Magnetic-Resonance Spectra of Mn in Au and Pd

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The electron-paramagnetic-resonance properties of Mn impurities in Au and Pd are reported for the first time. A small positive g shift was observed for Mn in Au. Although this result is in agreement with the Mn g shift in Ag and Cu the Mn linewidth in Au at 20°K was 725 G, which is more than five times larger than in Ag and Cu. It was found that, in contrast to the Gd resonance, nonmagnetic impurities such as Ag in Au broaden the Mn line appreciably. A large positive g shift has been observed for Mn in Pd. This shift is explained by a positive exchange interaction $J(\mathbf{S} \cdot \mathbf{s})$ of the Mn impurities with the Pd valence band and is opposite in sign to the exchange interaction observed previously for Gd in Pd. Comparison of the Mn additional g shifts with the additional Gd g shifts produced by the presence of other rare-earth impurities in Pd confirms the exchange-interaction mechanism and the polarization of the valence electrons by the rare-earth impurities.

INTRODUCTION

THE electron-paramagnetic-resonance (EPR) properties of magnetic impurities in metals have been observed directly only for the S-state ions Gd^{3+},[1-4] Eu^{2+},[5] and Mn^{2+}.[6,7] Of these impurity ions Gd^{3+} was investigated rather thoroughly as it has a stable $^8S_{7/2}$ configuration. Eu is most often in a nonmagnetic trivalent state, but the Eu^{2+} resonance in metals has been reported only in the two dense materials Eu metal and $EuAl_2$.[8] The magnetic moment of Mn varies in different metals. In some metals like Cu, Ag, and Mg, Mn has a moment close to that of the $^6S_{5/2}$ state and its resonance has been observed.[6] In other metals like Al^9 the Mn atoms do not show any localization of their magnetic moment and accordingly no EPR was observed.

In this paper we are concerned with the EPR properties of Mn and we present the results of our investigation of EPR of Mn in Au and Pd.[7] Au is an S-state host metals in which the Mn EPR has not been observed prior to this work. Since the Mn resonance in Ag and Cu have been reported, it is important theoretically to observe this resonance in Au. The EPR properties of Gd in Pd and in some Pd alloys were investigated extensively,[1,2,4] and it is of interest to compare them with the EPR properties of Mn in the same alloys with respect to the metallic properties of the host metals as reflected in the resonances of these two S-state atoms.

TABLE I. EPR of 2% Mn in full d band metals.

Temp.	Host metal	g value	Linewidth gauss $\pm 10\%$
20.4	Au	2.005±0.005	725
20.4	Cu	2.010±0.005	140
20.4	Ag	2.010±0.005	120

EXPERIMENTAL RESULTS AND DISCUSSION

The experimental technique has been described elsewhere.[1] The Mn alloys were prepared in silica crucibles in an induction furnace with an argon atmosphere. The Pd alloys containing small amounts of rare earths were quenched in ice water from 1100°C.

The electron paramagnetic resonance results for Mn in Au are shown in Table I. The g value is close to the ones for Mn in Cu and Ag. The linewidth is however much larger, and this may be the reason why we were the first ones to observe the resonance of Mn in Au, aided by the fact that our resonance apparatus works at the relatively high frequency of 50 kMc/sec. Our results on the g values of Mn in Ag and Cu which are also shown in Table I agree with those of Owen *et al.*[6] who were first to measure them.

