

Session V

MAGNETISM

CHAIRMAN: *H. Frauenfelder*

MAGNETISM IN DILUTE ALLOYS: *W. Marshall, T. E. Cranshaw, C. E. Johnson, and M. S. Ridout*

CONTRIBUTED PAPERS

Magnetism of Dilute Alloys*

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I. INTRODUCTION

This paper will review our present understanding of two classes of dilute alloys: (i) dilute ferromagnetic alloys with iron, nickel or cobalt as host metal; (ii) dilute alloys of transition metals with hosts such as copper, gold, silver, zinc. The emphasis will be upon the use of the Mössbauer effect to help understand the properties of these alloys. Because only a few Mössbauer experiments have been performed on these alloys to date, the discussion will, of necessity, be mainly theoretical and mainly a statement of possible experiments.

II. DILUTE FERROMAGNETIC ALLOYS

This topic has been reviewed in a paper by Friedel.¹ Friedel begins his discussion by reference to the famous Slater–Pauling curve which we reproduce here as Fig. 1. From this figure we recognize three classes of alloys:

- (a) Alloys based on Co or Ni giving the right-hand branch of the curve (CuNi, NiCo, CoFe);
- (b) Alloys based on Fe giving the left-hand branch;
- (c) Alloys based on Co or Ni giving a sharp drop in $\bar{\mu}$ as the impurity concentration (of Cr, Mn, or V) is increased.

The alloys of type (a) are the simplest to understand. Consider NiCo as an example. The band structure of Ni is shown symbolically in Fig. 2. This figure shows the d_α band as entirely below the Fermi surface: the d_β band is displayed to higher energy by the exchange interactions, and the Fermi surface intersects it so as to give 0.6 holes per atom in the d_β band, as deduced from the saturation magnetization of $0.6 \mu_B$.

When a Co atom is introduced into Ni, the electrons see it as a repulsive potential of one unit: they are scattered from this potential, and therefore the wavefunctions are no longer plane waves; the electron charge density is therefore changed in such a way as to reduce the electron density on the Co atom where the repulsive potential exists. This in turn changes the scattering potential seen by the electrons by providing a screening effect. The effective scattering potential must therefore be determined by some self-consistent calculation. We can, however, foresee the results of such a calculation by a very general argument: because the host is a metal, the effect of the Co impurity must vanish at sufficiently large distances. Thus, at large distances, the electron density must be that of pure Ni. This means that on the Co atom itself and in its immediate vicinity there must be room over-all for one less electron with energy below the Fermi surface. This then

* Presented by W. Marshall.

¹ J. Friedel, *Nuovo Cimento Suppl.* **7**, 287 (1958).

exactly compensates for the fact that Co brings with it one electron less than Ni. We can go beyond this exact result by observing that Co and Ni have the same electronegativity and, therefore, to a zero-order approximation, each unit cell will be neutral. Hence, to a zero-order approximation we can describe the alloy as having one less $3d$ electron in the Co unit cell with the Ni atoms left undisturbed.

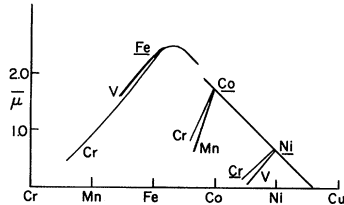


FIG. 1. A simplified Slater-Pauling curve giving the saturation magnetization $\bar{\mu}$ in units of the Bohr magneton as a function of electron number.

How do we arrive at this solution starting from the band picture of Fig. 2? The effective scattering potential may or may not be strong enough to pull bound states above the top of the d_α and d_β bonds: to zero order this point is of no consequence, provided all the d_α states remain below E_f . Because the d_α band is entirely below the Fermi surface, no perturbation of it can produce any change in charge density (on the tight binding model every atomic $3d_\alpha$ state is occupied and any arbitrary set of one-electron wavefunctions gives the same many-electron wavefunction and the same charge density). The perturbation and screening therefore involves the d_β band exclusively. (We ignore the conduction band to zero order because it has a much smaller density of states than the d_β band.) The d_β band is therefore displaced upwards so that it has exactly one electron less below the Fermi surface, and the detailed wavefunctions below this Fermi surface are charged so that they have less amplitude on the Co atom and slightly more on the Ni atoms. As a result, summing over all states below E_f , the last electron is entirely on the Co, and the Ni atoms are undisturbed. This model predicts the moments

$$\mu_{\text{Ni}} = \text{constant } 0.6, \quad \mu_{\text{Co}} = 1.6, \\ \bar{\mu} = 0.6 + 1.0c \quad (1)$$

The observed $\bar{\mu}$ is in excellent agreement with this. More generally if the impurity has nuclear charge Z relative to the host, we expect the results

$$\mu_{\text{host}} = \text{constant}, \quad \mu_{\text{impurity}} = \mu_{\text{host}} - Z, \\ \bar{\mu} = \mu_{\text{host}} - Zc \quad (2)$$

This last law is well obeyed by the alloys of type (a).

