

Paramagnetic Resonance of S-State Ions in Metals

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The interaction between conduction electrons and paramagnetic ions in metals has been investigated by observation of the paramagnetic resonance of gadolinium in alloys and intermetallic compounds. Spectra of Gd in powdered samples were observed at temperatures between 1.4 and 500°K and frequencies between 10 and 80 kMc/sec. A single line has been observed with g values varying between 2.01 and 1.88. A striking correlation has been established between the g shifts and the susceptibility and the specific heat of the pure Rh-Pd and Pd-Ag alloys, leading to the conclusion that the shifts are due to the interaction of the host conduction electrons with the paramagnetic ions. Linewidth considerations indicate that this interaction is mostly of scalar form. From the observed dependence of the g shift and linewidth on the magnetization we conclude that the interaction produces the electron Knight shift predicted by Yosida, rather than the shift predicted by Kittel and Mitchell. The observed negative shift indicates that there is a polarization of mostly negative sign in agreement with previous nuclear magnetic resonance observations on GdAl_2 by Jaccarino *et al.* A possible mechanism for this negative polarization is the Anderson-Clogston mechanism. Some experiments on line broadening due to different magnetic species, and their connection to the absence of the g shift of Gd and Mn in Ag are discussed briefly.

I. INTRODUCTION

THE phenomenon of paramagnetism in ionic crystals has been essentially understood since the pioneering work of Van Vleck.¹ The advent of the techniques of electron—and nuclear—paramagnetic resonance initiated a period of intense study of paramagnetic ions, and progress in the understanding of the mechanics of these ions was accelerated by optical spectroscopic studies to the point where, in some cases, it has become possible to predict the behavior of the paramagnetic ground state from the knowledge of the optical level structure.²

The behavior of paramagnetic ions in metals, on the other hand, remains much less understood. The metallic electrons interact with the magnetic ions, and this interaction seems to determine much of the magnetic characteristics of these ions. Recent experiments³ have, for example, shown a correlation between the conduction electron density and the occurrence of paramagnetism of iron dissolved in transition metals. Model calculations have been offered recently by Anderson⁴ and Wolff,⁵ which show how the ion-conduction electron interaction, the electron density, and the exchange effects determine the paramagnetic state of dilute ions.

The experimental data against which these theories are compared are almost exclusively dc susceptibility measurements. The parity-forbidden weak optical transitions which gave much useful information on paramagnetism in ionic crystals are here obscured by the conduction electron absorption. Paramagnetic resonance has only been observed in S-state ions. In other magnetic ions, the spin-lattice interactions have made resonance measurements very difficult. The search

for such resonances would have to be carried out at low temperature in order to reduce spin-lattice interactions. However, magnetic ordering tends to occur at these temperatures even at low concentrations, and a sensitivity problem arises. Since the microwave radiation penetrates only a thin layer of metal (less than a micron), the possibilities of observing resonances at high dilution are limited not only by the sensitivity of the resonance apparatus, but also by the oxide and hydroxide layers, which may form on the metallic surfaces and mask the desired resonance signals. It has, nevertheless, been possible to observe metallic ionic paramagnetic resonance in some special cases. The first observations were due to Owen *et al.*⁶ for the case of Mn in Cu, Ag, and Mg, and to Kip *et al.*⁷ for the case of metallic Gd. Later on, electron-paramagnetic resonance (EPR) measurements were also reported on Eu metal and on intermetallic compounds containing Gd and Eu.^{8,9}

Paramagnetic ions in orbital singlet states see the conduction electron cloud only as a relatively minor perturbation. A certain degree of analogy between paramagnetic resonance and nuclear resonance is therefore to be expected. In particular, if a significant part of the interaction can be described by a scalar term,

$$JS \cdot s, \quad (1)$$

connecting the angular momentum of the paramagnetic ion, S , with the conduction electron spin, s , then we would expect a shift of the paramagnetic g factor, which may be analogous to the Knight shift, a longitudinal relaxation mechanism analogous to the Korringa broadening, and a transverse relaxation mecha-

¹ J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, New York, 1932).

² E.g., S. Sugano and M. Peter, *Phys. Rev.* **122**, 381 (1961).

³ A. M. Clogston, B. T. Matthias, M. Peter, H. J. Williams, E. Corenzwit, and R. C. Sherwood, *Phys. Rev.* **125**, 541 (1962).

⁴ P. W. Anderson, *Phys. Rev.* **124**, 41 (1961).

⁵ P. A. Wolff, *Phys. Rev.* **124**, 1030 (1961).

⁶ J. Owen, M. E. Browne, V. Arp, and A. F. Kip, *J. Phys. and Chem. Solids* **2**, 85 (1957).

⁷ A. F. Kip, C. Kittel, A. M. Portis, R. Barton, and F. H. Spedding, *Phys. Rev.* **89**, 518 (1953).

⁸ M. Peter and B. T. Matthias, *Phys. Rev. Letters* **4**, 449 (1960).

⁹ V. Jaccarino, B. T. Matthias, M. Peter, H. Suhl, and J. H. Wernick, *Phys. Rev. Letters* **5**, 221 (1960).

nism analogous to the Bloembergen-Rudermann-Kittel mechanism, all of which are well-known effects in the case of nuclear resonance studies in metals.

