# CONDUCTION-ELECTRON POLARIZATION IN THE PARAMAGNETIC STATE OF A "GIANT-MOMENT" DILUTE ALLOY*

L. D. Graham and D. S. Schreiber

Department of Physics, Northwestern University, Evanston, Illinois

(Received 1 August 1966)

The study of local moments in metals, particularly the dilute iron-group elements in a Pt or Pd host matrix, has received much theoretical and experimental attention lately.[1-16] Macroscopic experimental techniques such as susceptibility measurements and neutron diffraction have yielded much useful information. The microscopic Mössbauer effect and spin-resonance techniques have proved fruitful for investigating the magnetic properties as seen by the dilute iron-group element. Also a spin-echo nuclear-magnetic-resonance study in the ferromagnetic state has been made on several of these systems.[3] We report here a microscopic investigation of the host matrix, the results of which may help to clarify and perhaps resolve some ambiguities on the role and effects of the matrix's conduction-band electrons, as inferred from these previous experiments.

By observing the nuclear magnetic resonance of $Pt^{195}$ in dilute alloys of cobalt in platinum (from 0.005 at.% Co to 0.2 at.% Co), we have made a measure of the conduction-electron spin polarization in the intervening Pt host matrix. We find that while an enhanced polarization of the Pt conduction electrons does exist in the paramagnetic state, it is not simply of one sign (positive or negative), nor is it in any way uniform. We find, in fact, that when averaged over all interspace (excluding the nearest neighbor Pt atoms), part of the conduction-electron polarization induced by the Co moments is nearly zero. The ordinary Pt conduction-electron susceptibility is all that survives, as far as the majority of the conduction electrons are concerned. There is, of course, the large temperature-dependent part of the susceptibility due directly to the localized Co moments and perhaps their nearest neighboring Pt atoms.

Some theoretical and experimental considerations of dilute iron-group elements in the platinum metals Pt or Pd have indicated that the enhanced paramagnetic-state conduction-electron moment is nearly uniform throughout the matrix,[9] or at least of one sign and monotonically decreasing away from the impurity, and

in one case this sign is thought to be negative.[6] Our results will be seen to be in some sense more in agreement with analyses like those of Dworin[11] and Scalapino,[10] where the majority of the conduction electrons contribute only the usual Pauli susceptibility.

In another case the magnetic-moment density on the host atom in the ordered state as observed by neutron diffraction[4] is found to be a relatively long-ranged monotonically decreasing function of distance from the localized impurity. If this induced moment with its monotonic behavior persists, although weakened, into the paramagnetic state, one would expect some net induced polarization on the intervening host atoms. Clogston et al.[2] and Geballe et al.[14] have suggested that the induced moment does persist into the paramagnetic state and have prescribed an expression to describe its temperature dependence.

Any induced moment, however, residing on the host will, of course, provide a hyperfine field at the nucleus in the same way that the $s$- and $d$-band electrons (the latter primarily through core polarization in the case of Pt) do even without an extra induced polarization. In other words we would, for example, expect to observe an enhanced Knight shift if some net polarization exists. This additional shift would be positive if the $s$ electrons were the ones primarily polarized, and negative if the $d$ electrons were the ones primarily polarized. The absence in our experiment of any net polarization (the precision of the experiment is such that we could detect changes in polarization corresponding to about a 1% change in the usual susceptibility) beyond the nearest Pt neighbors, but instead, the presence of an induced polarization which apparently varies in sign and magnitude at varying distances from the localized Co moment, suggests that our results can instead be best treated simply in terms of the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction.[17] The analysis is similiar to that of Owen et al.[18] and Behringer[19] for the Cu-Mn system, a system, however, which does not become ferromagnetic nor exhibit a giant moment as do the iron-group platinum or palla-

dium metal systems.[20]

For the very dilute concentrations used in this study, the vast majority of Pt atoms are further than nearest neighbors from the Co-impurity local moments. In this nmr experiment the nearest neighboring Pt atoms and perhaps even the next nearest neighbors are most likely shifted well out of resonance because of the large local polarizations on the near neighbors. The remaining Pt atoms (nuclei) are observed to be shifted either up field or down field corresponding to whether the polarization at a particular Pt site is positive or negative. However, the net shift of the center of gravity of the distribution is zero with respect to the ($s$ and $d$ conduction-electron-produced) Knight shift of pure Pt metal. Since there are equal amounts of resonant intensity at fields (or frequencies) greater than and less than those for the pure Pt metal, the average induced polarization as seen by the Pt sites must be nearly zero.