We have also studied the paramagnetic susceptibility of Mn in Au. Figure 1 shows a plot of $1/(\chi - \chi_0)$ versus temperature. Here χ is the measured susceptibility of the Au $+2\%$ Mn alloy and χ_0 the susceptibility of the host lattice alone (i.e., of pure Au). Over a large temperature range, the Curie-Weiss law $[1/(\chi - \chi_0) = (3Mk/L\beta^2 cp^2)(T - \theta)]$ is well obeyed. (M is the atomic wieght, L Avogadro's number, β the Bohr magneton, c the concentration, and $p = g[J(J+1)]^{1/2}$ the effective paramagentic moment.) We find from Fig. 1 the effective moment per Mn atom p to be 5.7 ± 0.2 and $\theta = 9$°K. Our value for p is very close to the theoretical value for $Mn^{++}(^6S_{5/2})$ of $p = 5.9$. The isotropic g value is close to the free electron value and it is consistent with an assignment of the $^6S_{5/2}$ state to Mn dissolved in Au.
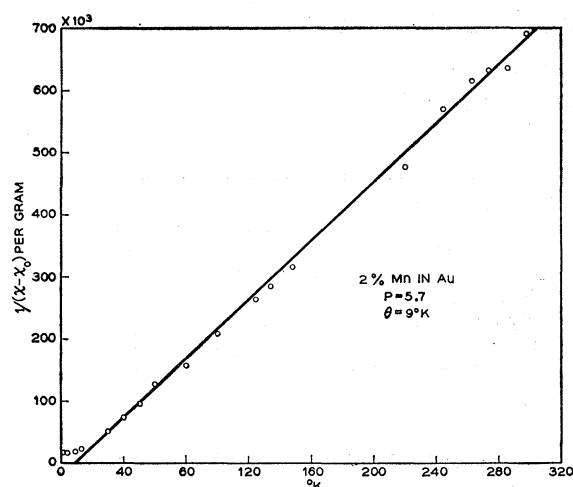
Susceptibility measurements of dilute Mn alloys in

[1] M. Peter, D. Shaltiel, J. H. Wernick, H. J. Williams, J. B. Mock, and R. C. Sherwood, Phys. Rev. **126**, 1395 (1962).

[2] M. Peter, D. Shaltiel, J. H. Wernick, H. J. Williams, J. B. Mock, and R. C. Sherwood, Phys. Rev. Letters **9**, 50 (1962).

[3] D. Shaltiel, J. H. Wernick, and V. Jaccarino, J. Appl. Phys. **35**, 978 (1964).

[4] D. Shaltiel, J. H. Wernick, H. J. Williams, and M. Peter, Phys. Rev. **135**, A1346 (1964).

[5] D. Shaltiel *et al.* (to be published).

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

[7] D. Shaltiel, M. Peter, J. H. Wernick, and H. J. Williams. A preliminary report of this work has been given in the 1963 Am. Phys. Soc. Meeting in Washington [Bull Am. Phys. Soc. **8**, 249 (1963)].

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

[9] E. W. Collings and T. F. Herdgcock, Phys. Rev. **126**, 1654 (1962).

FIG. 1. The $1/\chi$ versus temperature curve of Mn in Au.

Cu, Ag, Au, Mg, and Pd have been reported by several other authors.[3,6,9,10] Although the reported results differ in a few cases, perhaps due to the different temperature ranges in which the measurements were carried out, in most cases the effective magnetic moment according to the different authors agrees within 2%. It is found that Mn has a large magnetic moment of between 4 and 5 Bohr magnetons in Cu, Ag, Au, Mg, and Pd while in other metals, like Al, almost no moment is observed. Owen et al.[6] found $p=4.95$ for 1.4% Mn is Cu and $p=5.57$ for 0.4% Mn in Ag. These results are very close to that measured by Gustafsson[10] in alloys having similar Mn concentrations and they show that the magnetic moment of Mn obtained from the slope of the T versus $1/(\chi-\chi_0)$ curve is smaller than that expected theoretically for Mn^{2+}. This observation is also true for Mn in Au or Mg.

No hyperfine interaction has been observed for Mn in any of the above metal host lattices even for Mn-Cu alloys with less than 0.1% Mn.[6] For this alloy of low Mn concentration no exchange narrowing of the line is expected. However the linewidth was about 100 G indicating that the hyperfine constant to be at least five times smaller than that observed in ionic crystals. Despite the unresolved hyperfine structure and of values of p which deviate somewhat from the theoretical value $p=5.9$, Owen et al. have given the $^6S_{5/2}$ state as the ground state assignment for Mn in Cu and Ag so that in all the noble metals, this state appears as the best assignment.

The g values of Mn in the noble metals are larger by $0.01 \div 0.005$ than the g values observed for Mn^{2+} in ionic crystals. As we will explore more fully in the case of Mn in Pd the Mn magnetization is perturbed by an effective ion valence electron exchange interaction. It is likely that the slight g shift observed for Mn in Au, Ag, and Cu are due to exchange interactions.