It should be emphasized that the discussion given

above is correct only to a zero-order approximation. One important addition to the discussion is the fact that, because the electrons form a degenerate gas with a sharply defined Fermi surface, it is impossible to achieve the simple charge distributions described above. In particular, the host atoms cannot be left undisturbed because charge and moment oscillations, with a period related to the Fermi vector, and with an amplitude steadily decreasing with distance are set up. For a discussion of these effects see Yosida² and Blandin and Friedel.³

From the above discussion it is clear that we would expect observations on the hyperfine fields of the host nuclei [most conveniently performed by NMR techniques for type (a) alloys] to show only small deviations from the hyperfine field of the pure metal. These deviations would mostly come from the damped oscillations of the magnetic moment in both the conduction electron gas and the d electron gas. The NMR pattern would be a superposition of spectra arising from the hyperfine field at nearest neighbors, next-nearest neighbors, . . . distant neighbors. The lines from the first few neighbors should be resolvable from the main peak. A proper interpretation of the measurements would be hard because the hyperfine field does not have a simple relation to the moment density in the unit cell, and our understanding of these ferromagnetic alloys extends little further than the elementary discussion

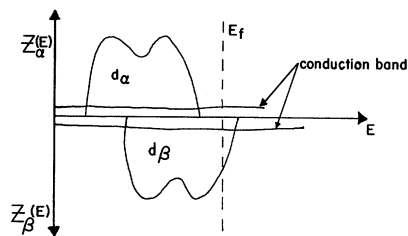


FIG. 2. A schematic diagram of the density-of-states $Z(E)$ curve for Ni.

sketched above; we do not even know if, in the pure metal, the conduction electron moment is parallel or antiparallel to the mean magnetic moment. Although for some years we have assumed parallel alignment, recent but inconclusive work by Shull and Yamada,⁴ and a theoretical discussion by Anderson⁵ suggest the antiparallel alignment may be correct.

² K. Yosida, Phys. Rev. **106**, 893 (1957).

³ A. Blandin and J. Friedel, J. Phys. Rad. **20**, 160 (1959).

⁴ C. Shull and Y. Yamada, J. Phys. Soc. Japan **17**, Suppl. B III, 1 (1962).

⁵ P. W. Anderson, Phys. Rev. **126**, 41 (1961).

Although several NMR experiments on Co-based alloys have been performed, they have not, so far as we are aware, produced meaningful results. There are several reasons for this: suppose, for example, the Co⁵⁷ resonance is examined in an alloy containing 1% Fe. The Co atoms which are nearest neighbors to the Fe impurity do not all have the same resonance frequency because the excess magnetic moment in the Fe unit cell produces a dipolar field at the Co nuclei in the neighborhood; and for the nearest neighbors this field is substantial (~ 1000 G) and, in general, different for the different neighbors because a dipolar field depends upon the angle between the magnetization and the vector joining the Fe atom to the nucleus concerned. Furthermore, Portis and Kanamori⁶ have drawn attention to the fact that the introduction of an impurity ion could distort the charge and spin distributions around the neighboring Co atoms in such a way that in some cases this effect could be enhanced. Also, the near-neighbor resonances are affected by the quadrupole interaction with the electric field gradient set up by the impurity, and finally, all these effects have to be averaged over the magnetization directions taken up in a domain wall. In view of all these complications, it is not clear if the nearest-neighbor shell should give several distinct resonances or if the signal from them should be so blurred that it should not be seen at all. Similar remarks apply, with less force, to the resonances from more distant atoms. In view of these difficulties of interpretation associated with the NMR alloys, the Mössbauer effect will probably remain the most effective way of studying the hyperfine field distributions in ferromagnetic alloys containing Fe⁵⁷.