There is experimental evidence that a strong interaction of the form $JS \cdot s$ does indeed occur in intermetallic compounds and alloys of Gd. The origin of this term is, however, at present not clarified, although the Anderson-Clogston polarization mechanism¹⁰ may, for reasons set forth below, play a dominant role.

Even after the presence of an interaction of the form $JS \cdot s$ is established, the analogy with the nuclear resonance experiments is not necessarily a close one. The orders of magnitude of the magnetic moments, the relaxation times and the interactions have to be established, and the case of nuclear resonance emerges as only one of several possibilities.

It has been stressed before^{6,11} that an electron gas can only interact with paramagnetic S -state ions if it has a sufficiently short relaxation time. In the presence of paramagnetic ions, the conduction electron polarization will consist of two parts, one produced directly by the external magnetic field, the other by the ionic magnetization. Different results are expected from paramagnetic resonance experiments depending on whether the paramagnetic ions interact both with the direct and indirect conduction electron polarization, or only with the direct part.¹²

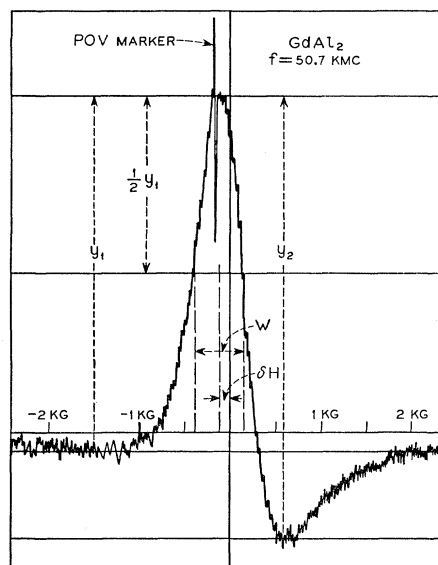


FIG. 1. Absorption dispersion line in $GdAl_2$ at $-35^\circ C$, with $f=50.69$ kMc/sec. This line is Lorentzian, because of strong exchange-narrowing. It was fitted to the proper combination of absorption and dispersion by determining $y_1/y_2=y$, and W . Then, by means of Fig. 2, DH and δH were determined and $F(x)=(1-1.2x-x^2)/(1+x^2)^2$ was found to fit the observed line. [$x=(H-H_0)/DH$; $H_0=18270$ gauss; $DH=500$ gauss.] DH is defined as the half-power half-width of the absorption part of the resonance line.

¹⁰ P. W. Anderson and A. M. Clogston, Bull. Am. Phys. Soc. **2**, 124 (1961).

¹¹ C. Kittel and A. H. Mitchell, Phys. Rev. **101**, 1611 (1956).

¹² H. Hasegawa, Progr. Theoret. Phys. (Kyoto) **21**, 483 (1959).

In the next section, we would like to present the result of a study of Gd in several intermetallic compounds and alloys, and attempt to give a description of the resonance processes involved with the help of the different models indicated above.

II. DESCRIPTION OF THE EXPERIMENTS

We have studied the factors determining line width and g values of the resonance of Gd in metallic lattices, by means of resonance experiments in $GdAl_2$ and alloys of $GdAl_2$ with other metals, and in dilute alloys of Gd with elements of the second transition series. The alloys with melting points below $1800^\circ C$ were prepared by melting them in an induction furnace in quartz crucibles and then reheated to $900^\circ C$ and quenched in water to retain as much as possible of the Gd impurity or other impurities in solid solution. The alloys with melting points above $1800^\circ C$ were melted in an arc furnace and quenched from $1100^\circ C$, as above. The samples used in resonance measurements, are put in powder form either by crushing in an agate mortar, or by filing. The crushed samples are then passed through a 400-mesh sieve, so that the maximum particle size is ~ 0.02 mm. These particles are still large compared with the penetration depth [$\delta=(2/\omega\sigma\mu)^{1/2}=1.45\mu$, for $\sigma=2\times 10^6$ mho/m and $\omega=3.7\times 10^{11}$ cps]. The surface of a powder with spherical particles of radius r , suspended with concentration f in a sheet of thickness d , is increased over the surface of a solid sample by a factor $F=3df/r$. This gives, for our powders with $d=0.05$ mm and $f=0.2$, a factor $F=15$. Comparison of intensities of measurements on powders and flat surfaces showed indeed an increase of signal intensities of this magnitude. Paraffin was found to stabilize even the more reactive metals investigated against oxide or hydroxide formation.

The apparatus used in these experiments has been described previously.¹³ The sample is introduced along the wall of a waveguide (RG 98 or RG 99). The absorption of the sample is modulated magnetically, and the change of power transmitted through the waveguide is detected by the low-frequency part of a Varian NMR spectrometer. The signal sources for all our experiments were experimental models of backward wave oscillators developed by C. F. Hempstead at the Bell Laboratories. Magnetic fields up to 28 000 gauss were available, and our experiments were conducted at 50 and 60 kMc/sec, corresponding to a field of 17.8 and 21.4 kgauss, respectively. From the fact that the permeability of the magnet iron changes as a function of the applied field, distortions may result in amplitude and phase of the modulating field. These distortions were found to be appreciable in the region where saturation sets in for the iron in the pole pieces. We, therefore, tried to make most of the measurements below this region. Corrections were applied where necessary.

