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Silver Nuclear Magnetic Resonance in Silver-Transition-Metal Solid Solutions

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The nuclear magnetic resonance of Ag^{109} has been studied in binary silver solid solutions containing Pd, Pt, Ni, and Mn. Knight shifts and cw absorption linewidths are reported as a function of solute concentration c, temperature T, applied field H, and annealing time. The silver absorption line is broadened rapidly by the addition of Mn and has an H, T, and c dependence given by $\Delta H_{\text{imp}}/H=[0.8+120/(T+55)]c\times 10^{-3}$ (T in °K). The presence of magnetic moments on the Mn ions is inferred, with, however, some interaction between moments. Only in Ag : Mn is the linewidth appreciably temperature dependent. The width is believed to be due to direct magnetic dipole coupling between Ag nuclei and Mn ions and Ruderman-Kittel-Kasuya-Yosida spin-density oscillations. Representation of $\langle S_z \rangle$ for Mn ions by a modified Brillouin function leads to qualitative agreement with experiment. A sharp narrowing of the linewidth following annealing is believed to be due to loss of solute by internal oxidation. The line shape becomes more Lorentzian as Mn is added to Ag. For Ag : Ni and Ag : Pt, the line broadening is only about one-third of that observed in Ag : Mn. The change in the Ag^{109} Knight shift K upon alloying with Ni, Pt, or Mn is small, $\Delta K/K \lesssim -1\%$. The shift in Ag : Pd is negative and nonlinear in concentration with $\Delta K/K = -3\%$ at 10% Pd and -10.5% at 20% Pd, in agreement with pulse measurements of Narath. The line broadening in Ag : Pd is proportional to c up to $c=10\%$ and varies as $\sqrt{c}$ for higher concentrations. The broadening is discussed in terms of simple band theory and virtual bound states. Line broadening produced by equiatomic percentage of d-shell impurities is compared. Finally, a comparison with other systems, particularly Cu : Mn, is made.

I. INTRODUCTION

This paper describes the results of the first comprehensive study of the steady-state NMR of a nonquadrupolar nucleus (Ag^{109}) in noble-metal–transition-metal alloys. Results are presented for the solutes Pd, Pt, Ni, and Mn[1] dissolved in silver. The purpose of this study is to gain a better understanding of the changes in electronic and magnetic properties of the host when impurities possessing an incomplete d shell are added. Several inhomogeneous line-broadening mechanisms may be present. Polarization of conduction electrons by unpaired d spins gives rise to Ruderman-Kittel-Kasuya-Yosida (RKKY) spin-density oscillations,[2] and screening of charge imbalance leads to Friedel-Blandin oscillations[3] in the charge density. Only spin-density waves are capable of interacting directly with the host-metal nuclei (via the hyperfine interaction), since the nuclear spin of Ag^{109} has value one-half. This should lend an important advantage over the considerable NMR results which have been reported on copper alloys, where a large part of the linewidth was due to quadrupolar shifts resulting from charge-density oscillations. Other sources of line broadening include the direct dipolar interaction between the moments of silver nuclei and transition ions. It is also thought[4] that for the $3d$ solutes dissolved in silver both long-range and short-range solute-solute interactions may exist. We attempt by various heat treatments to modify such order, if it exists, while monitoring the effects on the Ag^{109} resonance. Since internal oxidation was thought to exist in Ag : Mn alloys, it was also deemed desirable to study any loss of solute at elevated temperatures due to this mechanism. The effect of the Kondo bound state (for $3d$ solutes) on our measurements should be small due to the presence of high internal fields and relatively high temperatures since the Kondo temperature $T_k \approx 0.05$ °K.[5]

We describe the experimental apparatus and discuss sample preparation in Sec. II. The results of our measurements are presented in Sec. III. Some interesting features of the results are: (a) The impurity induced width in Ag : Mn is proportional to the applied field and consists of two components, only one of which depends on temperature; (b) the Ag : Mn line narrows sharply after annealing the as-filed particles; (c) line broadening due to Ni and Pt is independent of temperature and is only about one-third of that due to Mn; (d) the Knight shift in Ag : Pd decreases in a nonlinear way with increasing Pd concentration c while the linewidth increases proportional to c for $c < 10\%$ Pd and varies as $\sqrt{c}$ for $c > 10\%$.

In Sec. IV we discuss line broadening in these systems and compare theory and experiment for Ag : Mn. The conclusion is reached that it is not possible to account for the observed broadening in terms of a free-spin Brillouin function. The results of annealing are presented in Sec. V. Section VI contains a discussion of line broadening in terms of virtual bound states and simple band theory. The broadening produced by different *d*-shell impurities is compared and briefly discussed. The Ag : Mn and Cu : Mn systems are compared. We summarize in Sec. VII.

II. EXPERIMENTAL PROCEDURE

A. Apparatus

The experiments were performed with a Varian induction spectrometer, crystal stabilized between 3.5 and 5 MHz corresponding to polarizing fields between 17 and 25 kG. First derivative resonances of the absorption line were recorded on an *X-Y* plotter after passing through a lock-in detector with output time constant varying from 30 to 100 sec. Field modulation was limited to 20 Hz to avoid distortion effects. From relative rf-level studies it was deduced that the spin-lattice relaxation time T_1 in the alloys, surprisingly, is not much changed from that of pure Ag at corresponding temperatures.[6] The long T_1's in these alloys make it especially important to limit rf levels to values below the onset of saturation ($\lesssim 0.03$ G peak to peak).

Measurements were made on most samples at room, liquid-nitrogen, and liquid-helium temperatures. By pumping, temperatures down to 1.5 °K were achieved and measured by the helium vapor pressure.

