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Solute Knight Shift and Nuclear Spin-Lattice Relaxation in Ag- and Au-Base Solid Solutions*

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The solute Knight shifts and nuclear spin-lattice-relaxation times of dilute solutions of Cu, Ga, In, Al, and Sb in silver and of Cu, Ga, In, and Al in gold have been investigated at 4.2°K. No marked concentration dependence was observed. Knight factors (electron density ratio between the solute atom in the alloy and the solute free atom) determined from both types of measurements show good agreement in magnitude and valence dependence. The exchange enhancement of the Korringa product is found to be larger for the silver than for the gold alloys.

I. INTRODUCTION

THE electronic structure of metals and alloys can be examined through a study of various physical properties of dilute alloys. Nuclear-magnetic-resonance (NMR) methods can be used to probe the electronic structure in the immediate vicinity of both the solvent and solute atoms. Knight shifts of the solvent nuclei have been measured extensively in various noble-metal alloys[1–4] and the results interpreted according to theories based on impurity charge screening[5,6] and rigid-band models.[7]

Knight shifts of the solute atoms have also been studied in noble-metal alloys[8–10] and the results analyzed according to the existing theory.[11] The theory for the solute shift in dilute alloys at infinite dilution is based on the assumption that the same electrons provide the shift for both the solvent and solute nuclei. Daniel[12] introduced a polarization factor into the theory, to account for charge accumulation near the impurity site; however, this modification has not led to better agreement with experiment.[8] What is needed is a knowledge of the wave functions at the impurity nuclear sites in order to calculate the electron densities. Lacking this information an attempt was made in this work to correlate Knight-shift measurements with nuclear spin-lattice-relaxation times in a series of alloys. The study was made on dilute alloys of nontransition metals of different valencies in noble metals. The noble-metal–base alloys were chosen, first because an extensive amount of NMR information exists on these alloys[1–4,8–10] and second because they are more amenable to theoretical calculations.[5–7,10–13] The solute Knight shift K and the longitudinal nuclear spin-lattice-relaxation time T_1 of Cu, Ga, In, Al, and Sb in silver and of Cu, Ga, In, and Al in gold have been investigated. Some of the Knight shifts have been reported by other workers[8,10] and the agreement between the various investigators is usually within ±0.02%.

Section II reports the experimental method and techniques used, whereas Secs. III and IV describe and discuss the experimental results with respect to the Knight ξ factor, exchange enhancement, and linewidth.

II. EXPERIMENTAL METHOD

A. Knight-Shift Measurements

The Knight-shift measurements of the gold alloys were made at room temperature with a wide-line NMR spectrometer (Varian) and a field-regulated 22-in. magnet (Magnion). In order to obtain adequate signal-to-noise ratios, a signal averager was used (Northern Scientific, Model NS-544). The spectrometer frequency was crystal controlled, while the field was repeatedly swept through resonance. To calibrate the field sweep, a suitable reference substance was used whose resonance frequency was recorded at several fields during the sweep. This allowed a determination of the resonance frequency of the reference nuclei ν_R at the resonance field of the metal. The Knight shift

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for solute B in solvent A, ${}^{A}K_B$, was calculated using the relation

$$ {}^{A}K_B = \left(\frac{\gamma}{\nu}\right)_{\mathrm{R}} \left(\frac{\nu}{\gamma}\right)_{B} - 1 , \tag{1}$$

where ν_B is the resonance frequency for the solute and γ the nuclear gyromagnetic ratio (obtained from the Varian NMR table). For Cu and Ga, the reference was an aqueous solution of $AlCl_3$ and for In it was D_2O containing a small amount of $FeCl_3$.

The Knight-shift measurements of the silver alloys and Al in gold were made at 4.2°K with a phase-coherent crossed-coil pulsed NMR spectrometer. Aluminum metal was used as a reference, except for copper solutes, where the shifts were measured relative to metallic copper. The resonance fields of the solute H_B and the reference metal H_{RM} were determined at constant frequency and the Knight shifts calculated from the formula

$$ {}^{A}K_B = \left(\frac{H_{\mathrm{RM}}}{H_B}\right) \left(\frac{\gamma_{\mathrm{R}}}{\gamma_B}\right) (1 + K_{\mathrm{RM}}) - 1 , \tag{2}$$

where the known metal shifts K_{RM} for aluminum and copper were 0.161 and 0.233, respectively.[14]

B. T_1 Measurements

The T_1 measurements were made at 4.2°K. A frequency of 12 MHz was employed and the rotating magnetic field amplitude H_1 was usually 40 Oe or more. The T_1 values were derived from relaxation curves determined by two different methods. In the first method, the amplitude of the Bloch decay following the second pulse of a 180°–90° sequence was determined as a function of the pulse time separation. The second method utilizes a three-pulse sequence, where the separation between the second and third pulse was held constant. The echo amplitude generated by the second and third pulse was measured as a function of the time separation between the first and second pulse. This method is essential when the Bloch decay occurs appreciably within the dead time of the receiver (dead time is approximately 5–10 μsec).

