dently of considerable influence in the case of orientated molecules.

From measurements with (2, 3, 5, 6)-tetrachlorotoluene the ratio of the proton distances can be derived without any assumptions:

$$r(H_{ar}-H_{meth})/r(H-H)_{meth} = 3.225 \pm 0.025.$$

These examples show that by measurements in nematic solutions, precise information about the solute molecules may be obtained, some of which perhaps cannot be gained by other methods. Finally, we would like to mention that stable free radicals can also be dissolved in crystalline liquids in concentrations sufficient for electron spin resonance experiments.

We are indebted to Professor R. Mecke for the support of this investigation. We also wish to thank Professor W. Maier for helpful discussions.

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# MAGNETIC ORDERING IN DILUTE SOLID SOLUTIONS OF IRON IN GOLD

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Magnetic ordering in dilute alloys of Fe in Au has been discovered at low temperatures by means of the Mössbauer effect. Preliminary magnetization measurements[1] indicate typically ferromagnetic behavior. The extreme dilution of the paramagnetic solute precludes the possibility of direct exchange coupling between nearest-neighbor $d$-shell spins, and hence the magnetic ordering must result from some mechanism of indirect exchange.

Four absorber foils containing 0.84, 1.85, 7.38, and 11.5 at. % Fe were prepared by vacuum evaporation of enriched (91.2% $Fe^{57}$) Fe onto thin Au foils. Homogenization was then accomplished by holding the foils at 800°C for one hour. To insure against the possible precipitation of Fe, they were quenched by flooding the furnace with Ar and were subsequently stored in liquid nitrogen. A source foil containing 10.2 at. % Fe was also prepared by arc melting the constituent metals in a bottom furnace. The resulting ingot was cold rolled and remelted several times to insure homogeneity. A foil was then prepared and homogenized for several days at 900°C terminating with a water quench. This was then electroplated with 10 mCi of $Co^{57}$, vacuum annealed for one hour, and used as a source. Specimens were chemically analyzed to obtain the final compositions listed in Table I.

According to Hansen,[2] Au will dissolve up to about 11 at. % Fe at 300°C, and although it seems safe to assume that a solid solution obtained at all compositions, purposeful attempts were made to induce precipitation of the Fe in order to test this assumption. First, the absorber foil containing 7.38 at. % Fe was annealed at 200°C for two weeks. It was then manually cold worked and annealed for two days at 100°C followed by a one-day anneal at 200°C. After neither treatment did the Mössbauer spectrum of pure Fe appear nor had the spectrum changed significantly in any way. In this connection a foil containing 32 at. % Fe has also been investigated. As expected, nearly pure (~1% Au)[2] Fe precipitates and one observes two resolvable hyperfine spectra, one corresponding to that of pure Fe and the other presumably resulting from the solid solution. The hyperfine splitting of the latter disappears at approximately 370°K and at higher temperatures only the hyperfine spectrum of the Fe is observable. Thus we are confident that the five samples studied in this work (Table I) are true solid solutions.

The Au-Fe absorbers were used in conjunction with a stainless steel source; the single Au-Fe source was used with a 1-mil stainless steel absorber. Mössbauer resonant spectra were measured with a constant-velocity drive apparatus used as a transmission spectrometer.[3] Spectra were obtained at room temperature, 80, 27.3, 20.4, 17, 14, 4.2, and 2.2°K using liquified $N_2$, Ne, $H_2$, and He. The striking

Table I. Summary of measurements and results.