At this point it should be remarked that, although the ability of NMR or Mössbauer experiments to measure the hyperfine fields at successive neighbors to an impurity can be of potential value, this potential will only be realized fully if it can be shown empirically that there is some simple interpretation of the hyperfine field in terms of local magnetic moments. This question has been examined for Fe⁵⁷ in the more concentrated alloys by the authors,^{7,8} who found no simple relation between hyperfine field and the iron moment or the mean alloy moment. It is therefore specially valuable to compare the hyperfine field measurements in dilute alloys with the magnetic moments measured by diffuse magnetic scattering of slow neutrons. Some neutron experi-

ments of this type have been performed by G. Low and M. Collins⁹ on NiFe, NiMn, and NiV, and Ni-Cr alloys: experiments on the Fe-based alloys are now in hand.¹⁰ These neutron experiments give the magnetic moment on the impurity atom, on the nearest-neighbor shell, on the next-nearest-neighbor shell, and so on. They therefore give information of much more basic interest than the hyperfine field, but these neutron experiments are hard to perform, and it is worthwhile to supplement them with the easier NMR or Mössbauer experiments. The neutron results on NiFe confirm the simple discussion given above; they show that μ_{Fe} is 2.7 and μ_{Ni} remains 0.6. The Ni neighbors of each Fe are very little perturbed.

The alloys of type (b) are hard to understand. If the d_α band of iron were entirely below the Fermi surface, there would be 2.2 holes in the d_β band and only 0.2 conduction electrons per atom. This latter figure is too low to be reasonable, and therefore we deduce that the d_α band cannot be entirely below E_f . Hence, there are holes in both the d_α and d_β band, and consequently the discussion of these alloys becomes complicated. There exists no theory of their behavior which commands general acceptance. It is particularly surprising that so many impurities (Al, Au, V, Si) merely appear to dilute the Fe so far as the magnetic properties are concerned.

The Mössbauer absorption spectra of these alloys are, in general, complex, showing a six-line spectrum similar to that of natural iron; but superimposed on it are spectra corresponding to Fe atoms in which the hyperfine field is substantially different. It is natural to interpret this spectrum as being due to Fe atoms having no, one, two, etc., neighbors of the alloying element. In general, it is found that up to three neighbors the effects are additive and that the reduction in hyperfine field by each neighbor is about 7%. In some cases (FeAl, FeSi) the field for the Fe atoms with no impurity neighbors is the same as in natural iron, whereas in others (FeV, FeCr) the field is increased. The fact that this increase occurs without appreciable line broadening indicates that many more atoms than are contained in the next-nearest-neighbor shell must contribute. Alloys of Fe with V, Cr, and Mn have been investigated using the neutron technique by Collins and Low,¹⁰ who find that their observations on FeV and FeCr alloys can be described by supposing that the moment on nearest neighbors of V and Cr is reduced by 8% and that the moment on about 50 neighbors more distant than the nearest neighbors is increased by about

⁶ A. Portis and J. Kanamori, *J. Phys. Soc. (Japan)* **17**, 587 (1962).

⁷ W. Marshall and C. Johnson, *J. Phys. Rad.* **23**, 733 (1962).

⁸ C. E. Johnson, M. S. Ridout, and T. E. Cranshaw, *Proc. Phys. Soc. (London)* **81**, 705 (1963).

⁹ G. Low and M. Collins, *J. Appl. Phys.* **34**, 1195 (1963).

¹⁰ M. Collins and G. Low (private communication).

1.5%. If we assume that the hyperfine field at the Fe nucleus is proportional to the moment on the Fe atom, this is at least in qualitative agreement with the Mössbauer investigations. However, Low and Collins find that Mn atoms have no influence on the moment of neighboring Fe atoms, whereas the Mössbauer investigations show that the Fe hyperfine field is reduced by the usual 7%. This casts serious doubt on the assumption of proportionality between hyperfine field and magnetic moment.

The Mössbauer investigations can provide two other pieces of information. The first concerns the intensity of the lines which we have attributed to Fe atoms that have impurity atoms among their nearest neighbors. These intensities give a measure of the relative probabilities of each Fe atom having no, one, or two neighbors. In some alloys the probabilities differ markedly from those calculated on the assumption of a random distribution. Some alloys (FeV FeCr) show a tendency for Fe atoms to have one impurity neighbor. In others (FeMo, FeW, FeRe), Fe atoms tend to have zero or two impurity neighbors. Thus short-range order can be investigated.