On some alloys both methods were used with similar results. In practically all the measurements, signal averaging was accomplished either by means of a single-channel boxcar integrator or a multichannel high-speed digital averager (Fabritek, Models 952 and 1052). For all of the samples, the echo half-width was in the range of 7 to 20 μsec.

C. Samples

The solvent metals used for the alloys were of high purity (99.999%) obtained from the United Mineral and Chemical Corporation. The purity of the solute metals was at least 99.99%. The alloys were prepared by levitation melting in an argon-helium (99.999%) atmosphere, except for a few of the more concentrated samples, where alloying by induction heating was used, followed by casting into graphite crucibles. For the more dilute samples, master alloys were used. In the levitation technique, the melts were cooled in the levitated state with a flow of cold helium. The alloys were subsequently annealed for at least a day at 100°K below the melting point and quenched in a mixture of ice and brine.

TABLE I. Knight shifts ${}^{A}K_B$ (%) of various solutes in Ag and Au solid solutions and those of the pure solvent and solutes.

Solute (B)	Solvent (A) Ag	Solvent (A) Au	Isotropic Knight shift in the pure metals
^{63}Cu	0.23	0.17	0.23
^{109}Ag[a]	0.53	0.39	0.53
^{197}Au[a]		1.65	1.65
^{27}Al	0.15	0.16	0.16
^{71}Ga	0.39	0.67	0.115[b]
^{115}In	0.87	0.86	0.80[c]
^{121}Sb	0.20		

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The samples consisted of 325-mesh filings. For the gold alloys, it was necessary to embed the particles in vaseline, to provide sufficient electrical insulation.

III. EXPERIMENTAL RESULTS

The Knight-shift measurements were made at solute concentrations of 0.1, 1, and 5 at.%. No resolved concentration dependence was observed for the shifts of the various solutes in silver and gold. The values indicated in Table I are therefore, believed to be representative of those at infinite dilution.

Rowland *et al.*[8] studied solute linewidths in several copper and silver alloys. Results for the linewidth measurements of Cu, Ga, and In in gold are reported in Table II. For these solutes, the width is found to increase with solute concentration. In all cases the linewidths are much greater than the pure dipolar linewidths and reflect an interplay of several mechanisms such as quadrupole interaction, inhomogeneous Knight shift, and indirect exchange. In no case could a fit be made to Eq. (3) of Ref. 8, which treats the inhomogeneous Knight shift as the major source of broadening. Thus, as might be expected for nuclei with spin greater than $\frac{1}{2}$, quadrupole broadening is an important source of linewidth in these alloys.

Nuclear spin-lattice-relaxation data are presented in Table III. The Bloch decays for the solutes Cu, Al, and Sb in silver and gold were exponential; however, Ga and In deviated in this respect, presumably because of incomplete saturation of the spin system. The decay for the latter nuclei could generally be decomposed into

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TABLE II. Concentration dependence of linewidth ΔH, in dilute Au alloys. ΔH is measured from the peak-to-peak linewidth of the derivative and the values are corrected for modulation. H_0 is the external field.

Solute (B)	Concentration (at.%)	H_0(kOe)	ΔH(Oe)
^{63}Cu	13	13.540	6.2±0.5
	13	11.510	5.6±1
	7	13.540	4.7±0.5
	7	11.510	4.1±1
	7	8.850	3.0±1
	3	13.540	2.6±0.5
	3	11.510	2.0±0.5
	1	13.540	1.9±0.3
	1	11.510	1.8±0.5
	0.3	13.540	1.6±0.3
	0.3	11.510	1.8±0.5
^{71}Ga	5	11.700	10.7±1
	5	7.650	8.7±1
	1	11.700	7.1±1
	1	7.660	6.6±1
^{115}In	5	16.260	20.5±4
	5	10.640	20.5±6
	1	16.260	13.1±3
	1	10.640	12.5±4

two exponential components. The relaxation data for Ga and In were derived from the longer one.

