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MAGNETIC IMPURITY STATES IN LIQUID COPPER*

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(Received 30 June 1966)

We have measured the change in Knight shift of the solvent nuclear resonance produced by impurities of the first transition series dissolved in liquid copper. The apparatus and techniques used were similar to those described by Odle and Flynn.¹ While all the solutes cause a linear decrease in the Knight shift K with concentration c (see Table I), the effect due to Cr, Mn, Fe, and Co is strikingly large and exhibits an inverse temperature dependence which we attribute to the existence of localized magnetic moments on these four solutes in liquid copper. The resonance shift due to polarization of the electron gas by magnetic impurities has been discussed theoretically² and shown to have the same inverse temperature dependence as the fractional alignment of the impurity spins along the magnetic field. In what follows we show that the magnitude of the resonance shift leads to an estimate of 1 eV for the bandwidth of the virtual d states associated with these magnetic impurities.³

In liquid metals atomic diffusion is sufficiently rapid that the nuclear resonance is affected only by the spatial average of the electron redistribution caused by impurities. Thus, in the case of all alloys except those containing Mn, the Cu resonance linewidth was not significantly altered, and shifts caused by impurities could be measured accurately. In contrast, the resonance in solids is broadened and the shifts masked.⁴ Although the liquid copper linewidth was doubled by only 2% Mn, the broadening was much smaller than the resonance

shift and did not impair the accuracy of measurement. The broadening is probably due to an enhanced relaxation of Cu nuclei diffusing into sites near the large Mn magnetic moment.

The temperature dependence of the resonance shift is shown in Fig. 1 for a number of alloys containing magnetic impurities. In every case ΔK follows a Curie-Weiss law with a Curie temperature between 0 and 300°K, but the limited temperature range of 950°C (supercooled) to 1200°C precluded the possibility of determining these Curie temperatures accurately. In the case of V, which may well be magnetic, the solubility is so low that no shifts could be measured.

The electron density disturbance near an impurity which produces phase shifts $\eta_{li}(k)$ in the partial waves of electrons with wave vector k and spin i may be written² in the single orthogonalized-plan-wave approximation

$$\delta\rho_i(r) = \sum_k \rho_i(k, r) \sum_{l=0}^{\infty} (2l+1) \{ [n_l^2(kr) - j_l^2(kr)] \times \sin^2 \eta_{li}(k) - n_l(kr) j_l(kr) \sin 2\eta_{li}(k) \}, \quad (1)$$

where $\rho_i(k, r)$ is the undisturbed density of electrons with wave vector k and spin i , and is assumed in the following to be independent of k in the relevant range of $k \simeq k_F$.

We assume that for these magnetic impurities, only the d -wave phase shifts are important and $\eta_{li} = 0$ for $l \neq 2$. In the following we write $\eta \uparrow$ and $\eta \downarrow$ for the d -wave phase shifts

Table I. The fractional change in the Cu Knight shift per unit solute concentration at $T = 1100^\circ\text{C}$. Γ is independent of temperature for the solutes Sc, Ti, and Ni, but varies inversely with temperature for Cr, Mn, Fe, and Co.

Solute	Γ	Solute	Γ
Sc	-0.48 ± 0.10	Fe	-14.3 ± 0.3
Ti	-0.8 ± 0.3	Co	-7.6 ± 0.3
Cr	-13.2 ± 0.6	Ni	-1.2 ± 0.2
Mn	-19.2 ± 0.4		

of spin-up and spin-down electrons, respectively, and $\delta\rho_\uparrow$ and $\delta\rho_\downarrow$ for the corresponding density disturbances. The spin polarization in the lattice surrounding a magnetic impurity is

$$\delta\rho = \delta\rho_\uparrow - \delta\rho_\downarrow,$$

and the average hyperfine interaction at the nuclei is then proportional to $\langle\delta\rho\rangle$, in which the average is taken over all nuclear sites and over the spin states and orientations of the magnetic ions. The latter is proportional to the frac-

tional magnetization of the impurities and yields a factor $[(n+2)\mu_B/3\kappa(T-\theta)]$, with μ_B the Bohr magneton, κ the Boltzmann constant, θ the Curie temperature, and n the average excess number of electrons in the lower-lying subband. The final result is

$$\Gamma = \frac{1}{K} \frac{\partial K}{\partial c} = \frac{(n+2)}{3} \frac{E_F}{\kappa(T-\theta)} \frac{1}{k_F^3} \int_0^{k_F} k^2 dk \{A(k) \times [\sin^2\eta_\uparrow(k) - \sin^2\eta_\downarrow(k)] + B(k) [\sin 2\eta_\uparrow(k) - \sin 2\eta_\downarrow(k)]\}, \quad (2)$$

with

$$A(k) = 5 \int_0^\infty [n_2^2(kr) - j_2^2(kr)] D(r) dr,$$

and

$$B(k) = -5 \int_0^\infty n_2(kr) j_2(kr) D(r) dr,$$

where $D(r)$ is the radial distribution function, E_F the Fermi energy, and k_F the Fermi wave vector of liquid copper. Equation (2) differs from that of Blandin and Daniel² by a factor