[10] G. Gustafsson, Ann. Physik 25, 545 (1936).

The addition of nonmagnetic impurities such as Ag or Cu to Au or Ag to Cu and vice versa was found to broaden the Mn resonance line appreciably and above a certain concentration to make the line altogether disappear.[5] This observation is in contrast to the work on the EPR spectrum of metallic solutions containing Gd.[1,4] There we observed that only magnetic impurities such as other rare earth or Fe produce appreciable effects on the resonance linewidth. It is possible that the large linewidth of Mn in pure Au is in part also due to nonmagnetic lattice disturbances. Such disturbances could result from lattice defects or from distortion around the Mn impurities themselves.

As we mentioned above, Mn has a high moment in Pd,[4] and since Pd has a high valence electron susceptibility we would expect large Mn g shifts similar to that observed for Gd in Pd. We have therefore investigated the magnetic resonance of Mn in Pd. The results for 2 mole % of Mn in Pd are summarized in Table II. The linewidths at 20°K are big but they decrease quite appreciably at 4.2°K. The integrated intensities of the resonance lines at 4.2°K were much larger than we would expect for the absorption in the paramagnetic state of these alloys. Since susceptibility measurements have shown that these alloys are ferromagnetic at 4.2°K,[4] we conclude that the lines observed are due to ferromagnetic resonance. The narrow linewidth observed for these alloys which were in powdered form, indicates that the anisotropy constants are very small and that we can therefore neglect their effect on the line position. The g value of Mn in Pd at 20.4°K is 2.09 and is shifted by $+0.09$ with respect to the g value of Mn^{2+} in nonconducting crystals. No Mn line was observed at 78°K so that we estimate the lower limit of the linewidth to be 2500 G. The g value of Mn in the ferromagnetic state obtained by neglecting the anisotropy constants was 2.10 which is slightly larger than the g value at 20.4°K.

The effect of small amounts of rare-earth impurities on the Mn resonance in Pd was observed. Additional g shifts and broadenings occurred at 4.2°K as small amount of Ho and Pr were added to the Mn-Pd alloy, the g shift being positive for Pr and negative for Ho. As EPR experiments on Gd in Pd with small amounts of rare earth impurities have shown that the effect of the rare earths to the left of Gd in the periodic table (spin antiparallel to total momentum) is to increase the

TABLE II. EPR of 2% Mn in Pd alloys.

Temp. °K	Rare earth	g value	Δg $g-2.00$	DH gauss
78	...	...	...	>2500
20.4	...	2.09	0.09	1500
4.2	...	2.105	0.105	680
4.2	1% Pr	2.195	0.195	1300
4.2	0.2% Ho	2.055	0.055	1200
4.2	0.5% Tb	...	...	>2500

valence electron polarization, and for the rare earth to the right of Gd in the periodic table (spin parallel to total momentum) to decrease the polarization[2,4] we see that the observed effect of the rare earths on the g shift of Mn in Pd can be understood to be transmitted by the valence electrons. The theory of the EPR g values of ions in metals has been discussed previously.[2,4] This theory is based on an effective exchange interaction of the form $\bar{J}_a(\mathbf{S}_a \cdot \mathbf{s})$ between the paramagnetic ion a of spin $\mathbf{S}_a$ and the valence electrons of spin $\mathbf{s}$. From a measured g shift Δg_0 observed for the resonance of Mn in pure Pd, we obtain the exchange interaction of Mn with the Pd valence electrons $\bar{J}_{Mn} = 0.007$ eV. This value has been calculated from the expression

$$\bar{J}_{Mn} = \Delta g_0 / \chi_0 \beta^2 g_e.$$

Here, χ_0 is the susceptibility of Pd, β the Bohr magneton, and g_e the valence electron g factor. The presence of, for instance, Pr ions, give rise to the additional g shift

$$\Delta g_{Pr} = \Delta g_0 \bar{J}_{Pr} \chi_{Pr} (g_{Pr} - 1) / \beta^2 g_e g_{Pr}.$$

Here, g_{Pr} is the Landé g factor of Pr^{3+} and χ_{Pr} is the (measured) susceptibility due to the addition of the Pr to our alloy.