We have reached these conclusions on the basis of measurements of the linewidth and position of the Pt[195] resonance in our alloys as functions of magnetic field (8-16 kG) and temperature (1.5-4.2°K). The variation of the nmr linewidth as usually defined serves as a convenient measure of the breadth of the distribution of resonance shifts and is shown in Fig. 1. We find that the linewidth increases
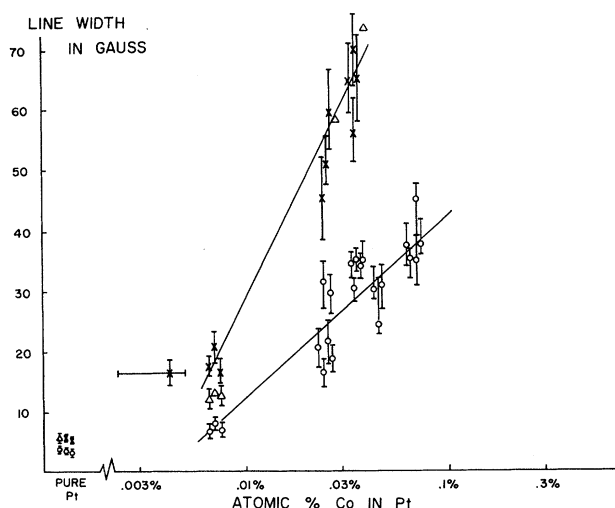
nearly linearly with magnetic field and somewhat less than linearly with $1/T$, and at least monotonically with Co concentration up to about 0.1 at.% Co. For samples of 0.2 and 0.4 at.% Co, we were not able to observe the resonance line within our temperature range; however, this may not be surprising since these alloys should be near ordering below 4.2°K. In all cases the resonance distribution is nearly symmetric and roughly Lorentzian in shape, and its center has a Knight shift which, to within the experimental error of ±0.02%, is identical to the Knight shift of $K = -4.01\%$ found in pure Pt metal. This is shown as a function of concentration in Fig. 2.

As Behringer[19] has demonstrated (for the case of the Cu-Mn system), it can be shown upon the basis of an RKKY interaction that the deviation from the resonant frequency of the $j$th platinum nucleus due to the average $z$ component of the magnetic moment of the $k$th cobalt local moment a distance $R_{jk}$ away is given by

$$\Delta\nu_{jk} = \frac{SB_s}{8\pi}\frac{aAm^*\Omega^2}{\hbar^3}$$

$$\times\frac{2k_m R_{jk}\cos 2k_m R_{jk} - \sin 2k_m R_{jk}}{R_{jk}^4},$$

where $a$ = hyperfine interaction of the conduction electrons with the Pt nuclei, $A$ = exchange coupling of the conduction electrons with the
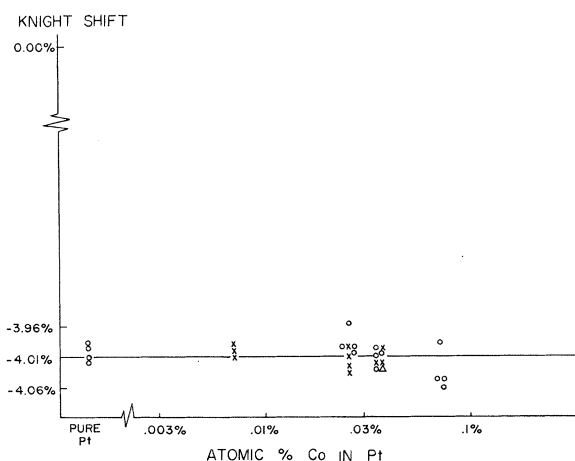


FIG. 1. Linewidth in G of the Pt[195] nuclear magnetic resonance as a function of atomic percent cobalt in samples of platinum-dilute cobalt alloy. Circles: 8 kG, 4.2°K; crosses: 16 kG, 4.2°K; and triangles: 8 kG, 1.6°K.



FIG. 2. Knight shift of the Pt[195] nuclear magnetic resonance as a function of atomic percent cobalt in samples of platinum-dilute cobalt alloy. Circles: 8 kG, 4.2°K; crosses: 16 kG, 4.2°K; and triangles: 8 kG, 1.6°K.

total Co complex, $m^* =$ effective mass of the conduction electrons, $k_m =$ wave number of the conduction electrons at the Fermi surface, $\Omega =$ atomic volume, and $SB_S =$ time-averaged $z$ component of the spin of a total local moment.