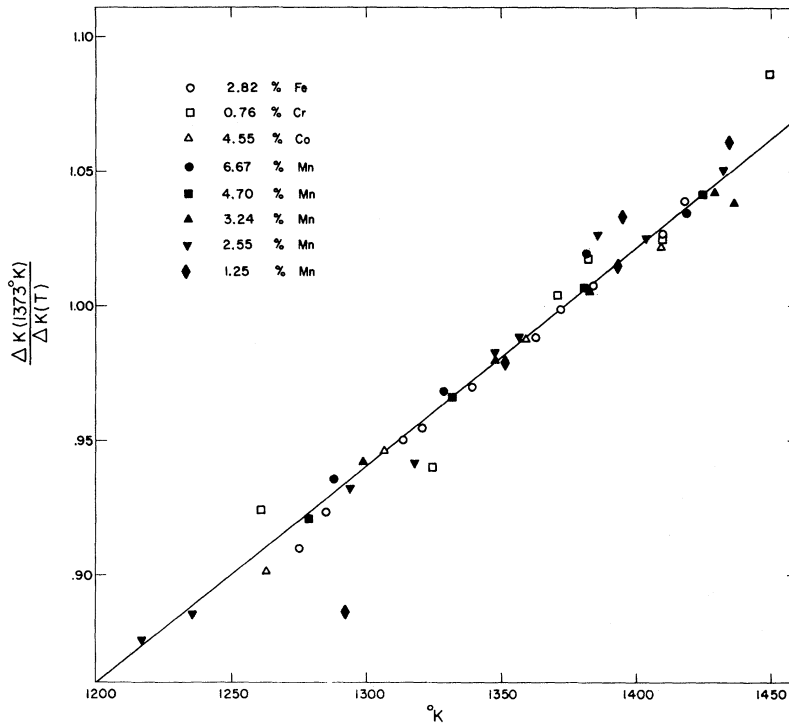


FIG. 1. Reciprocal of the Cu^{63} Knight shift change versus temperature for various magnetic impurities. ΔK for each alloy is scaled to unity at 1373°K (1100°C) for purposes of comparison. The line corresponds to a Curie-Weiss temperature dependence with $\theta = 150^\circ\text{K}$.

of 2 and by the inclusion of the Curie temperature θ .

We have also measured the magnetic susceptibility of the liquid Cu-Mn alloys and found that Mn has an excess, n , of 4.4 electrons in one spin direction, in good agreement with the work of Vogt⁵ and Gustafsson⁶ on solid Cu-Mn alloys and Nakagawa⁷ on concentrated liquid alloys. This is close to the maximum possible localized d spin of $\frac{5}{2}$ which occurs when one spin band is full and the other empty. For the case of a single filled band which is narrow and symmetric about k_0 , the second integral in Eq. (2) vanishes and

$$\Gamma \simeq \frac{(n+2)}{3} \frac{E_F}{\kappa(T-\theta)} \frac{k_0^2}{k_F^3} A(k_0) \int_0^{k_F} \sin^2 \eta \uparrow(k) dk. \quad (3)$$

Given the shape and center of the impurity band, the width can be calculated from Eq. (3) together with the observed Γ and a modified Friedel sum rule³ which relates the phase shifts $\eta_i(E)$ to the number $n_i(E)$ of d electrons with spin i bound at energies $E' < E$,

$$\eta_i(E) = \frac{1}{\pi} \pi n_i(E).$$

We have assumed that the Mn impurity can be represented by a narrow, filled band at the Fermi surface and have evaluated the width parameters α , β , and γ for the following band shapes:

$$\begin{aligned} \text{(a) Lorentzian} \quad & \frac{dn_i(E)}{dE} = \frac{5}{\pi} \frac{\alpha}{\alpha^2 + (E-E_0)^2}, \\ \text{(b) Gaussian} \quad & \frac{dn_i(E)}{dE} = \frac{5}{\beta\sqrt{\pi}} \exp \left[-\frac{(E-E_0)^2}{\beta^2} \right], \\ \text{(c) Square} \quad & \frac{dn_i(E)}{dE} = \frac{5}{2\gamma} \quad |E-E_0| \leq \gamma, \\ & = 0 \quad |E-E_0| > \gamma. \end{aligned}$$

The values for the width at half maximum are

$2\alpha = 0.6$ eV, $2(\log 2)^{1/2}\beta = 1.4$ eV, and $2\gamma = 2$ eV from which we conclude that the width of the virtual d states associated with a Mn impurity in Cu is ~ 1 eV.

Within the approximations leading to Eq. (2), this estimate contains uncertainties due to imperfect knowledge of $D(r)$ (since the radial distribution function of Cu has not been published, it was approximated by that of Ag⁸ as described by Odle and Flynn¹) and the approximation that the impurity band is narrow and located at the Fermi level. Particularly for the case of the Lorentzian line which has extended wings, the calculated linewidth is not compatible with the assumed proximity of the Fermi level and with the k dependence of $A(k)$. However, within the validity of Eq. (2) it is unlikely that the estimates are in error by more than 50%. An approach to the calculation of electron redistribution similar to that adopted in deriving Eq. (2) has proved reasonably successful in predicting the changes of Knight shift due to nontransition impurities in liquid copper.¹

We wish to thank Professor D. Lazarus for his encouragement and for partial support of this research, and Dr. D. Rigney for his cooperation in the experimental work.

*Work supported in part by the Advanced Research Projects Agency under Contract No. SD-131, and also by the U. S. Atomic Energy Commission under Contract No. AT(11-1)-1198, Report No. COO-1198-373.

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