| Sample | | 1a | S-1 | 1 | 3 | 2 |
|---|---|---|---|---|---|---|
| Iron concentration (at. %) | | 11.5 | 10.2 | 7.38 | 1.85 | 0.84 |
| Ground-state splitting (mm/sec)[a] | 2.2°K | 3.23 | ⋯ | 3.10 | 2.90 | 2.75 |
| | 4.2°K | 3.25 | 3.65 | 3.07 | 2.88 | 2.53 |
| | 14.0°K | 3.18 | ⋯ | ⋯ | ⋯ | ⋯ |
| | 17.0°K | 2.93 | ⋯ | ⋯ | ⋯ | ⋯ |
| | 20.4°K | 2.78 | 3.05 | 2.33 | 0 | 0 |
| | 27.3°K | 2.55 | 2.55 | ≈0.74[b] | ⋯ | 0 |
| Excited-state splitting (mm/sec)[a] | 2.2°K | 1.81 | ⋯ | 1.75 | 1.70 | 1.51 |
| | 4.2°K | 1.81 | 2.06 | 1.75 | 1.63 | 1.39 |
| | 14.0°K | 1.74 | ⋯ | ⋯ | ⋯ | ⋯ |
| | 17.0°K | 1.70 | ⋯ | ⋯ | ⋯ | ⋯ |
| | 20.4°K | 1.65 | 1.79 | 1.34 | 0 | 0 |
| | 27.3°K | 1.40 | 1.35 | ≈0.42[b] | ⋯ | 0 |
| Curie temp (°K) | | 35 ± 1 | 31 ± 1 | 28 ± 1 | 12 ± 2 | 7 ± 2 |
| $g_0(0)/g_0(0)_{\mathrm{Fe}}$[c] | | 0.81 | 0.91 | 0.77 | 0.73 | 0.70 |
| $g_1(0)/g_1(0)_{\mathrm{Fe}}$[c] | | 0.80 | 0.90 | 0.76 | 0.75 | 0.68 |

[a] Probable error 0.05 mm/sec.

[b] Definite broadening but lines unresolved. Assuming all broadening due to magnetic hfs, $H_n$ is about 24 % of the 0°K value.

[c] $g_0(0)_{\mathrm{Fe}} = 4.015$, $g_1(0)_{\mathrm{Fe}} = 2.290$ (reference 3).

feature of these spectra is the appearance of the six-line magnetic hyperfine spectrum of $\mathrm{Fe}^{57}$ and the complete disappearance (less than 1 % of the ordered spectra) of the paramagnetic resonance line, demonstrating magnetic ordering at sufficiently low temperatures. No such splitting occurs at room temperature or at liquid $N_2$ for any composition containing less than 11.5 at. % Fe.

A graphical analysis of the spectra yields the values of the splitting of the ground state, $g_0$, and the excited state, $g_1$, which are presented in Table I. The magnitude of the splitting is proportional to the magnetic field at the nucleus, $H_n$, which we assume proportional to the spontaneous magnetization, $M$, as is the case for pure Fe.[4] Thus

$$g_0(T)/g_0(0) = g_1(T)/g_1(0)$$

$$= H_n(T)/H_n(0) = M(T)/M(0). \quad (1)$$

If the temperature dependence of $H_n$ in these samples is known, the transition temperatures can be obtained by extrapolation. The temperature dependence of the hyperfine splitting data for samples 1a, S-1, and 1 (Table I) is best described by the empirical relationship of Preston, Hanna, and Heberle.[4] This curve describes the temperature dependence of $H_n$ as well as the spontaneous magnetization for pure iron. (Brillouin functions could also be used but the fit of the data is slightly less satisfactory.) The results of our analysis are shown in Fig. 1. The calculated transition temperatures are given in Table I. The transition temperature of foil 1 is nearly equal to that of liquid neon, i.e., 27.3°K. In this case we were able to confirm that the transition temperature as calculated by extrapolation from the resolved spectra does indeed correspond to the temperature at which the observed hfs is rapidly approaching zero. The uncertainties assigned to the transition temperatures in Table I are statistical probable errors. Possible systematic differences between our method of determining transition temperatures and other methods are not considered here.