B. Samples

The alloys were melted in clay-graphite crucibles under carbon monoxide (plus argon for manganese containing alloys). They were poured between 2000–2100 °F and cast in ingot form in graphite molds, after which they were annealed for 1 h at 1000 °F and water quenched. The annealing atmosphere consisted of a mixture of one part N_2 and three parts H_2 (cracked ammonia) to avoid internal oxidation or scaling.[7] Silver with a purity better than 99.99% was used along with commercially pure solute material. Spectrographic analysis indicated that the alloys contained typically less than 0.001-at.% Fe, and about 0.003-at.% Cu, which should be insignificant quantities compared with the major impurity content. The samples were examined metallographically and found to be single-phase solid solutions. They were filed in air from the cast ingots and the particles were magnetically sieved and washed in a 0.5 *M* solution of Na_2S to provide electrical isolation. The powder samples usually had particle sizes less than 400 mesh; accordingly no skin effect correction has been applied to the data. This is consistent with the absence of mode mixing in the detected signal and the observation of rather symmetric line shapes.

III. EXPERIMENTAL RESULTS

Measurements of the Ag^{109} resonance were made between 1.5 and 4.2 °K and at 77 and 300 °K at frequencies 3.5, 4.0, and 4.9 MHz in binary silver alloys containing 0.01-, 0.03-, 0.05-, 0.075-, and 0.1-at.% Mn, 0.01- and 0.1-at.% Ni, 5-, 10-, 15-, and 20-at.% Pd, and 0.05- and 0.1-at.% Pt. Measurements were first made on the powder samples as-filed, then remeasured after various annealing times. Some characteristics of the resonance were significantly changed by the annealing process.[1]

The pure-silver absorption line has a peak-to-peak derivative width of 0.64 G at room temperature independent of applied field within the total experimental error which is about 10%. The widths at both 77 and 4.2 °K are 0.77 G, slightly larger than at room temperature. The center of gravity of the pure-metal absorption was shifted to higher applied fields by 0.8 G at 77 °K and 1.1 G at 4.2 °K at 4 MHz. Resonances were usually measured with a peak-to-peak field modulation limited to 60 to 75% of the linewidth. A small correction for finite modulation[8] has nevertheless been applied to all linewidths reported in this paper.

Line shapes of the derivative of the absorption curves were determined by comparing the experimental curves with ideal Lorentzian and Gaussian curves.[9] The curves were normalized by requiring the peak height and width at half-maximum intensity to be equal for experimental and theoretical curves. The pure-silver resonance is well approximated by a Gaussian at all temperatures and fields.

A. Ag-Mn

The center of gravity of the broadened symmetrical lines in the alloys is very little different from that in pure silver. The average of many resonances indicates that the Knight shift *decreases* by only about 1% of its absolute value (0.52%) at low temperatures and higher (> 0.075 at.%) Mn concentrations. This shift is smaller and in the opposite direction to that observed[10] in Cu-Mn alloys at comparable temperatures and concentrations. Such small shifts are consistent with an oscillatory spin polarization and are incompatible with theories requiring a uniform polarization of the conduction band or a monotonic distance dependence. Such a small decrease in the Knight shift can be accounted for by the demagnetization field[11] within the sample due to the bulk susceptibility.

The derivative width of the Ag^{109} absorption line was measured as a function of Mn concentration, temperature, and magnetic field. Since we are interested in the effect of the addition of Mn atoms on the Ag NMR, we shall plot only the impurity contribution $\Delta H_{\rm imp}$ to the total linewidth. In Fig. 1,

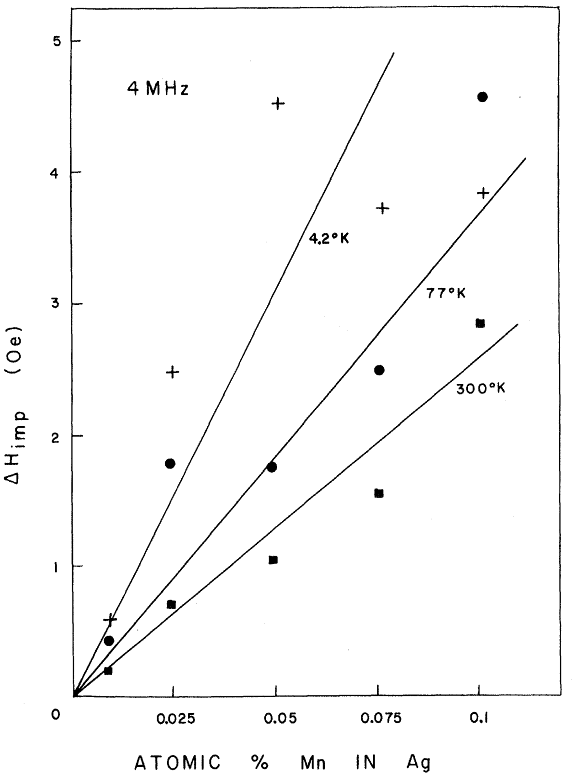

FIG. 1. Impurity contributions to the Ag^{109} derivative linewidth ΔH_{imp} as a function of Mn concentration at 4 MHz for different values of sample temperature (+4.2 °K; ● 77 °K; ■ 300 °K). The straight lines represent linear approximations to the low concentration data.

we show ΔH_{imp} vs Mn concentration at 4 MHz for different values of the temperature. The linewidth is approximately proportional to the Mn concentration c for $c \leq 0.05$ at.%. However, for $c > 0.05$ at.% and especially at low temperatures, there is considerable scatter in the data. Since impurity interactions become important at higher c and lower T, the scatter strongly suggests such interactions. Figure 1 also shows that the broadening is greater at the lower temperatures, as is expected for a line-broadening mechanism associated with polarization of the impurity spins.