In Fig. 2 we show schematically the results of our experiments with dilute solution of Pr and Ho in Pd containing Gd or Mn. The position of the resonance lines of Mn and Gd in pure Pd are indicated. The arrows show the directions in which Pr and Ho displace the resonance lines of Mn and Gd. We see that $\bar{J}_{Mn} > 0$, whereas $\bar{J}_{Gd} < 0$. The g shifts induced by Pr and Ho are then of opposite sign in Mn and in Gd, in accord with our theory. The parameters $\bar{J}_{Pr}$ and $\bar{J}_{Ho}$ can now be obtained from two independent determinations— once from the experiments on Mn in Pd and once from the experiments on Gd in Pd. The results of these two determinations are shown in Table III, where we find satisfactory agreement between the two sets of values. The fact that $\bar{J}_{Gd}$ is negative and $\bar{J}_{Mn}$ is positive for Gd and Mn in solution in Pd illustrates the complex nature of the effective exchange interaction. Koida and Peter[11] have recently stated that the effective exchange interactions are the result of several contributions: a direct exchange interaction which is always positive, and indirect terms which are predominantly negative. In Pd, as in Ni_5La and Ni_5Y, the negative terms pre-
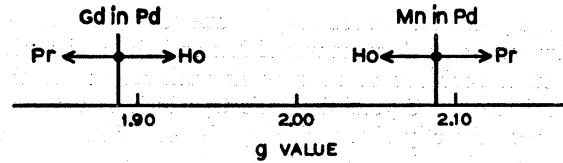

FIG. 2. The sense of the additional g shift of Mn and Gd produced by rare earth. Though the effect on Mn and Gd is opposite, the origin is the same. Pr increases the polarization of the conduction electrons and therefore increases the absolute value of the g shift whereas Ho decreases the polarization and shifts the line in the opposite sense.

dominate for the dissolved rare earths, giving rise to negative parameters $\bar{J}_{RE}$.[4] Koida and Peter[11] also discuss the fact that $\bar{J}_{RE}$ is biggest for the rare earths with the lowest atomic numbers. Our results in Table II are in agreement with this trend.

Evidence for the interaction of the Mn atoms with the Pd conduction electrons can be obtained from the low-temperature susceptibility measurements of Mn in Pd.[4] There it was observed that the Mn moment p is a linear function of the temperature-dependent Pd susceptibility χ_{Pd}:

$$p = p_0(1 + \alpha \chi_{Pd}),$$

where p_0 equals to 4.59 Bohr magnetons is the Mn magnetic moment without the Pd interaction and $\alpha = 373$ (emu/mole)$^{-1}$ is the enhancement coefficient. Using the value of $\chi_{Pd}(20°K) = 7.77$ emu/mole we obtain p at 20°K equal to 6.2 Bohr magnetons. This gives a 5% increase of the magnetic moment with respect to the pure ground state of $^6S_{5/2}$ and is close to the 4.5% increase that we would expect from the positive g shift of Mn in Pd. Although this agreement lends support to the assumption of a $^6S_{5/2}$ ground state of Mn in Pd, the problem of the relatively low magnetic moment observed for Mn in Cu, Ag, and Au, discussed earlier, remains outstanding.

As we have discussed previously[4,11,12] the nonlocal susceptibility of the valence electrons in Pd is of very long range (several lattice distances), so that dilute magnetic impurities will cause only a small broadening of a magnetic ion. In particular, the broadening of the Gd resonance in Pd by other rare earths was found to be smaller than the shifts caused by the same rare earths. We would expect the broadening by magnetic impurities to be similar in the cases of Gd and Mn, since they should both depend on the same nonlocal susceptibility of the valence electrons in the host metal. Instead, we observe that comparable concentrations of the rare earth impurities cause a much larger broadening of the Mn resonance than of the Gd resonance, all of the alloys being in the paramagnetic state. We believe that this is linked to the observation discussed above that Mn, unlike Gd, is also broadened by nonmagnetic im-

TABLE III. $\bar{J}_{RE}$ in Pd derived from Gd or Mn additional g shift.