¹³ M. Peter, Phys. Rev. **113**, 801 (1959). J. B. Mock, Rev. Sci. Instr. **31**, 551 (1960).

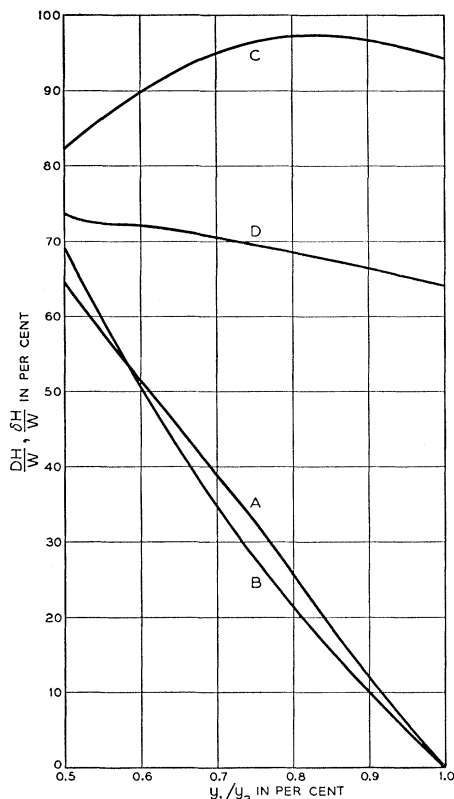


FIG. 2. *A* and *B* give $\delta H/W$, and *C* and *D* give DH/W , for all ratios $y=y_1/y_2$. For definition of these quantities, see Fig. 1. *A* and *C* apply to Lorentzian curves, *B* and *D* to Gaussian curves. A series of these curves was calculated by computer, and the calibration curves were then derived graphically.

The two main advantages of a cavity system, enhancement of absorption and separation of absorptive and dispersive effects, are partly lost in spectroscopy with metal powders. Specimens of reasonable size are at our frequencies so lossy as to destroy the cavity Q factor, and absorptive and dispersive effects become mixed due to the complex metallic impedance. We found, therefore, the use of a waveguide transmission system well suited for metallic paramagnetic resonance studies.

Since we are seeing 10^{13} spins at 20°K in phosphor-doped silicon ($\Delta H=2$ gauss), we can expect to see paramagnetic Gd in 0.01% dilution at the same temperature assuming 500 gauss for ΔH and a modulation of 100 gauss, and that we observe transitions for all values of m . The observed intensities are consistent with these assumptions although such intensity measurements are quite uncertain. However, the absence of satellite lines^{14,15} both in strongly exchange-narrowed concentrated GdAl₂ and in dilute Gd, LaAl₂ confirms our view that the observed line comprises all Zeeman levels. If the dilute Gd, LaAl₂ had shown a splitting of the order found in insulating crystals, then the concen-

trated and exchange narrowed compound would have reduced this splitting to within the magnitude of the linewidth.¹⁶ But no irregular structure was observed in either dilute or concentrated compounds. The lines were considered to be arbitrary mixtures of the dispersive and absorptive parts χ' and χ'' , described by the shape function $g(\nu)$ defined by Pake and Purcell.¹⁷ These authors have discussed the resonance signals under the assumption of Gaussian and Lorentzian line shape. The line position was, in our case, deduced by finding a mixture of the absorptive and dispersive part of either Lorentzian or Gaussian shape that fitted the observed line best.

Figure 1 shows how the parameters W , y_1 , and y_2 helped, by means of the graph given in Fig. 2, to pick the right trial shape for final correlation. The line in this figure was exchange narrowed and therefore of a truncated Lorentzian shape.

It is well known that a field for resonance is reduced by approximately $2\pi M$ for a flat sample if the magnetic field is applied parallel to its plane, and increased by $4\pi M$ if the field is applied perpendicular. The ferromagnetic resonance frequency will therefore appear to be proportional to the sample magnetization. We have tried to use the surface of a single crystal of GdAl₂, but were not able to obtain shifts corresponding to the above limits. Instead, we observed the occurrence of two resonances, an effect which we ascribe to an insufficiently polished surface. In powders we observed only single lines, and the frequency was different for fields parallel or perpendicular to the supporting powder surface. This is illustrated in Fig. 3. We find that the field varies indeed roughly proportionally to the sample magnetization, and that the values for the two orientations coincide for zero magnetization. Hence, we are able to measure the g values for zero magnetization by extrapolation without knowing the magnetization dependence of the frequency. The magnetization was calculated from the susceptibility measurements which

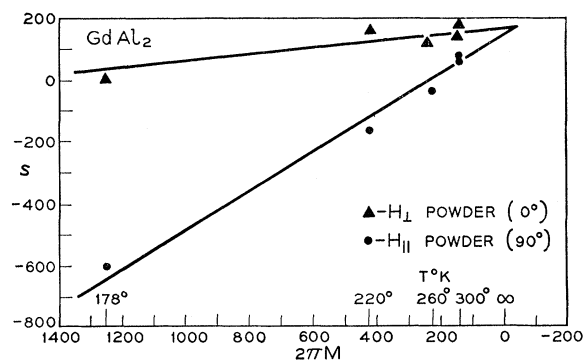


FIG. 3. Line shifts vs $2\pi M$ as observed on powder samples. M is the magnetization, calculated from the dc susceptibility measurements. For flat surfaces, the lines would have the slopes +1 and -2, respectively.