The relaxation times do not show any marked concentration dependence, except for Ga. It can not be excluded, however, that this deviation stems from metallurgical difficulties.

IV. THEORY AND DISCUSSION

The Knight shift of a nontransition solute element (B) in a noble metal as the solvent (A) is described by[11]

$$ {}^{A}K_B = \frac{1}{\beta} H_{\text{eff}}{}^{(B)} \chi_p{}^{(A)} \xi(K) \,, \tag{3} $$

where β is the Bohr magneton and $H_{\text{eff}}{}^{(B)}$ is the hyperfine field characteristic of the valence electrons of solute B in the free atom. The Pauli spin susceptibility per atom of solvent metal A is indicated in Eq. (3) by $\chi_p{}^{(A)}$, and $\xi(K)$ represents the ratio of the electron density at nucleus B in matrix A, averaged over the Fermi surface, to that of an atomic valence electron of B. The Knight factor $\xi(K)$ as defined in the present work indicates that ξ is determined from Knight shift data. This definition of ξ is identical to that of Bennett *et al.*[10]

TABLE III. Values of T_1T in (sec°K) for various solutes in Ag and Au and of the pure metals.

Solute (B)	Solvent (A) Ag	Au	Pure metals
^{63}Cu	2.15	2.0	1.27
^{109}Ag[a]	9.6	17.0	9.6
^{197}Au[a]		4.6	4.6
^{27}Al	3.07	2.54	1.85[b]
^{71}Ga	0.42	0.08	0.63[c]
^{115}In	0.15	0.076	0.086[d]
^{121}Sb	4.13		

[a] References 4 and 17.

[b] J. J. Spokas and C. P. Slichter, Phys. Rev. **113**, 1462 (1959).

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The measured nuclear spin-lattice-relaxation rate of solute B in A will be related to $\xi(T_1)$ by means of[15]

$$ {}^{A}(\gamma^2 T_1 T)_B{}^{-1} = \frac{\pi\hbar k}{\beta^4} [H_{\text{eff}}{}^{(B)} \chi_p{}^{(A)} \xi(T_1)]^2 \,, \tag{4} $$

where T is the absolute temperature and k is the Boltzmann constant. The Knight factor $\xi(T_1)$ indicates that ξ is determined from relaxation measurements. Equation (4) is based on the assumption that for the alloys used here, only the contact interaction is important in the relaxation process. Several sets of values for the solute atom s-valence electron hyperfine fields $H_{\text{eff}}{}^{(B)}$ and the spin susceptibilities $\chi_p{}^{(A)}$ for the noble metals have been recently discussed by Bennett *et al.*[10] The H_{eff} and the Pauli susceptibility χ_p calculated semi-empirically from

$$ \chi_p = \chi_{\text{expt}} - \chi_{\text{diam}}(\text{core}) - \chi_{\text{diam}}(\text{conduction}) \tag{5} $$

were used in this analysis and are described by these authors in Tables II and VI (C), of Ref. 10, respectively.

A. Knight Factor

A comparison between the Knight factors as determined from the Knight shifts and relaxation times for the various solutes in silver and gold by means of Eqs. (3) and (4), respectively, is made in Table IV. The agreement between the two distinct types of measurements is gratifying, considering the approximations made in deriving Eqs. (3) and (4). The valence dependence of the Knight factor of the solutes in gold is reversed from that for silver for $\xi(T_1)$ as well as $\xi(K)$, in agreement with Bennett *et al.*[10]

The smallest value for the Knight factor in the current work and by Bennett *et al.*[10] is obtained for Sb in silver and P in copper, respectively, indicating that these small values are perhaps characteristic of group-V solutes in copper and silver. It can not be excluded however, that H_{eff} calculated for Sb is inaccurate.

There is considerable speculation on the exact interpretation of the behavior of the Knight factor.[10] In fact, even for pure copper, which has been investigated extensively both experimentally and theoretically. ξ is known only to within ±20%. Davis[13] recently calculated a value of 0.43 for the Knight factor in copper, well within the range of the different experimental determinations which vary from 0.36 to 0.52.