The second concerns the isomer shift produced in Fe atoms by an impurity neighbor. In general, we may expect that an impurity atom will disturb the s electron density at neighboring Fe nuclei. Si (Stearns¹¹), Ge, and Sn all produce positive isomer shifts on neighboring Fe atoms of the order of 0.05 mm/sec, corresponding to a reduction in s electron density. It is not clear whether the effect is a direct reduction of $4s$ electron density or an increase in $3d$ electrons causing a shielding of $3s$ electrons.

The alloys of type (c) are partially understood. The magnetic moment behavior is explained by Friedel¹ as follows. The effective repulsive potential is very much stronger for these alloys than for those of type (a), and therefore bound states can certainly be pushed out of the top of the d_α and d_β bands, for example, NiV has $Z = -5$. We suppose the potential is strong enough to push the d_α bound states above the Fermi surface and that the full fivefold degeneracy of the d_α band is retained so that five d_α electrons empty mainly into the d_β band (a small fraction empty into the conduction band). Hence the third equation of (2) is modified to read

$$\bar{\mu} = \mu_{\text{host}} - (10 + Z)c, \quad (3)$$

and this law holds approximately for the alloys concerned. It is easy to see that the bound states pushed

out of the band cannot be compact in space. If, for example, they were dominantly the $3d$ atomic states of the impurity, say V, then because both the d_α and d_β bound states are empty, the V atom would have no $3d$ electrons at all. This strongly violates the rough rule that every unit cell is electrically neutral, and therefore we deduce that the self-consistent effective potential must be such that the bound states are not compact in space but must have appreciable amplitude on the nearest-neighbor and next-nearest-neighbor atoms. For the case of NiV the charge difference Z is -5 , so we deduce that the bound states must have about half their weight on the V atom and half on the Ni atoms in the immediate vicinity. In these circumstances we expect appreciable disturbance of the magnetic moments on the nearest-neighbor Ni atoms. This argument is confirmed by the neutron experiments of Low and Collins⁹ on NiV and NiCr, which show a large reduction in the magnetic moment of the nearest neighbors to each V or Cr atom. In the Co-based alloys (CoV, CoCr), the NMR signal from the nearest neighbors has been searched for but not found.^{12,13}

III. DILUTE ALLOYS OF TRANSITION METALS WITH CU, AG, AU, AND ZN

As an example of these alloys, we consider CuFe, but we should emphasize that there appear to be at least two types of alloys of this kind: one typified by CuMn and the other by CuFe.¹⁴ In detail, therefore, the discussion of these alloys varies from case to case. All of them show remarkable specific-heat values at low temperatures. For CuMn Hoare and Zimmerman¹⁵ find a specific heat above that of pure Cu, which is linear in temperature and independent of concentration at low enough temperatures and over an appreciable range of concentrations. For CuFe Franck, Manchester and Martin¹⁶ find qualitatively similar results but with some important differences in detail (an alloy of 0.2% Fe gave the specific heat linear in T , but alloys of 0.1% and 0.05% give specific heats with some considerable curvature in their dependence on T).

The first explanation of these results was given by Overhauser¹⁷ in terms of static spin-density waves.

¹² R. C. LaForce (private communication).

¹³ M. Rubinstein (private communication).

¹⁴ D. L. Martin, in *Proceedings of the Eighth International Conference on Low Temperature Physics* (Butterworths Scientific Publications, Ltd., London, to be published).

¹⁵ F. E. Hoare and J. E. Zimmerman, *J. Phys. Chem. Solids* **17**, 52 (1960).

¹⁶ J. P. Franck, F. D. Manchester, and D. L. Martin, *Proc. Roy. Soc. (London)* **263**, 494 (1961).

¹⁷ A. W. Overhauser, *J. Phys. Chem. Solids* **13**, 71 (1960).

¹¹ M. B. Stearns, *Phys. Rev.* **129**, 1136 (1963).