Table I also gives the ratio of the 0°K splitting of each alloy to that of pure Fe for both the ground and excited states. This provides a check on the internal consistency of the measurements as well as a measure of the saturation magnetization relative to pure Fe. The sign of $H_n$ is not determined by our measurements. If we make the reasonable assumption that $H_n$

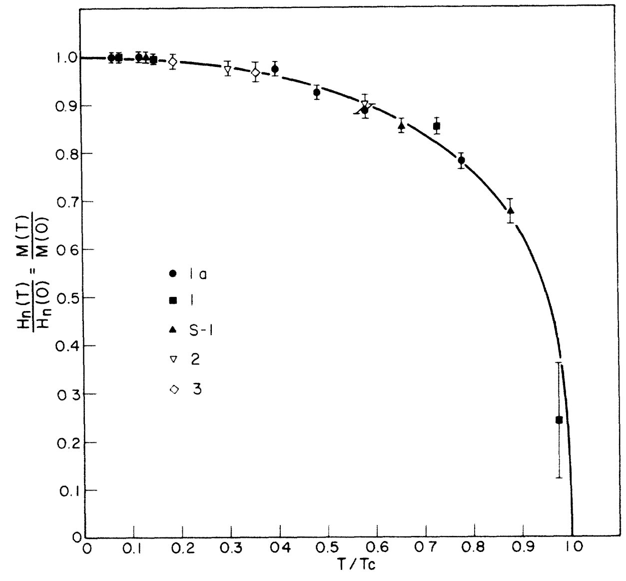

FIG. 1. Temperature dependence of Au compared with the curve of Preston, Hanna, and Heberle. In the case of samples 2 and 3 the number of observations equals the number of unknown parameters ($H_n$, $T_c$); therefore these points are located directly on the curve.

is negative in these alloys, as it is known to be in metallic Fe, it is noteworthy that $H_n$ is an appreciable fraction of its value in pure Fe.

The isomer shift for all samples relative to pure Fe at room temperature is

$$\delta = +0.84 \pm 0.04 \text{ mm/sec}.$$

The positive sign indicates[5] that the electron density at the Fe nucleus in a Au matrix is less than in pure iron.

The dependence of the transition temperature upon the concentration of the paramagnetic solute has been the subject of several theoretical studies.[6-8] For long-range forces (e.g., Curie-Weiss model) this dependence is linear at all compositions, whereas for short-range forces (nearest-neighbor interactions) the Curie temperature is zero until a critical concentration is attained. While differing in detail, the theories based on direct coupling of the solute atoms predict this critical concentration to be $\approx Z^{-1}$ where $Z$ is the number of nearest neighbors. Kaufman, Pan, and Clark[9] interpret their data on Au-Fe solutions as evidence for a critical concentration of about 6.5 at. %. Sato, Arrott, and Kikuchi[6] consider a readjusted value of Kaufman's critical concentration[10] (≈12 at. %) to be in reasonable agreement with a calculated value of 16.7 at. % obtained from their theoretical considerations (average-coordination-number method).

Our experimentally determined transition temperatures are plotted against iron concentration in Fig. 2. The predicted dependence on concentration based on short-range forces is shown schematically with a critical concentration of $1/Z = 8.25$ at. % for the face-centered cubic gold lattice. If a critical concentration exists in these alloys it must be at least an order of mag-