The impurity induced linewidth in Ag–0.03% Mn is plotted vs applied field at different temperatures in Fig. 2. The linewidth data at fixed temperature can be fitted by a straight line which extrapolates approximately to zero at zero applied field. The increase of linewidth with decreasing temperature shows saturation and cannot be described by a simple $1/T$ function. For example, in 0.01, 0.03, and 0.05% Mn samples, ΔH_{imp} increased by only 10 to 20% as the temperature was lowered from 4.2 to 1.5 °K. A spin-$\frac{5}{2}$ (or $\frac{3}{2}$) Brillouin function is not expected to show much saturation even at our highest experimental H/T ratios. The dependence of ΔH_{imp} on H, T, and c, between 4.2 and 300 °K in the range linear in c (expressed in at.%) can be represented[1] approximately by $\Delta H_{\mathrm{imp}}/H = [0.8 + 120/(T+55)]c \times 10^{-3}$, indicating the presence of two broadening mechanisms only one of which depends on temperature. For comparison we note that these linewidths are an order of magnitude smaller than those reported[10] in the CuMn system. In addition, the impurity-induced linewidths in that system varied by more than a factor of 2 between 1.5 and 4.2 °K. This may be only partly due to quadrupole broadening in the latter alloy. The broadening per impurity atom is, on the other hand, almost an order of magnitude larger than that found in silver alloys containing nonmagnetic solute atoms.[12]

As manganese is added to silver the line shape changes slowly from Gaussian toward Lorentzian. For Mn concentrations less than 0.03% the shape fits a Gaussian better than a Lorentzian. For higher concentrations the experimental curve fit a Loretzian somewhat better; however, the intensity in the wings of the line remains lower than the ideal curve.

B. Ag-Ni

As in the Ag-Mn system, the center of gravity of the line is essentially unshifted ($\Delta K/K \lesssim -1\%$) at

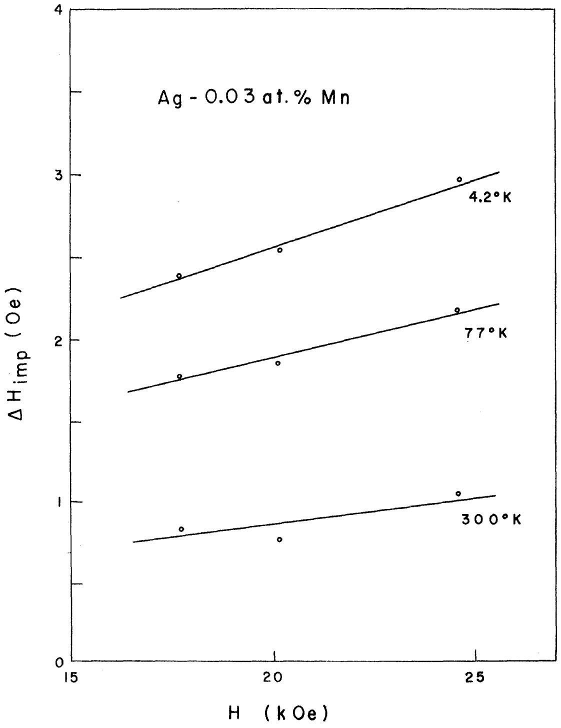

FIG. 2. Impurity-induced linewidth in Ag–0.03% Mn vs applied field at different temperatures.

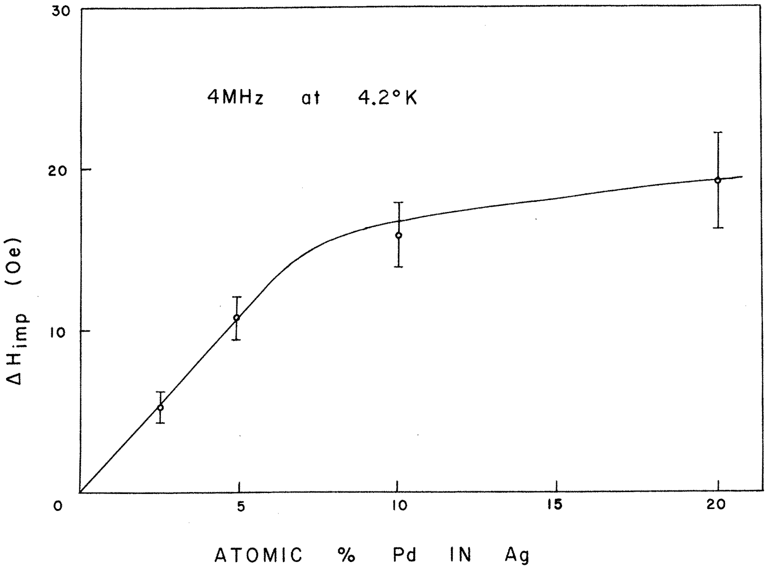

FIG. 3. Ag^{109} linewidth vs Pd concentration at 4 MHz and 4.2 °K.

any temperature or field. The peak-to-peak derivative width in a Ag–0.1-at.% Ni sample at 300 °K was roughly twice that of pure Ag. The temperature dependence of the width was much less pronounced than in Ag-Mn, the linewidth at 4 °K being only about 20% greater than that at 300 °K. An increase in width somewhat less than linear in applied field was observed. The noted behavior is consistent with the conclusion that Ni does not possess an appreciable magnetic moment in Ag.

C. Ag-Pd

While it is possible to form solid solutions of Mn in Ag at room temperature up to 10- or 15-at.% Mn, the high Mn susceptiblity renders the Ag cw absorption line unobservable at any temperature for Mn concentrations above about 0.1 at.%. Nickel, on the other hand, is much less magnetic, but unfortunately does not dissolve in silver in concentrations higher than about 0.1%. Palladium is completely miscible in silver and, in addition, is not sufficiently magnetic to render the Ag NMR unobservable. We report measurements out to 20% Pd in Ag.

The Ag^{109} Knight shift K decreases in a nonlinear fashion with increasing Pd concentration: $\Delta K/K = -3\%$ at 10% Pd and -10.5% at 20% Pd. The shift is independent of temperature and applied field. The results agree within experimental error with pulse measurements[13] of Narath on this alloy system.