He applied his theory to the CuMn alloys and found excellent agreement with experiment. An alternative theory was also advanced by one of the authors¹⁸ who used the well-known Ruderman-Kittel-Yosida spin interaction as the basis for an explanation. The latter theory has recently been made quantitative by Klein and Brout¹⁹ and by Klein.²⁰ The feature common to all these theories and essential to explain the results is that there is some degree of randomness in the alloy. Because of this randomness the exchange field acting on any particular impurity spin has a probability distribution which is a continuous function instead of a sharp δ function as it would be for a concentrated and pure ferromagnetic. In the Overhauser theory the randomness comes from the phase of the static spin-density wave as it passes over the impurity; because the wave has a wave vector incommensurate with the lattice, all phases are possible. In the alternative theory the randomness comes from the variation in distance apart and spin orientation of every possible pair of impurity atoms.

The probability distribution function is easy to construct in the Overhauser theory. The field acting on a spin j is supposed to be

$$H_j = \Delta \cos \mathbf{k} \cdot \mathbf{R}_j = \Delta \cos \varphi_j, \quad (4)$$

where \mathbf{k} is the wave vector of the spin-density waves and Δ is proportional to its amplitude. If k is incommensurate with the lattice, all phases φ_j are equally likely and it follows immediately that, if $p(H)dH$ is the probability the field lies between H and $H + dH$,

$$p(H) = (1/\pi)[1/(\Delta^2 - H^2)^{1/2}] \quad (5)$$

for values of H between $-\Delta$ and $+\Delta$, and is zero otherwise. Overhauser also shows that, to a good approximation, Δ is given as a function of temperature by the relation

$$\Delta(T) = \Delta(0)[1 - (T/T_c)^2]^{1/2}, \quad (6)$$

where T_c is the ordering temperature of the alloy. It is important to note at this point that CuFe does not show a sharp ordering temperature proportional to concentration as is the case for the CuMn alloys. Thus it is not clear if it is possible to extend the Overhauser theory to CuFe: certainly if it is found that spin-density waves are absent in CuFe, it implies nothing about their existence in CuMn.

The alternative theory is very much more qualitative in nature; in fact the $p(H)$ curve could be

given only as a rough sketch. For *heuristic purposes only* we can represent the $p(H)$ by the sum of two Lorentzians: thus,

$$p(H) = \frac{1}{\pi} \left[\frac{\Delta}{\Delta^2 + (M - \delta)^2} + \frac{\Delta}{\Delta^2 + (H + \delta)^2} \right], \quad (7)$$

where Δ and δ both have a slow dependence on T , and $\delta > \Delta$ at low T . Thus at low T , $p(H)$ has a local minimum at $H = 0$ and two maxima, one on each side. At low T , Δ and δ should be proportional to c . It should be strongly emphasized that the theory did not deduce (7) or any other expression as a precise form; we introduce (7) merely to give a convenient qualitative representation of the result.

It can be shown that the low-temperature specific-heat results are sensitive only to the value of $p(0)$ and, therefore, cannot by themselves distinguish between these theories. However, in principle, the Mössbauer effect can measure the complete $p(H)$ curve as a function of temperature and concentration. To see how this can be done, consider CuFe as an example. From the specific-heat results the magnetic entropy can be calculated, and Franck, Manchester, and Martin¹¹ show that it approaches $R \log 2$ at high T . They therefore deduce that the Fe has spin $\frac{1}{2}$ in this alloy. It follows that the mean z component of spin of a particular atom is

$$\langle S \rangle = \frac{1}{2} \tanh \mu H / kT, \quad (8)$$

where H is the exchange field on that particular Fe atom. But in this alloy, because it is so dilute ($c \lesssim 1\%$), we can take the hyperfine field to be proportional to $\langle S \rangle$ to an excellent approximation; hence

$$h = 2a\langle S \rangle, \quad (9)$$

where h is the hyperfine field and a is a constant of the order of 10^5 G. From (8) and (9),

$$h = a \tanh \mu H / kT. \quad (10)$$

This equation shows that there is a one-to-one relationship between the exchange field H acting on the Fe electron spins, and the hyperfine field h acting on the Fe nuclear spin. Hence, if there is a distribution function for the first, there must be a distribution function for the second. In principle, the distribution of hyperfine fields $P(h)$ can be measured by a Mössbauer experiment, and therefore, using (10), the distribution for the exchange field can be deduced. The experiment is difficult because the Fe concentration is low and the Mössbauer spectrum from each h value is the sum of six lines, each with a natural width.

¹⁸ W. Marshall, Phys. Rev. 118, 1519 (1960).

¹⁹ M. W. Klein and R. Brout (to be published).