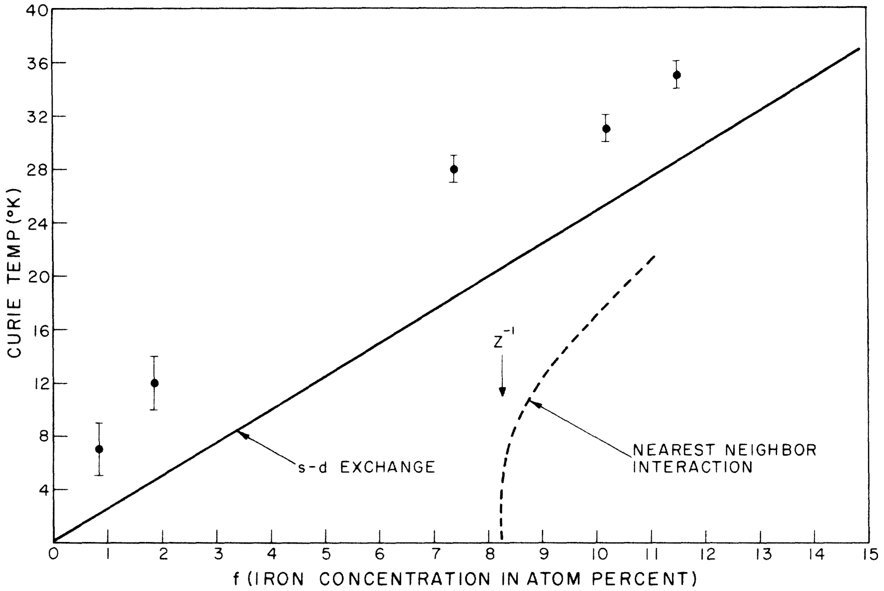

FIG. 2. Transition (Curie) temperature as a function of iron concentration.

nitude less than $Z^{-1}$ as magnetic ordering is observed even when the iron concentration is as low as 0.84 at.% (foil 2).

The transition temperature on the basis of the Curie-Weiss model and $s$-$d$ exchange[11] is given by

$$kT_c = \frac{1}{8}\frac{S(S+1)}{(S+\frac{1}{2})^2}\frac{(h\Delta\nu)^2}{E_{\mathrm{F}}}\frac{f}{100}. \qquad (2)$$

To calculate $h\Delta\nu$ we assume the splitting in the solid solution to be the same as for the free ion $\mathrm{Fe}^+$.[11] Spectroscopic measurements give for the configuration $3d^6 4s$ the separation $^6D_{9/2}-{}^4D_{7/2} = 7955\ \mathrm{cm}^{-1}$. Using this to obtain $h\Delta\nu$, taking the spin of the iron atom in the gold lattice as $S=2$, and the Fermi energy $E_{\mathrm{F}}$ of the gold conduction electrons as $0.88\times10^{-11}$ erg, we obtain

$$T_c = 2.5f\,^\circ\mathrm{K},$$

where $f$ is the at.% iron in gold. The coefficient of $f$ is insensitive to the choice of $S$. The trend of the experimental transition temperatures with concentration (Fig. 2) is consistent with the $s$-$d$ exchange curve but the points appear to be significantly higher. Magnetization measurements[1] on a 5 at.% sample yield a saturation moment about one-fourth that of pure iron. However, the Mössbauer data show that (1) the magnetic order is complete (no paramagnetic component), and (2) the saturation moment on the Fe atom, assuming no contribution from its surroundings, is 70-90% of that in pure iron. These apparently conflicting observations could be resolved if Fe atoms are preponderantly aligned in an antiferromagnetic rather than a ferromagnetic configuration.[12] However, the positive value of the paramagnetic Curie temperature[1] and the relatively high remanence would seem to argue against the presence of significant amounts of an antiferromagnetic phase.

Although the magnetic coupling must result from indirect exchange, it is difficult to reconcile the present findings with the theories thus far proposed to account for such interactions. Yosida[13] concluded that the polarization of the conduction electrons by $s$-$d$ exchange would be severely restricted to the immediate vicinity of the paramagnetic atom and hence could not produce long-range order. Overhauser[14] has developed a theory for long-range antiferromagnetic coupling which is consistent with the behavior of the much studied Cu-Mn system. This theory can predict a linear dependence of $T_c$ upon concentration similar to Eq. (2). It is not yet clear whether this theory can be applied to the Au-Fe system because of its pronounced ferromagnetic character.

We are continuing to investigate the Au-Fe as well as ternary (Au-Fe-X) systems.

We have profited from discussions with A. Arrott, E. Catalano, and W. E. Henry.

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