The Ag^{109} linewidth vs Pd concentration is shown in Fig. 3 for 4 MHz and 4.2 °K. The absorption line is observable in all samples, the peak-to-peak width increasing to somewhat greater than 20 G (30 times the pure Ag width) in the 20% Pd alloy at 4 °K. The width measured between half-intensity points of the derivative curve is 35 G. The increase is linear in concentration up to 5% Pd, but departs from linearity at higher concentrations, being approximately proportional to $\sqrt{c}$. The linewidths are independent of temperature from 1.5 to 300 °K, in sharp contrast to the Ag-Mn system. They are, however, approximately proportional to the applied field. The Ag^{109} line shape shows little change upon addition of Pd atoms, remaining closely Gaussian even for 20% Pd in Ag. The shape is insensitive to temperature or field.

Pulse measurements[13] at high fields (55 kG) have shown the spin-echo width to be about 110 G in a 20% Pd in Ag sample. When normalized to the field of the present experiment, the pulse determination of the "linewidth" is only a factor of 2 larger than the value reported here. Since these linewidths are much greater than those deduced from the measured value[13] of the spin dephasing time T_2, the cw line-broadening mechanism may be associated with spatial variations of the Knight shift not included in T_2. If the discrepancy between the cw and pulse determinations of the linewidth were due to the removal of the absorption from silver nuclei which are near neighbors to palladium atoms, then one would expect a large decrease in the intensity of the Ag–20% Pd resonance, which is not observed.

D. Ag-Pt

Two samples were measured: Ag–0.05-at.% Pt and Ag–1% Pt. The Pt contribution to the Ag^{109} linewidth is 0.45 and 4.2 G at 4 MHz and 300 °K for 0.05% Pt and 1% Pt, respectively. Thus, whatever the mechanism for line broadening, the net broadening per atomic percent impurity is about the same for Ag-Pt and Ag-Ni. The linewidths exhibited no field dependence, but did broaden at 77 °K;

ΔH_{imp} was 0.8 G for Ag–0.05 Pt. The center of gravity of the line was shifted to higher applied fields by less than 1% of the Knight shift.

IV. COMPARISON OF THEORY AND EXPERIMENT–LINEWIDTH IN Ag:Mn

The major sources of field- and temperature-independent line broadening in silver alloys include (a) nuclear magnetic dipole interactions and (b) indirect exchange coupling between nuclear spins. Field- and/or temperature-dependent mechanisms include (c) direct magnetic dipolar interaction between silver nuclei and transition ion cores, (d) indirect exchange coupling, via the conduction electrons, of silver nuclei and transition ion cores (RKKY broadening). In addition, there may be inhomogeneous Knight shift broadening due to a nonrandom distribution of impurities. For completeness, we also list the broadening due to the bulk magnetism of the sample.[11]

It is straightforward to show that the broadening due to *nuclear* dipole interactions is negligible. In this case the Van Vleck formula[14] yields for the impurity contribution to the rms second moment $\Delta H = 0.07$ G for 0.1% Mn in Ag and $\Delta H = 0.13$ G for 20% Pd in Ag. These widths are small compared with the experimental linewidths and will be neglected. Similarly, T_1 is too long (30 msec for pure Ag at 300 °K) to make an important contribution to the linewidth. It is believed that T_1 does not shorten sufficiently in the alloys to warrant further consideration of this source of line broadening.

While indirect exchange broadening between unlike nuclei is important in pure Ag metal, it is not expected to play an important role in the alloys. The field dependence of the widths confirms that this mechanism is not important. It is thus believed that the broadening in the Ag:Mn system can be roughly accounted for by a combination of (c) and (d) above.

A. Magnetic Dipolar Interaction between Silver Nuclei and Manganese Ion Cores

If we assume, following Behringer,[15] that the reorientation time for Mn 3*d* spins is determined by a $J\vec{S}\cdot\vec{s}$ interaction (where $\vec{S}$ is the impurity spin and $\vec{s}$ the conduction electron spin), then T_1 for Mn in Ag is given by $T_1 = 0.6\times10^{-9}/T \approx 10^{-11}$ sec. Since $T_2(\text{Ag}) \approx 10^{-2}$ sec,[12] $T_1(\text{Mn}) \ll T_2(\text{Ag})$ and we are justified in treating the effect of the Mn spin as adding an additional magnetic field along the applied field direction. The contribution to the linewidth from this source is then given[15] by

$$\Delta H = 7.21 c \bar{\mu}_z / (\tfrac{1}{4}) a_0^3 \,. \tag{1}$$

In this expression c is the atomic concentration of impurities, a_0 is the length of the cube edge in the fcc lattice and $\bar{\mu}_z$ is the thermal average dipole moment of the Mn ion core given by $\bar{\mu}_z = g\mu_B S \times B_S(g\mu_B SH/kT)$, where z is the direction of the applied field H, g is the spectroscopic splitting factor, μ_B is the Bohr magneton, S is the spin of the Mn ion core, and B_S is the Brillouin function. The field and temperature dependence of the linewidth enter through the Brillouin function.