$\bar{J}_{RE}$	Determination from the Gd resonance	Determination from the Mn resonance
$\bar{J}_{Pr}$	-0.09 ± 0.01 eV	-0.11 ± 0.01 eV
$\bar{J}_{Ho}$	-0.06 ± 0.01 eV	-0.07 ± 0.01 eV

[11] S. Koida and M. Peter, Rev. Mod. Phys. 36, 160 (1964).

[12] M. Peter, J. Phys. Radium 23, 730 (1962).

purities, an effect which may be due to the differences between the level structures of Mn and Gd, and to the different positions of their levels with respect to the Fermi energy. Crystal-field effects, which so far have not been directly observed, may also contribute to the difference in behavior of the two ions. The difference in broadening by rare-earth impurities in the cases of Mn and Gd can then be understood, since Gd reacts only to the magnetic disturbances of the other rare earths, whereas Mn is also broadened by the nonmagnetic disturbances set up by these impurities.

1s–2p Transition of H and D in Solid Argon*

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The 1s–2p transition of hydrogen and deuterium atoms diluted in solid inert gases has been observed and its energy and half-width measured. In argon, absorption occurs at the energies of 10.55 and 10.565 eV and the half-widths are 0.27 and 0.23 eV, respectively, for H and D. An analysis of these results leads to an estimate of the frequency of a localized vibrational mode associated with the H and D impurities.

I. INTRODUCTION

AMONG the several methods used to investigate the properties of a solid is the introduction of impurities in the otherwise pure matrix. By studying the properties of the impurities as perturbed by the host lattice, it is possible to gain some knowledge about the electronic and vibrational structure of the lattice. Hydrogen, and its isotope deuterium, may be considered the simplest impurities and their unperturbed electronic structures are essentially known exactly; therefore they are convenient probes when introduced in the appropriate solids. If the optical absorption of these impurities is to be investigated there are only a few solids that can be used as hosts, the reason being that the resonance transitions of H and D occur above 10 eV, i.e., in the Lyman region of the vacuum ultraviolet where almost all solids absorb strongly.

The present paper reports the study of Ar and Ne films containing H or D as impurities.[1] The experiments show isotope effects, and one interpretation of the results leads to a determination of the frequency of a localized mode interacting with the $1s-2p$ transition of the H or D impurity centers.

II. EXPERIMENTAL

Hydrogen and deuterium atomic impurities have been produced by applying radio-frequency voltage at $\simeq 30$ Mc/sec to the gases in their molecular form. The

rf was applied either to the H_2 (or D_2) gas alone or to Ar (or Ne) containing a small fraction of H_2 (or D_2). In the first case, two separate deposition systems, one for Ar (or Ne) and the other for H, were employed, each of them ending in a capillary pointing toward a cooled substrate. When the rf was applied to a pyrex capillary with H_2 or D_2 flowing, it produced a red glow very rich in Balmer lines and only a very weak molecular spectrum, thereby indicating the predominance of atoms over molecules. The alternate method was to apply the rf to a mixture of Ar (Ne) and H (D) while it flowed toward the LiF film holder. The ratio of H to Ar was of the order of 2%, and even in this case the Balmer lines could be easily seen among the Ar lines.

The LiF substrate was at a temperature of $5 \pm 1°K$ at the end of a liquid helium-cooled cryostat, as described along with the rest of the experimental apparatus in a previous paper.[2]

III. EXPERIMENTAL RESULTS

The spectra of H- or D-doped argon films investigated between 1050 and 2200 Å exhibit absorption in the Lyman α spectral region as shown in Fig. 1. The open-circle spectra correspond to films produced by applying the rf to H or D only, while in the case of full-circle spectra, Ar:H (D) mixtures were treated with rf. The H and D bands occur at 10.56 ± 0.01 eV, with the D band shifted by ≈ 0.015 eV from the H band toward higher energies. The energy of the transition for the trapped atoms is thus 0.36 eV greater than for the free atoms. The half-widths of the absorption bands are

[1] For preliminary results, see G. Baldini, Bull. Am. Phys. Soc. 9, 217 (1964).

[2] G. Baldini, Phys. Rev. 128, 1562 (1962).