¹⁴ N. Bloembergen and T. J. Rowland, *Acta. Met.* **1**, 731 (1953).

¹⁵ G. Burns, *J. Appl. Phys.* **32**, 2048 (1961).

¹⁶ J. S. Van Wieringen, *Discussions Faraday Soc.* **19**, 118 (1955).

¹⁷ G. E. Pake and E. M. Purcell, *Phys. Rev.* **74**, 1184 (1948).

TABLE I. g values and half-width at half power of gadolinium in various metallic solvents.

	g value	DH (gauss)	$T(^{\circ}\text{K})$	
Gd metal	1.95	470 ± 70	378°	a
GdAl ₂	1.982 ± 0.003	500 ± 30	260°	b
Gd 3%, Rh 97%	1.989 ± 0.010	760 ± 80	47°	c
Gd 3%, Pd 97%	1.887 ± 0.007	750 ± 80	20°	c
Gd 3%, Ag 97%	1.995 ± 0.007		20°	c
Gd 3%, Ag 67%, Cd 30%	2.010 ± 0.007		20°	c

^a A. F. Kip, Revs. Modern Phys. 25, 279 (1953). DH has been defined differently than in the present paper.

^b See reference 32.

^c Present work. Measurements taken at 48.4 kMc/sec.

were performed on our samples at fields between 2000 and 14 000 gauss and temperatures between 1.4°K and 300°K . The apparatus used for the susceptibility measurements has been described elsewhere.¹⁸ The analysis of our samples was inferred from the susceptibility measurements and x-ray diffraction studies by Compton.¹⁹

The susceptibility vs temperature curves permitted determination of the effective moment per gadolinium ion. It turned out to be in satisfactory agreement with the values expected for a spin of $\frac{7}{2}$ and a g value of approximately two in all samples on which the paramagnetic resonance measurements are reported here. This is taken as an indication that gadolinium does not exhibit the polarization effects shown by iron and in the palladium series.³ In addition, x-ray examinations¹⁹ showed no second phase in these samples but a distinct increase in the spacing of the host lattice.

These facts are good evidence that the gadolinium was indeed contained in about the nominal concentration and in homogeneous dispersion, in the alloys of Rh, Pd, Ag, Cd on which the measurements are reported. The limits of this range were established as follows: towards both higher and lower atomic numbers the structure of the alloys changes from fcc to hexagonal.²⁰ The metal with the lowest atomic number investigated was elemental rhodium ($A=45$). The binary alloy with highest possible atomic number according to available metallurgical data²⁰ was the alloy 70% Ag, 30% Cd ($A=47.3$). Gd-doped platinum and gold were melted in the induction furnace, and Gd-doped iridium was melted in the arc furnace but in all these cases we found only a small susceptibility, no change in spacing of the host lattice as measured by x-ray and no resonance lines. Finally, we also tried alloying Gd into copper. There both resonance and the expected susceptibility were found. However, x-ray examination showed the presence of an additional phase in these alloys, so that we could not assume a simple dilute alloy.

Table I shows the observed paramagnetic g values of gadolinium in several metallic solvents. The shift in

¹⁸ R. M. Bozorth, H. J. Williams, and J. E. Walsh, Phys. Rev. 103, 572 (1956).

¹⁹ Mrs. V. B. Compton (private communication).

²⁰ W. B. Pearson, *Handbook of Lattice Spacings and Structure of Metals and Alloys* (Pentagon Press, New York, 1958).

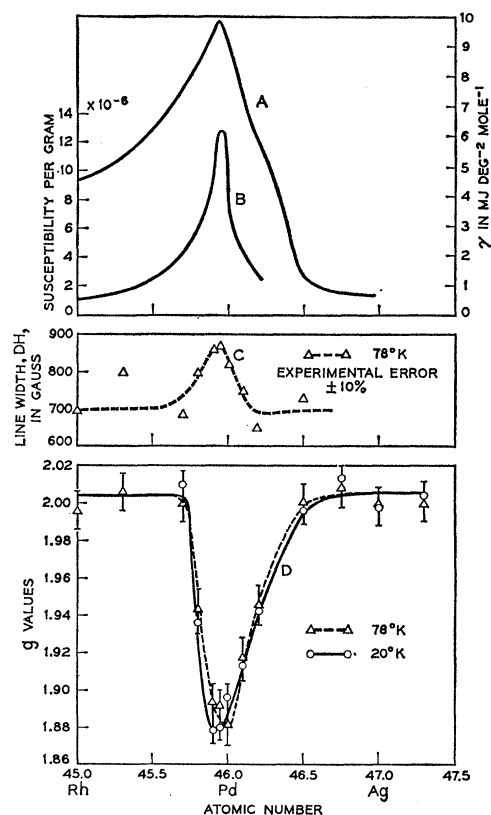


FIG. 4. Correlation between electronic properties of alloys of the second transition series (A, B) (without paramagnetic impurities) and the resonance properties of three atomic per cent Gd impurities into this series (C, D). A (right scale): electronic specific heat; B (left scale): susceptibility at 20°K . (For A and B , see reference 5). C : half power, half linewidth at 78°K and D : g value of gadolinium paramagnetic resonance at 20°K and 78°K .

resonance has shown no large explicit temperature dependence in the dilute Gd-Pd alloys. There is, however, the implicit dependence via magnetization, which is displayed in Fig. 3, for the case of GdAl₂. The g values for Gd in the palladium metal series are of particular interest since there we have an opportunity to study the dependence of the g shifts on the susceptibility of the solvent metal. This susceptibility, along with the specific heat, has been studied by Budworth *et al.*²¹ Our measured g shifts and linewidth along with the susceptibilities and specific heat data are displayed in Fig. 4.