ΔH in Eq. (1) refers to one-half the "wing-width" ΔH_2 (width between points where the intensity has fallen to one-half the peak value). For our lines $\Delta H_2^{\text{imp}} \approx 2\Delta H_{\text{pp}}^{\text{imp}}$ where ΔH_{pp} refers to the peak-to-peak separation of the derivative linewidth. We therefore compare the calculated widths directly with the measured $\Delta H_{\text{pp}}^{\text{imp}}$. A comparison of the values of ΔH calculated from Eq. (1) with $S = \frac{5}{2}$ corresponding to Mn^{2+} ions in a $^6S_{5/2}$ state to the experimental values shows that the observed widths cannot be accounted for by a free spin $S = \frac{5}{2}$ Brillouin function. The calculated widths represent only 10% of the observed widths at 300 °K but become even larger than the observed widths at low temperatures. This is in contrast to the CuMn system where even at low temperatures the calculated dipolar widths could account for at most 20% of the observed width.[15] It might perhaps be more reasonable to allow phenomenologically for the possibility of impurity-impurity interactions by assuming a Brillouin function of $1/(T+\theta)$, where $\theta \simeq 55$ °K, the value obtained earlier from a fit to the experimental data (Fig. 1). Owing to experimental uncertainties, it is not possible to determine the variation of θ with concentration; the physical meaning of θ, therefore, remains uncertain. [One may also obtain a Curie-Weiss–type dependence of the form $C/(T+\theta)$, where $\theta > 0$ for *isolated* impurities interacting with a sea of conduction electrons.[16,17]] This has the effect of greatly reducing the low-temperature contributions and is more in line with experiment. This approach is preferred to that of, say, assuming $S = \frac{3}{2}$, which while reducing $\bar{\mu}_z$ does not reproduce the experimental temperature dependence. The ΔH values obtained using Eq. (1) with this modification are shown in Table

TABLE I. Comparison of calculated and experimental ΔH values in Ag:Mn alloys at various temperatures and concentrations for an applied field of 20 000 G. The calculated values were obtained from Eq. (1) using a modified Brillouin function as described in the text.

ΔH	Calculated (G)			Experimental (G)		
			Temperature			
c (at. %Mn)	300 °K	77 °K	4.2 °K	300 °K	77 °K	4.2 °K
0.01	0.02	0.05	0.10	0.19±0.03	0.44±0.07	0.6±0.3
0.03	0.05	0.15	0.31	0.72±0.05	1.8 ±0.3	2.5±0.4
0.05	0.09	0.24	0.52	1.1 ±0.2	1.8 ±0.5	4.6±0.4
0.075	0.13	0.35	0.77	1.6 ±0.2	2.5 ±0.3	3.8±0.8
0.10	0.18	0.48	1.00	2.9 ±0.4	4.6 ±0.5	3.9±1.0

I together with the experimental values. The calculated widths are now seen to account for 10–20% of the observed widths.

B. RKKY Indirect Exchange Coupling

This broadening mechanism assumes that the Mn ion spins and the silver nuclear spins are indirectly coupled by the conduction electrons involving an initial exchange interaction between the Mn spins and conduction electrons and subsequent interaction of these polarized conduction electrons with silver nuclei via the hyperfine interaction.

The oscillations in conduction electron spin density which decrease in a nonmonotonic way with increasing distance from an impurity site can cause large positive and negative shifts at intervening nuclear sites and thus a line broadening of inhomogeneous type. Theoretical expressions for these oscillations patterned after the Ruderman-Kittel interaction have been obtained by Yosida,[2] Kasuya,[18] Behringer,[15] and others, and are commonly referred to as RKKY oscillations.

We now estimate the local hyperfine field at a silver nucleus due to the indirect interaction with a Mn ion located at the origin of coordinates, and with the applied field in the z direction. The internal field is given by[2]

$$\Delta H = \frac{-|\langle S_z\rangle|}{g_N\mu_N}\left(\frac{3n}{N}\right)^2 \frac{2\pi}{E_F} AJF(2k_m r) , \qquad (2)$$

where $F(x) \equiv (x\cos x - \sin x)x^{-4}$, r is the position of the nucleus with respect to a Mn ion, $g_N\mu_N I$ is the magnetic moment of the nucleus, $2n$ and N are the number of conduction electrons and lattice points in unit volume, respectively, k_m and E_F are the wave number and energy of a conduction electron at the Fermi surface, A is the hyperfine energy of a conduction electron with a silver nucleus, and J is the s-d exchange energy of a conduction electron with a Mn ion core. In order to calculate the line broadening from the above expression it is necessary to assume a line-shape function, a given distribution of impurities, and then to sum over all resonating nuclei.

By making certain assumptions and without explicitly carrying out the sum, one can estimate the magnitude and sign of the hf field at successive silver shells surrounding a central Mn. To obtain this crude estimate we assume that $\langle S_z\rangle = SB_s$ and that $S=\frac{5}{2}$. Free-electron theory gives $k_m = 1.20 \times 10^8\ \mathrm{cm}^{-1}$, $E_F = 5.51$ eV; $A = h\xi\nu_a$, where $\nu_a = 0.0659\ \mathrm{cm}^{-1}$ is the observed hyperfine splitting in a free silver atom and $\xi = \frac{1}{3}$ is the ratio[19] of the average probability density of a valence electron at the nucleus in the metal to that in the free atom. Since we have assumed that $J < 0$, the sign of ΔH is determined by the oscillating function $F(x)$. The internal fields calculated from Eq. (2), assuming $|J| = 0.31$ eV,[5] are much too large to agree with the observed widths, for example, at 4.2 °K, the field at first neighbors to a Mn is 7 kG. As in the case of dipolar broadening, in order to account for interactions, we now calculate $\langle S_z\rangle$ from a Brillouin function of $1/(T+55\ ^\circ\mathrm{K})$. The results of this calculation are given in Table II at 300 and 4.2 °K.

From Table II we can deduce that only about three shells of silver nuclei at 300 °K and four or five shells at 4.2 °K are expected to undergo shifts greater than the observed cw linewidth. At these low impurity concentrations, this represents a decrease in Ag^{109} intensity of only about 3%, which is too small to detect experimentally.