We have taken a free-electron model for the conduction-band $s$ electrons with a contribution to the band of 0.2 $s$ electrons per platinum atom.[21] We take $m^* = m$. From this we calculate $k_m = 0.73 \times 10^8$/cm. We have taken $a = (\frac{8}{3}\pi)\gamma_e\gamma_n\hbar^2|u(0)|^2/\Omega$. $|u(0)|^2$ has been estimated from predicted values of the direct $s$-electron portion of the Knight shift on the basis of hfs data. If we take $K_S = 1.4\%$ [21] $[K_S = (\frac{8}{3}\pi)|u(0)|^2\chi_S]$, and if we calculate again on the basis of the above free-electron model, we get $|u(0)|^2 = 3.3 \times 10^3$/cm$^3$, which yields $a = 1.95 \times 10^{-16}$ erg. Using as the total moment per cobalt-atom complex a value $p \approx 2.5$ deduced from the magnetization data of Crangle and Scott,[16] and assuming that it carries over roughly from the ferromagnetic state, we can determine $SB_S = p^2\mu_B H/g3kT$, assuming $g = 2$. Typical values of the exchange coupling constant $A$ which have been used in the analysis of susceptibility measurements[2] and magnetic-resonance data[19] are the order of $1.6 \times 10^{-13}$ to $2 \times 10^{-12}$ erg. We find that taking a value $A \approx 6 \times 10^{-13}$ erg provides us with a reasonable fit to our data. We have obtained this fit by constructing a histogram of the RKKY polarization over the 260 typical lattice points of a Pt/0.048 at.% Co structure under the assumption that the cobalt enters the matrix in a roughly cubic array. The histogram reproduces the shape and breadth of the resonance absorption distribution and leaves the center of the distribution unshifted.

We have also constructed such a histogram using instead the simple dipole fields of magnetic moments $\langle\mu_z\rangle = p^2\mu_B^2 H/3kT$ at the cobalt sites, and we have found that this interaction fails by an order of magnitude to explain our linewidth.

A detailed analysis of the Pt linewidth dependence on Co concentration and temperature is presently in progress and will be presented in a more comprehensive article.

We wish to thank Professor M. Bailyn for several helpful discussions.

[1]P. W. Anderson, Phys. Rev. 124, 41 (1961).
[2]A. M. Clogston et al., Phys. Rev. 125, 541 (1962).
[3]S. Kobayashi and J. Itoh, J. Phys. Soc. Japan 20, 1741 (1965).
[4]G. G. Low, in Proceedings of the International Conference on Magnetism, Nottingham, England, 1964 (The Institute of Physics and The Physical Society, London, 1965), p. 133.
[5]R. M. Bozorth, D. D. Davis, and J. H. Wernick, in Proceedings of the International Conference on Magnetism and Crystallography, Kyoto, Japan, September, 1961 [(Suppl. J. Phys. Soc. Japan 17, 112 (1962)].
[6]W. C. Phillips, Phys. Rev. 138, A1649 (1965).
[7]R. M. Bozorth et al., Phys. Rev. 122, 1157 (1961).
[8]S. Ehara, J. Phys. Soc. Japan 19, 1313 (1964).
[9]Duk-Joo Kim, Phys. Rev. 149, 434 (1966).
[10]D. J. Scalapino, Phys. Rev. Letters 16, 937 (1966).
[11]L. Dworin, Phys. Rev. Letters 16, 1042 (1966).
[12]D. Shaltiel et al., Phys. Rev. 135, A1346 (1964).
[13]P. P. Craig et al., Phys. Rev. Letters 9, 12 (1962).
[14]T. H. Geballe et al., J. Appl. Phys. 37, 1181 (1966).
[15]T. A. Kitchens and P. P. Craig, J. Appl. Phys. 37, 1187 (1966).
[16]J. Crangle and W. R. Scott, J. Appl. Phys. 36, 921 (1965).
[17]M. A. Ruderman and C. Kittel, Phys. Rev. 96, 99 (1954); K. Yosida, ibid. 106, 893 (1957).
[18]J. Owen et al., Phys. Rev. 102, 1501 (1956).
[19]R. E. Behringer, J. Phys. Chem. Solids 2, 209 (1957).
[20]The system Gd:LaAl$_2$ has been shown by A. C. Gossard, V. Jaccarino, and J. H. Wernick {in Proceedings of the International Conference on Magnetism and Crystallography, Kyoto, Japan, September, 1961 [(Suppl. J. Phys. Soc. Japan 17, 88 (1962)]} to be amenable also to the RKKY interaction treatment, but this system, like Cu-Mn, is not a "giant-moment" dilute alloy, nor is LaAl$_2$ (unlike Pd or Pt) expected to be triggered to a ferromagnetic state with the addition of an extremely dilute magnetic impurity by some long-ranged interaction. It is essentially because of the well-established existence of polarization on at least the nearest neighbors (the giant moment), and of the extreme long range of the interaction, that one might not unreasonably be lead to suspect a perhaps uniform or monotonic polarization of the intervening conduction electrons for the case of the iron-group platinum-group dilute alloys. As we will try to show, this is, in fact, probably not the case.
[21]A. M. Clogston, V. Jaccarino, and Y. Yafet, Phys. Rev. 134, A650 (1964).