The g values and linewidth of these alloys were measured by averaging a large number of recorded lines from different samples. In a few isolated cases, anomalous results were found. However, when the alloys in question were reproduced these discrepancies disappeared.

To avoid magnetization corrections of the g values and to avoid the low-temperature broadening, discussed

²¹ D. W. Budworth, F. E. Hoare, and J. Preston, Proc. Roy. Soc. (London) A257, 250 (1960).

below, the measurements were made above the Curie point, where the magnetization as taken from susceptibility measurements was small. Figure 4 does not show the g for some alloys at liquid hydrogen for this reason. The scattering of the measured g values was small in almost all the samples. However, the linewidth measured has shown a larger scattering. At compositions above 50% Ag the spread in linewidth is too large and their corresponding points have therefore been omitted from Fig. 4. We found in these samples a dependence of the linewidth on the mode of sample preparation.

Figure 5 shows the influence of the absorption linewidth on temperature for several samples of Gd in Pd. We observed that these curves possess minima with a steep increase of the linewidth towards the low-temperature side and a slow increase towards the high-temperature side. The linewidth below the minima is increasing with frequency whereas at high temperatures the width becomes nearly frequency independent. A small increase of the linewidth with concentration is also observed. At higher temperature, the shape of all observed resonance lines was found to be nearly Lorentzian. Finally, strong broadening was observed upon addition of different species of paramagnetic ions.

III. DISCUSSION OF RESULTS

Table I shows that the g values for gadolinium ions vary significantly in different host lattices. This is in contrast to the results of measurements in ionic crystals. The measurements on Gd^{+++} ions in insulating crystals all give g values higher than 1.990.²² The spectrum of the free Gd ion shows that the first excited state, 6P_3 , is situated $3.3 \times 10^4 \text{ cm}^{-1}$ above the ground state. Lacroix²³ has shown that, in this case, the g value is determined by the ionic spin orbit interaction and influenced very little by crystalline field effects. Effects due to covalency can also be assumed to be small, as evidenced by the absence of fluorine hyperfine structure in Gd-doped CaF_2 .

It could be argued that the shielding effect of the conduction electrons might decrease the intraionic fields, and, thereby, produce a decrease in term separation with a resulting increase in the ground-state perturbation, thus introducing bigger g shifts than in ionic crystals. However, even if such a hypothesis would provide an explanation of the observed decrease in g values, it would still fail to explain the strong broadening observed, due to the presence of other magnetic impurities.

Similar arguments can be brought forth against the assumption that crystalline fields or covalent bonding effects could cause the metallic g shifts. Such effects should reflect the symmetry of the ionic site and give rise to ground-state splittings. These splittings would in turn give rise to irregular line shapes similar to the ones found in nuclear magnetic resonance (NMR) ex-

periments in the presence of quadrupolar interactions.^{14,15} However, we have failed to detect any such irregularities. The ground-state splittings are therefore smaller than our observed widths. This means that any changes of g due to these effects should also be small, since zero-field splittings of the magnitude occurring in ionic crystals would have been quite visible in our experiments. A scalar interaction of the form (1), can account both for the coupling effects between different magnetic species, and for the shifts in magnetic resonance. The interaction must be of scalar form because, if it would not commute with the S_+ operator, it would give rise to a large broadening that has not been observed.²⁴

The effects on paramagnetic resonance that can be expected from interaction (1) have been discussed by several authors. Kittel and Mitchell¹¹ point out that if the g values accompanying S and s are identical, then expression (1) will commute with the magnetic interaction part of the Hamiltonian, which means that no change in the observed g value can result. It is the presence of relaxation processes acting on the conduction electrons which breaks down this rule. Each ion sees the average polarization produced in the conduction electron cloud by the external magnetic field. The g shift,

$$\Delta g = \bar{J} \eta(E_f) / n_0 \quad (2a)$$

then results, where $\eta(E_f)$ is the density of states at the Fermi surface, \bar{J} is the special average of J , and n_0 is the total number of lattice sites. This is the shift proposed by Yosida²⁵ in analogy to the nuclear Knight shift.²⁶ At higher concentrations of magnetic ions the conduction electrons will be polarized by the ions as

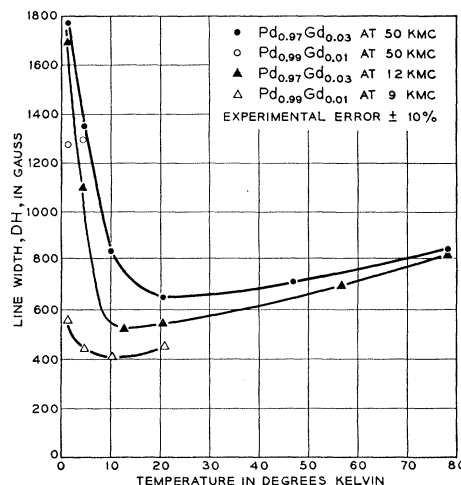


FIG. 5. Dependence of linewidth on temperature for different fields and Gd concentrations in Pd.