V. RESULTS OF ANNEALING

Kouvel[4] has suggested an interpretation of magnetic measurements in these alloys in terms of "antiferromagnetic" clusters of impurities, whereby spin pairing can reduce the net moment of the Mn ions. Owen *et al.*[20] have reported the coexistence of both antiferromagnetic and ferromagnetic interactions in dilute Cu : Mn alloys. To investigate the possibility of such ordering effects we have monitored the Ag linewidth as a function of annealing time at 770 °K for several Ag : Mn samples. The results[1] for Ag–0.05-at.% Mn measured at 300 °K is shown in Fig. 4. The plot shows a surprising sharpening of the total linewidth ΔH as a function of total annealing time. The decrease in ΔH is accompanied by a large increase in the peak-to-peak height. ΔH narrows to a little less than half the as-filed value after 4 h annealing but levels off, after subsequent anneals, to a value 35% greater than the pure Ag ΔH. The Ag^{109} linewidth in a Ag–5% Pd alloy remained unchanged after similar anneals, while ΔH of a 0.01% Ni sample was unobservable. In addition, the amplitude of the echoes observable[21] in these samples increased by about a factor of 2 after annealing. The Knight shift was unaffected by the annealing process. Similar narrowing effects on the linewidth in Cu : Mn alloys have been reported.[22,23] In contrast to the Cu : Mn

TABLE II. Hyperfine fields (in G) in the silver matrix, due to RKKY oscillations, calculated from Eq. (2) using a modified Brillouin function discussed in the text. The applied field is 20 kG. The numbers in the column labeled "silver shell" represent 1st, 2nd, ··· silver neighbors to a Mn ion.

Silver shell	$T = 300\ ^\circ\mathrm{K}$	$T = 4.2\ ^\circ\mathrm{K}$
1	67	600
2	−28	−250
3	16	150
4	1.8	17

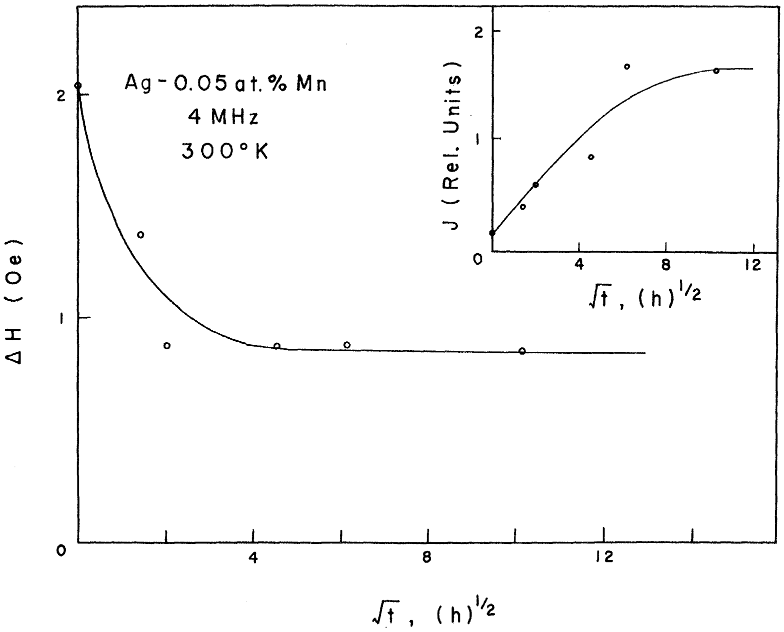

FIG. 4. Total linewidth ΔH vs $\sqrt{t}$, where t is the running total of separate annealing times at 500 °C. The depth of internal oxidation is expected (Ref. 25) to be proportional to $\sqrt{t}$. The increase in peak-to-peak height J is also shown.

system, the narrowing of ΔH in Ag : Mn cannot be attributed to a reduction of the quadrupolar broadening.

The net effect of the annealing on the NMR line is, then, in some ways equivalent to a reduction of solute concentration. The Ag : Mn phase diagram indicates, however, that the Mn is not expected to precipitate, in contrast with the Ag : Ni system. Besides influencing clustering, the heat treatment may modify grain size which affects the net moment if the spin ordering is antiferromagnetic,[24] or it may anneal out stacking faults and other imperfections arising from the comminution process. However, we believe that the observed effects find a reasonable explanation in the phenomenon of internal oxidation.

It has been known[25] for some time that Ag (and certain other metals, including Cu) containing a homogeneously dissolved solute metal B can be dispersion hardened by diffusing oxygen into them. The hardening is produced by a chemical reaction of the solute metal B with oxygen diffusing into the solid solution Ag + B and the subsequent internal precipitation of an oxide of the solute. The conditions that favor internal oxidation in general can be summarized[23,25] as follows: (i) Oxygen must dissolve and diffuse in the alloy. (ii) The affinity of oxygen for B must be sufficiently greater than for the solvent. (iii) The solute oxide must be insoluble in the alloy.

Now oxygen diffuses more freely through solid silver than through any other metal,[26] and with a speed considerably greater than metallic elements.[25] Its affinity for Ag is so small that Ag_2O is not formed when Ag is heated above 190 °C in O_2 of normal pressure. A recent detailed study[23,27] on Cu-Mn alloys using NMR, x-ray, and electron microscopy shows that solute loss by internal oxidation can result from comminution or vacuum anneals. We believe it is most likely that our NMR results are due to this phenomenon. In the above-cited work the dominant oxide was identified as MnO. The conditions for internal oxidation should be even better satisfied in Ag : Mn than Cu : Mn since the affinity of Ag for oxygen is even less than that of Cu. Since the affinity of Pd for O is expected to be less than that of Mn, we can understand, at least in a qualitative way, why no change in NMR parameters was observed in a Ag : Pd alloy after annealing. We shall report more detailed results on this and other silver alloy systems elsewhere.

