicate that the effect of exchange integral is stronger than that of interband mixing between $4f$ and conduction electrons, which gives rise to a negative contribution.[11] However, it should be emphasized that no undue importance should be attached to the values of $J(0)$ quoted in Table I, because of the several approximations inherent in the RKKY theory.

The above discussion makes clear the difficulties involved in determining the sign, much less the magnitude, of $J(0)$. It is therefore surprising that some authors are still casual on this point and do not emphasize the complex nature of the problem while interpreting the data. On the other hand, the early epr workers[12,13] tried to fit data with the equivalent of Eq. (1) but understandably failed, due to the

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Table I. Values of $J(0)$ (in eV) obtained in the $R\mathrm{Pt}_2$ and $R\mathrm{Pt}_5$ intermetallics from the various experimental data.

		From $^{195}\mathrm{Pt}$ Knight shift			From Gd^{3+} g shift	From θ_P data
		Ce	Pr	Nd		
$R\mathrm{Pt}_2$		0.30	0.35	0.16	-0.45 0.05^a	± 0.2
$R\mathrm{Pt}_5$	Pt_I	0.10	0.22	0.16	0.20^b	± 0.4
	Pt_{II}	0.36	0.21	0.24		

[a]See Ref. 6.   [b]See Ref. 7.

nature of the polarization they were dealing
with. They then resorted to other models with
interior cutoffs, etc., and at least obtained
the correct signs of $J(0)$. Part of the difficul-
ty is that Eq. (1) is an extremely poorly con-
vergent series, violently sensitive to errors
in either F or setting $J(q) = J(0)$. Evaluation
of the conduction-electron polarization in var-
ious RE alloys using more rigorous procedures[8]
is currently underway.

The authors wish to thank the Metallurgy
Division of the Bhabha Atomic Research Cen-
tre for help in preparing the alloys, V. R. Ma-
rathe for making the susceptibility measure-
ments, and K. V. Lingam and P. G. Nair for
taking the epr spectrum.

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SIZE EFFECTS IN THE ELECTRONIC THERMAL CONDUCTIVITY
OF GALLIUM SINGLE CRYSTALS*

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(Received 27 November 1967)

Recent work[1,2] on the electrical conductiv-
ity of 99.9999% gallium single crystals has
shown that the ideal resistivity ρ_i varies as
the square of the absolute temperature between
1.1 and 4.2°K. This variation may be caused
either by collisions between electrons from
different branches of the Fermi surface or
by electron-phonon Umklapp processes. In
a specimen of 0.95-cm diam, Newbower and
Neighbor[1] also found a small peak in the resis-

tance temperature curve at about 1.7°K; the
exact temperature depended on the measuring
current and on the earth's magnetic field. Spe-
cific-heat measurements on the same materi-
al by Shiffman and Neighbor[3] showed no cor-
responding effect, and this suggests that the
resistance peak is not a property of the bulk
metal, but may be due to the onset of boundary
scattering for a particular group of electrons.
(The average mean free path of electrons for