²⁴ J. H. Van Vleck, Phys. Rev. **74**, 1158 (1948).

²⁵ K. Yosida, Phys. Rev. **106**, 893 (1957).

²⁶ W. D. Knight in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 2, p. 93.

²² J. W. Orton, Repts. Progr. in Phys. **22**, 204 (1959).

²³ R. Lacroix, Helv. Phys. Acta **30**, 374 (1957).

well as by the applied field. Owen *et al.*⁶ point out in a footnote to their paper that this polarization will act on the energy levels only if the relaxation is rapid enough to prevent its alignment with the ionic spins, or if the electron spin-lattice time is short compared with the precession time of the conduction electrons around the ionic spin. If this condition $T_2 \ll 1/\gamma\lambda M_f$ is fulfilled, the expression (2a) is modified:

$$\Delta g = \bar{J}\eta(E_f)(1 + \lambda\chi_f)/n_0. \quad (2b)$$

χ_f is the ionic part of the susceptibility, and λ , the molecular field constant, is connected to \bar{J} by $\lambda = \bar{J}/2g\beta^2 n_0$. In addition to a shift, the ions also relax to the conduction electrons. The contribution to the broadening from relaxation effects which may be denoted by DH_K is connected to the shift Δg by the Korringa relation²⁷ for case a:

$$g\beta DH_K = 2\pi(\Delta g)^2 kT. \quad (3a)$$

For case b (rapid relaxation), Hasegawa finds¹²

$$g\beta DH_K = 2\pi(\Delta g)^2 kT/(1 + \lambda\chi_f). \quad (3b)$$

For $\lambda\chi_f \ll 1$, the two cases a and b will not be distinguishable, but for $\lambda\chi_f > 1$ and case b, we find that the shift Δg is inversely proportional to the temperature and that the width DH_K is temperature independent. Intermediate cases are treated by Hasegawa.^{27a}

Line Shifts

In GdAl₂ we find $E_f = 5.1$ eV from the free-electron picture if we assume $n_0 = 1.622 \times 10^{22}$, $n = 2\alpha n_0$, $\alpha = 1.5$. Since, in this approximation, we have $\eta(E_f) = 3\alpha n_0/2E_f$ we obtain, from $\Delta g = -0.01$, the value $\bar{J} = -0.03$ eV, as already indicated earlier.

A determination of J for Gd in Pd cannot be based on a single-band free-electron picture, as is indicated by the anomalous behavior of specific heat and susceptibility. If we assume the free electron density of states, we arrive at the value $\bar{J} = -0.33$ eV for the Gd_{0.03}Pd_{0.92}Rh_{0.05} alloy. A more reasonable interpretation is that the electron density is at least an order of magnitude above the free-electron value. The specific heat value is larger by 16.5 than the free-electron value, and the susceptibility value is larger by 135. If we assume $\bar{J} = -0.03$ as in GdAl₂, we obtain a factor of 11 for the density-of-state ratios. Figure 4 shows clearly that the g shift undergoes the same anomaly as the susceptibility and the specific heat of the palladium-

rhodium alloys. This correlation gives strong support to our contention that the g shifts are due to an ion-conduction electron interaction. Further support is shown by the fact that the g values of Gd in Pd-Rh alloys up to 30% Rh, from 20° to 40°K show a slight increase, while the g value of Gd in Pd metal in this temperature range remains essentially constant. This is in agreement with the susceptibility measurements of these alloys by Budworth *et al.*²¹

For $\bar{J} = -0.03$ and $n_0 = 1.6 \times 10^{22}$ for GdAl₂ and 6.8×10^{22} for Pd, we find: $\lambda = 8 \times 10^4$ for GdAl₂ and 2×10^3 for Pd. The volume susceptibilities are $\chi_f = 2 \times 10^{-3}$ for GdAl₂ at 270°K and $\chi_f = 6 \times 10^{-4}$ for 3% Gd in Pd at 40°K. The contribution in (2b) to the g shift would be of the order $\Delta g \lambda \chi_f$, and therefore bigger in both cases than the demagnetization effects, which are of order $2\pi\chi_f$. The observed temperature dependence of our g shifts does not exceed the one expected from demagnetization shifts, except in the case explained above where the temperature dependence of the susceptibility of the host lattice is involved, and permits thus the conclusion that, in the representative case of GdAl₂ and Gd in Pd, the conduction electron polarization must indeed follow the ionic magnetization, so that the formulas (2a) and (3a), rather than (2b) and (3b), must apply.