Since the Knight factor can be considered as the ratio of the average s-contact hyperfine field in the alloy to that in the free solute atom, it may be justified to

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state that a change in ξ is a manifestation of a change in the radial dependence of the s part of the conduction-electron wave function, an admixture of non-s components into the wave functions at the Fermi surface, or both. A correct description of the Knight factor must take into account the anisotropy of the Fermi surface, so that the susceptibility, hyperfine fields, and ξ factor are appropriate to specific segments of the Fermi surface.

B. Korringa Relation and Exchange Enhancement

When collective electron effects are neglected, the Korringa relation is given by[15]

$$K^2T_1T=S, \tag{6}$$

where

$$S=2(\beta/\gamma)^2(hk)^{-1}. \tag{7}$$

In Eq. (6), the Knight shift K is related to the uniform conduction-electron spin susceptibility χ, which is expressible in terms of the bare density of electronic states at the Fermi level, $N(0)$, (i.e., devoid of electron-phonon interactions, etc.) through the relation

$$\chi=2\beta^2N(0). \tag{8}$$

Since electron-electron interactions are neglected in Eq. (8), the susceptibility is underestimated and the experimental Korringa product is usually larger than that predicted theoretically from Eq. (6). Narath[4] has demonstrated that, for the noble metals and for silver-gold alloys, the ratio K^2T_1T/S exceeds unity by a considerable amount.

Moriya[16] included exchange in the theory, leading to an enhancement of χ whereby the Korringa product is modified to

$$K^2T_1T=S[K(\alpha)]^{-1}, \tag{9}$$

where $K(\alpha)$ is a function of the enhancement factor α, which measures the enhancement of the $\mathbf{q}=0$ component of the generalized susceptibility over that of the independent particle model. Recently, Narath *et al.*[17] corrected a numerical error in the results of Moriya, leading to enhancement factors for the spin-lattice-relaxation rate which are too large relative to experiment. Nevertheless, lacking a better theory, Eq. (9) is used in the current analysis.

Table IV. Values of the ξ factor evaluated from Eqs. (3) and (4). The H_{eff} and χ_p are from Ref. 10, Table II and row C of Table VI, respectively.

Solute (B)	H_{eff} (MOe)	χ_p(10^{-6} emu/mole)	Ag		Au	
			$\xi(K)$	$\xi(T_1)$	$\xi(K)$	$\xi(T_1)$
Cu	2.6	11.2	0.38	0.22	0.28	0.23
Ag	5.0	12.9	0.45	0.31	0.35	0.25
Au	20.6	12.2			0.36	0.31
Al	1.9		0.37	0.26	0.41	0.30
Ga	6.2		0.30	0.18	0.51	0.44
In	10.1		0.31	0.26	0.39	0.39
Sb	18.6[a]		0.047	0.025		

[a] Calculated from R. G. Shulman *et al.*, Phys. Rev. **100**, 692 (1955).

Table V. Value of K^2T_1T(expt), $[K(\alpha)]^{-1}$, and α for the pure metals and dilute alloys of Ag and Au.

Pure metals	K^2T_1T(expt) (10^{-6} sec°K)	$[K(\alpha)]^{-1}$	α
Cu	6.85	1.83	0.68
Ag	270.00	2.22	0.76
Au	1255.00	1.40	0.50
Al	4.74	1.2	0.33
Ga	0.84	0.3	···
In	5.78	5.5	0.13
Solutes in Ag			
Al	6.91	2.04	0.73
Cu	11.57	3.10	0.85
Ga	6.49	2.29	0.77
In	11.30	2.07	0.73
Sb	17.18	3.73	0.88
Solutes in Au			
Al	6.59	1.68	0.63
Cu	6.00	1.60	0.60
Ga	3.63	1.28	0.40
Ag	2.68	2.17	0.75
In	5.97	1.10	0.18

In the theory of exchange enhancement, two simplifying approximations are made:

(1) Effects of exchange and correlation can be represented by an effective potential, whose magnitude depends on the momentum transfer $\hbar\mathbf{q}$ between interacting electrons.

(2) The metals possess nearly spherical Fermi surfaces and they lie within the first Brillouin zone.

Narath *et al.*[17] showed that $K(\alpha)$ is not strongly dependent on α, except for values of α approaching unity. Table V summarizes the experimental Korringa products $[K(\alpha)]^{-1}$ and the corresponding α obtained from Narath's tables[17] for the pure metals and for the solutes in silver and gold. It is evident that except for In and Ga in gold, $K(\alpha)^{-1}$ exceeds unity by a substantial amount.