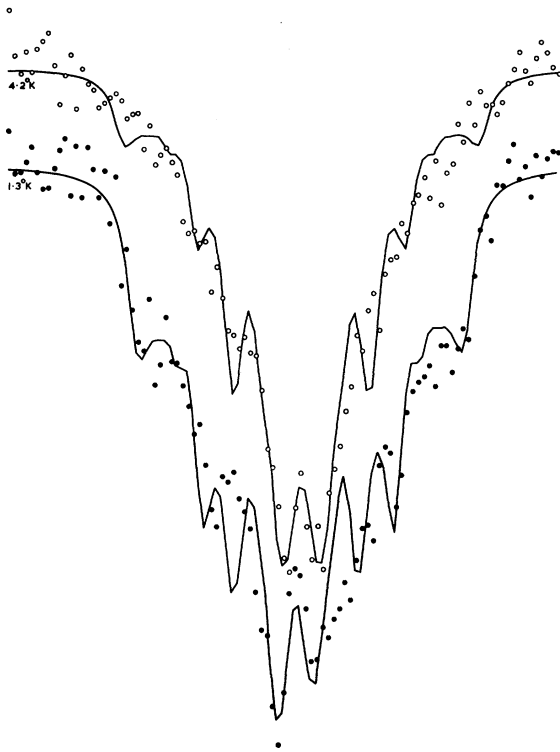
²⁰ M. W. Klein (private communication).

The interpretation can be simplified by approximating (10) by the result

$$\begin{aligned} h &= a\mu H/kT && \text{for } H < kT/\mu, \\ h &= a && \text{for } H > kT/\mu, \end{aligned} \quad (11)$$

$$P(h) = \{kT/a\mu\}p(kTh/a\mu) + \{\delta(h - a) + \delta(h + a)\} \int_{kT/\mu}^{\infty} dHp(H), \quad (12)$$

and it is understood that in the first term of (12), h is restricted to be less than a . The distribution of hyperfine fields indicated by (12) is complex. The second term gives sharp hyperfine fields and gives rise to the familiar six-line Mössbauer spectrum of Fe⁵⁷. The first term of (12) gives a continuous distribution of hyperfine fields and therefore a very broad absorption signal. A detailed comparison of experiment to the results predicted by (5) and (7),



ABSORPTION SPECTRUM 1.3% Fe IN Cu

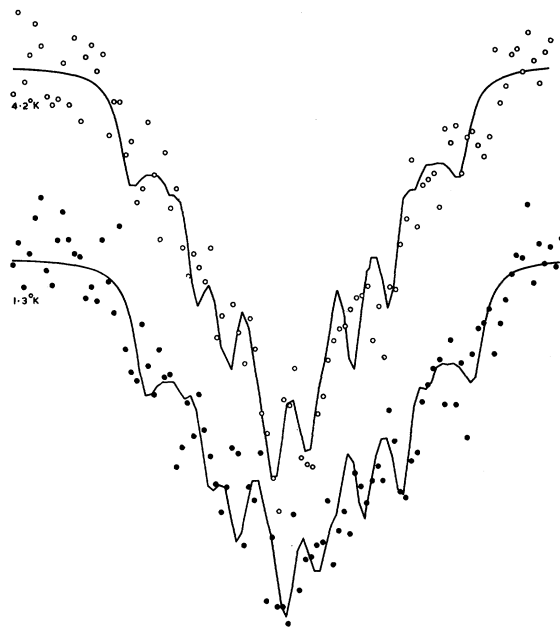
FIG. 3. The data for a CuFe alloy of concentration 1.3%. The curve is the least-squares fit using Eq. (7) for $p(H)$.

respectively, should provide important information on the mechanism of the magnetic ordering in these materials.

The main qualitative difference between the results predicted by the theories is in the way the δ

functions appear in (12). In the higher temperature region the alternative theory gives δ functions because $p(H)$ is nonzero even for large H . But the Overhauser theory gives no δ functions until T is below a limiting value T_l given by

$$kT_l/\mu = \Delta(T_l). \quad (13)$$



ABSORPTION SPECTRUM 2.6% Fe IN Cu

FIG. 4. The data for a CuFe alloy of concentration 2.6%. The curve is the least-squares fit using Eq. (7) for $p(H)$.

Substituting from Overhauser's equations this becomes

$$T_l = T_c \{1 + \pi^2(s + 1)^2/36\}^{-1/2}.$$

Below this temperature the amplitude of the δ function rises very rapidly. The alternative theory gives a more gradual increase in the amplitude of the δ function.