The shift disappears completely as we approach silver (Fig. 4). Thus Gd in Ag₅₀%Pd₅₀% behaves analogously to Mn in Ag, where Owen *et al.*⁶ failed to detect any significant g shifts. One possible reason for this behavior would be that the conduction electron relaxation time to the lattice, T_{sL} , is longer than T_{sf} , the interaction time to the Gd ions. This possibility has been eliminated by an experiment where the conduction electron relaxation time was shortened by introducing a terbium concentration of comparable magnitude to the Gd concentration in Ag₅₀%Pd₅₀%. The coupling of the conduction electrons to the two rare earth species would be of comparable strength. However, terbium relaxes at a rate T_{fL}^{-1} to the lattice which is larger²⁸ than its coupling to the conduction electrons, T_{fs}^{-1} . It can therefore be considered in equilibrium with the lattice. The conduction electrons are now coupled via the terbium to the lattice, so that $T_{sL} \sim T_{sf}$ and the adiabatic condition is no longer possible. From the fact that the gadolinium resonance showed no shift even under this condition, we conclude that the absence of spin lattice relaxation is indeed not the reason for the absence of the g shift.

Linewidths

Figure 5 shows an increase in linewidth with temperature, in qualitative agreement with (3a). This formula would predict $DH_K = 4.6T$ gauss for GdAl₂ and $120T$ gauss for Gd in Pd. The experimental values are smaller by a factor of 2 in the first case, and by an order of magnitude in the second case.

²⁸ P. G. deGennes, C. Kittel, and A. M. Portis, Phys. Rev. **116**, 323 (1959).

²⁷ J. Korringa, Physica **16**, 601 (1950).

^{27a} Note added in proof. Wangness [Phys. Rev. **111**, 813 (1958)] has pointed out that for thermodynamic reasons relaxation should always take place towards the instantaneous field acting on the relaxing sublattice in a two sublattice system. If we consider the Gd ions and the conduction electrons as two magnetic sublattices, Eq. (2a) can be derived in the limit of strong electron relaxation, as will be shown in a later publication. Hasegawa obtains (2a) and (3a) under the assumption of relaxation towards the instantaneous field, hence they should hold rather than (2b) and (3b). As shown below, (2a) and (3a) are indeed the equations that are consistent with our experiments.

Both in GdAl_2 and Gd in Pd there exists a critical temperature, below which the linewidth increases again. In both cases we correlate the low-temperature rise with magnetic ordering. In GdAl_2 , the broadening is of the magnitude expected from demagnetization effects in ferromagnets, whereas the much steeper rise in the Gd-Pd alloys must be due to the onset of a more complex ordering pattern.

Formula (3a) also predicts a correlation between line width and coupling strength at constant temperature. It is seen in Fig. 4 that the linewidth shows indeed an anomaly in the same concentration range where the shifts and susceptibilities have their maxima.

The dipolar broadening by impurities of different paramagnetic species is subject to the same exchange narrowing that reduces the broadening caused by dipolar interaction between the paramagnetic ions under study.²⁹ Partial replacement of the Gd ions by other rare earths should therefore change the observed linewidths only slightly, and should, in particular, decrease it if the different species had a smaller effective magnetic moment. The strong broadening found in a number of doping experiments can therefore not be explained by dipolar broadening. Instead, it must be correlated with the strong coupling between two neighboring ions which results from the fact that both ions are coupled to the conduction electron cloud.^{14,25,30-32} The fact that this mechanism leads to values for the scalar interaction in the other rare earth metals which are in reasonable agreement with values deduced by NMR measurements³³ has been pointed out previously.³²

The large anomalous linewidths introduced via the conduction electron coupling to paramagnetic impurities persist even when the shifts disappear. This observation may look like a contradiction to our contention that both broadening and shift may be attributed to an interaction of form (1). However, the spatial dependence of this interaction gives rise to a nonuniform polarization, and to a finite range in the interionic coupling. For the special case of a δ -function-like behavior of $J(x)$ this range function is the well-known Ruderman-Kittel³⁰ function. We have seen that the g shift in our experiments depends only on the uniform component of this polarization. The coupling, however, is generated by all the Fourier components $\bar{J}(q)$ of $J(x)$, and is in general not zero even if the average polarization is zero.

The fact that the observed g shifts are mostly negative shows that the interaction (1) is not predominantly a direct exchange interaction. The interaction $\bar{J}(q)$ is positive definite for $q=0$ and, therefore, always gives rise to a positive g shift.

The negative sign is, however, in agreement with the NMR measurements by Jaccarino *et al.*^{9,33} in the Al_2 compounds of different rare earths. These experiments showed a negative conduction electron polarization at the site of the Al^{27} nuclei. It has been proposed by Freeman and Watson³⁴ that this polarization could result from strong spatial dependence of the exchange polarization. Our measurements of the negative paramagnetic shifts are inconsistent with this hypothesis, whereas the original assumption of a negative average polarization⁹ is consistent with both the NMR and EPR results. Note that the NMR measurements in the rare earth aluminum compounds made clear that the scalar interaction is acting on the ionic spin only rather than on its total angular momentum.

Finally, a recent investigation should be mentioned which may contain an explanation of the observed negative coupling. Anderson and Clogston¹⁰ have investigated the effects which result from the matrix element V_{ss} between a localized f electron and the itinerant s electron. They find first-order changes in the electronic s and f wave functions. These changes, however, bring on no change in the net spin, as was pointed out by Anderson.⁴ It is therefore not clear whether these effects will influence the observed g values. In addition, they find that if this coupling mechanism is eliminated to second order it leads to a spin dependent energy shift of the order $|V_{ss}|^2/(E_f - E_s)$, where E_f is the Fermi energy and E_s is the energy of the localized polarized electron ($E_s < E_f$).