In view of the likelihood of internal oxidation in Ag : Mn and Cu : Mn alloys it is clear that serious errors in interpretation can arise if measured parameters are correlated with solute concentrations obtained from chemical analysis. In special cases the appropriate solute concentration with which to correlate data may be just some fraction of the nominal concentration. (We believe this to be the case for Ag : Mn.) In other cases (for example, resonance data involving quadrupolar nuclei or electrical resistivity measurements) the consequences of internal oxidation may be more drastic. For example, in addition to reducing the effective concentration, the precipitated oxide may appreciably perturb the system under measurement (e.g., by scattering electrons or creating electric field gradients). It is likely that internal oxidation is responsible for some of the strange magnetic behavior observed by Kouvel.[4]

VI. DISCUSSION

The Ag:Pd system shows a large decrease in Knight shift K with alloying, in contrast to Ag:Mn. In addition, the Ag^{109} line broadening was field dependent, temperature independent, and about one-tenth the magnitude of that produced by Mn, which is known to possess a magnetic moment when dissolved in Ag. One can understand qualitatively these facts on the basis of simple band theory and the concept of Friedel virtual bound states. In pure Pd, susceptibility measurements[28] have borne out the early suggestion of Mott[29] that the Pd d band is incompletely filled, containing about 0.4 hole, and overlapped by an s band. As Ag is added to Pd the magnetization decreases approximately linearly and becomes zero at 40–50% Ag. This behavior is accounted for by the gradual filling of the Pd $4d$ holes by some fraction of the extra Ag $5s$ electrons.[30] For the Ag-rich alloys on which we are reporting, essentially all Pd d holes are filled at some expense of shielding charge at nearby Ag sites. This neutralizes the Pd magnetism which is consistent with the observed absence of any temperature dependence of the linewidth. This decrease in both the local susceptibility and the charge density at Ag nuclei results in a decreased hf field at Ag nuclei and accounts for the observed decrease in K. The field dependence of the width may be attributed to inhomogeneous Knight shifts resulting from the relatively weak spin waves associated with a Pauli-type paramagnetism.

The case of Ag:Mn is quite different. The two $3d$ subbands of Mn are exchange split, one almost completely full and lying just below the Ag Fermi level, the other empty and lying above, thus producing a net magnetic moment. The essential correctness of this picture of the virtual level structure for Mn in the noble metals has been verified by recent photoemission and optical studies.[31–33] The field and temperature dependence of the NMR linewidth are in qualitative agreement with these ideas; however, as seen above, calculations based on Eq. (1) or (2) assuming that the alignment of impurity spins with the external field is opposed only by their thermal energy, predict enormous linewidths which are not observed. In order to bring the calculated widths into better agreement with those observed it is necessary to account, albeit in a crude way, for interactions among impurities by assuming $\langle S_z \rangle$ to be given by a Brillouin function of $1/(T+\theta)$ instead of $1/T$.

The solute elements Ni, Pd, and Pt occur one column to the left of Ag in the Periodic Table and therefore each (electrically neutral) free atom possesses 10 outer electrons (s and d). By comparing the line broadening produced by equal amounts of different impurities in the Ag host, one may obtain at least qualitative information concerning, for example, the degree of ionization and the presence of impurity magnetic moments. *A priori*, the number of holes in the impurity atom d shells when substituted in Ag is unknown. The number of such holes determines the degree of polarization of the conduction band and is therefore reflected in the line broadening of the host. However, in the absence of incomplete spin pairing among d electrons, the silver linewidths may be broadened from an increase (due to Coulomb and exchange interactions) in the temperature-independent susceptibility. Table III compares Ag^{109} linewidths at 300 °K and 4 MHz due to different d-shell solutes. In order to make comparison, the widths have been normalized to 1-at.% impurity assuming a linear dependence on concentration for alloys with limited solid solubility. It is seen from the table that, at room temperature, the broadening due to Pt and Ni is comparable and is about 4 times that due to Pd. We note that the ratio of ΔH's for Ag:Pt to Ag:Pd is the same as the ratio of their residual resistivities.[34] Mn, which presumably has near the maximum number of unpaired $3d$ spins, produces a broadening three times that of Pt or Ni and ten times that of Pd. Ag:Cd is included in the table to contrast the greatly decreased broadening per impurity concentration produced by a non-transition-metal solute. As pointed out earlier, only in Ag:Mn is the linewidth appreciably larger at low temperatures. The lack of temperature dependence and only a weak field dependence of the NMR linewidth associated with Pd and Ni indicate that no d holes remain and therefore the impurity d levels lie below the Fermi level. A recent analysis[35] of the energy distribution of photoemitted electrons from a Ag:Pd alloy confirms the existence of resonant bound states of the Pd $4d$ electrons lying just below the Fermi level. The transference of conduction electrons into the d holes creates a charge imbalance, the screening of which leads to charge- and spin-density oscillations, which in turn account for the broadening due to Pt, Ni, and Pd. (The temperature-dependent linewidth in Ag:Pt may indicate, however, that the Pt d levels in these alloys are incompletely filled. Susceptibility measurements would help resolve this problem.)

It is also interesting to compare the Ag:Mn linewidths to those observed by a similar cw technique in Cu:Mn. The impurity induced width in Cu–0.05% $Mn^{10,20,36}$ at 4 °K is some six to nine times larger than that in Ag–0.05% Mn (linearly extrapolated to the same field). If we assume that this width is mostly due to an RKKY mechanism and that the spin of the Mn ion is $\frac{5}{2}$ in both hosts, then Eq. (2) predicts that the ratio of Cu^{63} to Ag^{109} linewidths is 0.8. This number is obtained by taking $E_F(\mathrm{Cu}) = 7.04$ eV, $E_F = 5.51$ eV, the known magnetogyric

TABLE III. Ag^{109} absorption linewidth contributions at 300 °K and 4 MHz for equiatomic percent of various d-shell impurities.