In general, there is a larger enhancement for the solutes in silver than in gold or in the solute metals. This is consistent with the results of Narath *et al.*,[17] indicating $\alpha(\text{Ag})>\alpha(\text{Cu})>\alpha(\text{Au})$. These authors attribute the excessively large values of α to a breakdown of the δ-function contact interaction used in the electron exchange.

Until a more realistic theory is formulated, taking into account the non-s character of the electrons and allowing for other relaxation mechanisms in the Korringa product, these values for α must serve only as guidelines.

V. CONCLUSION

No marked concentration dependence is observed in the Knight-shift and T_1 measurements. The Knight

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factors for the solutes, determined from Knight shifts and relaxation times, are in good agreement. The solute valence dependence of ξ for the gold alloys exhibits an opposite behavior from that in silver. Linewidth analyses indicate that quadrupole interactions play a major role. The exchange enhancement factor for the solutes in the silver alloys exceeds that for the gold alloys. In order to comprehend the results for the Knight factors and exchange enhancement, however, a more sophisticated theory of dilute alloys is needed.

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Electron Relaxation of Fe Ion in Antiferromagnetic Cobaltous Carbonate*

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A Mössbauer study of $CoCO_3$ doped with Fe^{57} was made above and below the Néel temperature. The magnetic hyperfine field at Fe^{57} nuclei below T_N is observed to be perpendicular to the principal axis of the maximum electric field gradient. Asymmetric line broadening at low temperatures was observed and interpreted in terms of *spatial* distribution of the average magnetic hyperfine field over the nuclear observation time. $H=72\pm2$ kG and $\frac{1}{2}e^2qQ(1+\frac{1}{3}\eta'^2)^{\frac{1}{2}}=1.95\pm0.04$ mm/sec at 4.9°K were observed.

RECENTLY, the problem of electronic relaxation in paramagnetic or ferromagnetic materials has been attracting considerable attention in the Mössbauer field.[1–10] However, very little experimental observation of relaxation phenomena has been published for Fe^{2+} ion in antiferromagnetic materials. The purpose of this paper is to present the experimental observation of Fe^{2+} ion relaxation in $CoCO_3$, and to explain the observed phenomena in terms of *spatial* distribution of the average magnetic hyperfine field over the nuclear precession period instead of *linearly* fluctuating magnetic field between $+H$ and $-H$, which was theoretically developed by some authors.[4,5,9]

The symmetry of $CoCO_3$ is rhombohedral,[11] with a bimolecular unit cell which has the dimensions $a_0 = 5.665$ Å, $\alpha = 48°33'$ at 26°C. $CoCO_3$ becomes antiferromagnetic with weak ferromagnetism[12,13] below 18.1°K. On the basis of the existence of weak ferromagnetism (1440 cgs emu/mole at $T=0$[13]) Dzialoshinskii[14] has concluded that in the first appriximation Co^{2+} spin must lie in the (111) plane which is perpendicular to the trigonal axis.

The Fe^{57}-doped $CoCO_3$ sample was obtained by heating a mixture of a solution of $CoSO_4$ doped with $Fe^{57}SO_4$ (about 1% of $CoSO_4$) and a solution of $NaHCO_3$ at 210°C for 3 h in a closed autoclave. Considerable effort was exercised to prevent oxidation by doing the preparation in a glove bag filled with N_2 or CO_2 gas. A part of the sample was checked by x-ray diffraction technique to make sure that the sample is $CoCO_3$. The x-ray diffraction peaks taken by using Cr $K\alpha$ radiation were sharp enough to rule out any possibliity of ultrafine particels, which may show the so-called superparamagnetic relaxation. A Mössbauer spectrometer with an electromechanical drive system manufactured by Elron Co. and stabilized up to ±0.001 mm/sec[15] was used with a 15-mCi Co^{57} source in Pd which was kept at room temperature. Temperature measurement and control above 30°K were carried out by a platinum resistance and a heater within an accuracy of 0.5°K. A carbon resistance thermometer calibrated at liquid-nitrogen, liquid-hydrogen, and liquid-helium temperatures was used for temperature measurement and control below 30°K with an accuracy of 0.1°K. The Mössbauer spectra of Fe^{57} in $CoCO_3$ at various temperatures are shown in Figs. 1 and 2. Above the transition temperature of 17.6°K the Mössbauer spectra consist of two lines split by quadrupole interaction of Fe^{57} nuclei with the axially symmetric electric field gradient by surrounding electric charges. The measured Néel temperature T_N of (17.6±0.1)°K

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