This energy shift could be partially represented by an effective interaction of the form (1), and it turns out that this mechanism would lead to a negative $\bar{J}(0)$. This interaction would, therefore, produce a negative polarization and, hence, shifts of the observed sign.

CONCLUSION

(1) Gadolinium in metallic lattices gives rise to paramagnetic resonance lines whose g values are shifted by their interaction with conduction electrons. Experiments with gadolinium dissolved in alloys of the palladium alloys have established that these shifts show strong correlation with the susceptibility of the metallic matrix. The shifts are therefore attributed to an interaction between the paramagnetic ions and the conduction electrons of the matrix. The interaction must be mainly of scalar form since it would otherwise give rise to excessive broadening of the resonance lines.

(2) The effects of the interaction $J(\mathbf{S} \cdot \mathbf{s})$ depend on the relative strength of the conduction electron-lattice relaxation processes. From the observed dependence of shift and width on magnetization, we conclude that the interaction produces the electronic Knight shift predicted by Yosida, rather than the shifts predicted by Kittel and Mitchell. This result agrees with a predic-

²⁹ P. W. Anderson and P. R. Weiss, *Revs. Modern Phys.* **25**, 269 (1953); R. Kubo and K. Tomita, *J. Phys. Soc. Japan* **9**, 888 (1954).

³⁰ M. A. Ruderman and C. Kittel, *Phys. Rev.* **96**, 99 (1954).

³¹ R. E. Behringer, *J. Phys. Chem. Solids* **2**, 209 (1957).

³² M. Peter, *J. Appl. Phys.* **32**, 338S (1961).

³³ V. Jaccarino, *J. Appl. Phys.* **32**, 102S (1961).

³⁴ R. E. Watson and A. J. Freeman, *Phys. Rev. Letters* **6**, 277 (1961).

tion that can be made from two sublattice model. (See reference above.)

(3) Owen *et al.* observed that essentially no Knight shift appears in the resonance of Mn in dilute solution in copper and silver. We have found that the gadolinium resonance shift disappears as we extend the measurement to the silver-rich alloys of palladium. The absence of these shifts cannot be explained by excessively long conduction-electron relaxation times, since we have observed no shifts even after these times were shortened by addition of paramagnetic impurities of different species into the Cu and Ag alloys. The conduction-electron interaction must still be considerable in these alloys, since the foreign atoms produced large broadenings.

(4) The g shifts observed in the Gd resonances are of negative sign. Their origin is, therefore, not the simple exchange interaction which is always positive.

Instead, we must have a polarization of mostly negative sign, in agreement with previous NMR observations. A possible mechanism for this negative polarization is the Anderson-Clogston mechanism.

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Size Effect in Electrical Resistivity of Alloys*

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Harrison's hypothesis on the effect of atomic size of impurities on the electrical resistance is shown to predict the resistance of alkali solutes in liquid sodium to an accuracy as high as the data warrant. The impurity resistance was calculated numerically over a range of assumed dilutions. The predicted resistance is not proportional to $(\Delta V/V)^2$ but is approximately fitted by the empirical equation, $\Delta\rho = \text{const}[bx - 1 + \exp(-bx)]$, where $x = \Delta V/V$. New measurements on Na-K alloys are also reported.

INTRODUCTION

A WAY to treat the effect of atomic size of impurities on the resistivity of metals has been suggested by Harrison.¹ In the case of an impurity larger than the host, the dilation is regarded as lowering the positive charge density of the lattice at the scattering center. This drop in charge density creates a repulsive scattering potential for electrons.

In this paper we examine the predictions of a square potential model based on this idea. The excess resistivity $\Delta\rho$ due to 1 at.% of solute is calculated as a function of the dilation $\Delta V/V$. The results, to a good approximation, obey the empirical relation,

$$\Delta\rho = \text{const}[bx - 1 + \exp(-bx)], \quad (1)$$

where $x = \Delta V/V$. The predictions are compared with recent measurements of the excess resistivity due to alkali solutes in liquid sodium.

Calculations of this kind have been made by Blatt,² who has tabulated the predicted excess resistivity for many solid alloys, and by Daniel,³ who calculated the excess resistivity for the liquid alkali solutions just as we do here. What is new in the present work is the consideration of the form of the relation over a range of dilation, a new comparison with experiment, and the presentation of some new measurements on Na-K alloys.

THE MODEL

The conduction electrons are considered free except for their interaction with spherical scatterers. The potential is assumed to be square, a "well" in the case of small solutes (Li), a "barrier" for large solutes (K, Rb, and Cs). The radius of the potential is taken as the "radius" of the solute atom, as estimated from its partial molar volume in the solution.

The depth of the potential is chosen to satisfy Friedel's sum rule.⁴ This rule is a condition on the

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¹ W. A. Harrison, reported in F. J. Blatt, *Phys. Rev.* **108**, 285 (1957).

² See reference 1.

³ E. Daniel, *J. Phys. Chem. Solids* **13**, 353 (1960). Also see the Erratum, to be published in the same journal.

⁴ J. Friedel, *Phil. Mag.* **43**, 155 (1952).