Alloy	ΔH_{imp}(1 at. %) (G)
Ag : Ni	8.0 ± 2.0
Ag : Pd	2.2 ± 0.3
Ag : Pt	8.0 ± 2.0
Ag : Mn	22.0 ± 3.0
Ag : Cd	0.2

ratios for Cu^{63} and Ag^{109}, and hyperfine coupling constants of 6.6×10^8 Hz and 38×10^8 Hz for Ag^{109} and Cu^{63}, corrected for the metal using the Knight factor (~0.3 for both Cu and Ag).[19] $\langle S_z \rangle$ has been accounted for by extrapolating the experimental linewidths to equal fields. We now attempt to resolve this discrepancy of a factor of 10 between our crude theoretical estimate and experiment: (a) There is some evidence[5] that $J_{s\text{-}d}$ for Mn is comparable in silver and copper. We assume that this is the case and is therefore not the source of the discrepancy. (b) It is likely that even at 4 °K an appreciable part of the copper linewidth is due to quadrupole interaction. We feel that this is confirmed in the original work of Owen *et al.*[20] by the presence of a temperature-independent term which is comparable in magnitude to the $1/T$ term even at at 4 °K. This broadening mechanism is independent of RKKY broadening and would help resolve the above discrepancy. The lattice and conduction electron contributions to electric field gradients in metals have been discussed by Watson *et al.*[37] (c) If short-range ordering, clustering, or internal oxidation of Mn in Ag reduced the effective concentration of Mn, then ΔH(Ag) would be reduced and the discrepancy made worse. (d) Similarly, agreement between theory and experiment is worsened if we assume that in Cu:Mn some RKKY shifted satellites do not contribute to the measured linewidth. (e) In addition to (b) above, it is also possible that some Ag nuclei are not being observed. If we assume there is no contribution from source (b), then to reproduce the ratio of linewidths calculated from Eq. (2) the Ag width would have to be about ten times larger than that measured, i.e., 35 G for 0.05-at.% Mn at 4 °K and 4 MHz.

The Knight shift K is an interesting quantity but more complicated to interpret than line broadening. For alloys such as Ag: Mn, where inhomogeneties in the shift (suggested by field-dependent and temperature-independent broadening) may play an important role, one should perhaps stress that the quantity obtained experimentally is the center of gravity of the envelope of a distribution of spin packets arising from a distribution of local hyperfine fields. This quantity for Ag: Mn indicates that a few more nuclei are located in regions of smaller internal fields than are located in larger fields. The Knight shift, being proportional to the product of the *local* susceptibility and the square of the wave function at the nucleus, can thus vary considerably as a function of position in the lattice. It is therefore risky to draw conclusions concerning hyperfine fields and charge or spin distributions on the basis of NMR measurements alone. Bulk susceptibility measurements do not resolve this problem although they do provide a poorly defined "average value" for the hyperfine field. In addition, the interpretation is problematic because of the likelihood of near-neighbor nuclei going undetected in the steady-state experiment. Pulse experiments which should help resolve this problem are currently in progress. No large shifts are observed (with the interesting exception of Ag: Pd) because the function $F(x)$, defined in Eq. (2), oscillates rapidly in the region of large r which is probed by cw experiments.

The $\Delta K/K$ values reported are not much larger than the experimental precision. For that reason it is not possible to establish the concentration dependence of the shift. $\Delta K/K$ for Ag–0.05% Mn is -0.01; for Cu–0.05% Mn, $\Delta K/K = +0.03$.[10] The shifts reported may not be "small" if normalized to unit impurity concentration c. For example, compare $\Delta K/cK$ for Ag: Mn and a non-transition-metal alloy, say, Ag:As.[11] The values are -0.1 and -0.01, respectively.

VII. SUMMARY

We have presented the results of an NMR study of the effects of the transition metals, Pd, Pt, Ni, and Mn dissolved in silver. The fact that the nuclear spin of the Ag^{109} isotope has the value one-half lends an important advantage over previous work in the Cu system where quadrupole effects complicated the interpretation. The silver absorption line is broadened rapidly by the addition of Mn, with a field, temperature, and concentration dependence given by $\Delta H_{\text{imp}}/H = [0.8 + 120/(T + 55)]c \times 10^{-3}$. Such a temperature and field dependence is consistent with the presence of a magnetic moment on the Mn, with, however, some interaction between different moments. Only in Ag: Mn is the linewidth appreciably temperature dependent. The width is believed to be due to direct magnetic dipole coupling between Ag nuclei and Mn ions and RKKY spin-density oscillations, however, quantitative agreement with theory is lacking. If, in the calculation of dipolar and RKKY broadening, it is assumed that impurity spins are not free, but are rather represented by a Brillouin function of $1/(T + 55\ °\text{K})$, then calculated linewidths are in rough agreement with those observed, if it is assumed that about 4 shells of silver nuclei are shifted too much to be observed in the cw spectrum. A sharp narrowing of the linewidth after annealing is believed to be due mostly to loss of solute by internal oxidation, but may be partly due to spin ordering caused by modified grain size. The line shape becomes more Lorentzian as Mn is added to Ag. For Ag: Ni and Ag: Pt the line broadening is only about one-third of that observed in Ag: Mn. The change in Knight shift upon alloying for the above three alloys is small, $\Delta K/K \lesssim -1\%$. Measurements out to 20% Pd in Ag show a decrease in Knight shift which is nonlinear in concentration with $\Delta K/K = -3\%$ at 10% Pd and -10.5% at 20% Pd, in agreement with pulse measurements of Narath. Difficulties in interpreting the Knight shift measured with cw techniques in inhomogeneous systems are stressed. The line broadening at 4.2 °K in Ag: Pd is proportional to c for $c < 10\%$ Pd and varies as $\sqrt{c}$ for higher concentrations. The broadening is discussed qualitatively in terms of simple band theory and virtual bound states. Line broadening produced by equiatomic percentage of d-shell impurities is compared. Finally, a comparison with other similar systems, particularly Cu: Mn, is made.

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