Some preliminary results have been obtained on the CuFe system and are shown in Figs. 3 and 4, and the parameters obtained by a least-squares fit using computer programs based upon (7) are shown in Table I. The solid curves shown in the diagram are these least-square fits. We were unable to obtain any good fit based on (5) and therefore do not give any details; also, as we have emphasized, there is no reason to expect (5) to be appropriate for these particular alloys. For these first experiments we used Fe concentrations of 2.6%, 1.3%, and 0.5%. These concentrations are far too high to expect agreement with either of the two theories described above (the

highest concentration used by Martin was 0.2%), but to establish the technique it was advisable to use high enough concentrations for a Mössbauer absorption spectrum to be observed easily.

The results clearly show that the samples contain both fully aligned and partially aligned spins at the temperatures of 1.3 and 1.2°K. The displayed pattern was divided into 100 channels of such a width that a room-temperature linewidth equalled only 4 channels. In view of this fact and in view of the statistical error, we believe the fit to the data using (7) to be reasonable. At 77°K the spectrum was a single line, only slightly broader than that observed at room temperature.

The concentrations used in our experiments are beyond the solubility limit for Fe in Cu; they were therefore prepared by a fast quench from 900°C. Some samples were annealed at 500°C, and they then showed a different Mössbauer pattern (a broad rectangular absorption) which we ascribed to fcc aggregates of Fe. Subsequent cold working produced

TABLE I. Values of the parameters found in the least-squares fits shown in Figs. 3 and 4. The parameters Δ and δ are defined in the text.

Data fitted to Eq. 7				
Temp °K	4.2		1.3	
Concentration %	1.3	2.6	1.3	2.6
Δ kg	16 ± 1.0	25 ± 1.5	8.5 ± 0.4	9.0 ± 0.6
δ kg	19 ± 0.7	28 ± 1.6	9.8 ± 0.5	10.2 ± 0.7

bcc Fe which was detected by its characteristic Mössbauer absorption spectrum. In view of their results we are confident that the main samples used have the iron in solid solution, but we have no way of testing for homogeneity.

The Mössbauer patterns shown in the figures have several characteristic features. The over-all shape is triangular and this qualitatively is to be expected from any broad hyperfine field distribution; for example, a rectangular distribution of hyperfine fields would produce an absorption spectrum which would be a superposition of three rectangles of different widths with the inner narrow rectangle the deepest and the outer rectangle the shallowest. Making allowance for the natural width of the absorption line, this becomes modified into a rough triangle with shoulders appearing at the points corresponding to the extreme limits of each rectangle. Superimposed on this "triangular" absorption spectrum is a weak six-finger spectrum which, at the temperatures used, is visible to the eye only for the 2.6 alloy. The spectra

observed at 1.3°K clearly show the shoulders expected from this description. One important additional feature displayed in all the spectra is the split pattern of two lines in the center. These lines are too strong to be the central two lines of a six-finger spectrum (if they were, the other four lines of the spectrum would be exceedingly strong) and therefore must reflect some feature of the $p(H)$ curve. Because this part of the spectrum reflects $p(H)$ at small H , we deduce that the $p(H)$ curve has a local minimum at $H = 0$, and the minimum is reasonably sharp. The asymmetry in the computed curve arises from the fact that the computer program allowed for a possible isomer shift correlated with the local magnetic field.

A glance at Table I shows that the theory described above does not account for the experimental results. A major feature of the results is that the width of the $p(H)$ curve increases with increasing temperature, whereas the Overhauser theory gives a width decreasing with increasing T , and the alternative theory gives a roughly temperature-independent width. It is therefore clear that alloys of these concentrations in this temperature range are displaying phenomena quite different from that which the theories were attempting to describe. This in itself is not surprising because the concentrations used in our experiments are an order of magnitude larger than those where the specific-heat measurements were performed.

Nevertheless, it is worthwhile to speculate on the cause of this increasing width of $p(H)$ with increasing temperatures. One possibility we believe can be dismissed is that it is due to increased spin disorder, and to understand this point it is necessary to consider carefully what $p(H)$ represents. At low temperatures we assume that each spin is locked parallel to the local exchange field (without real justification we ignore zero-point motion). The exchange field then has a distribution solely because of the geometrical disorder associated with an alloy; each site has a different exchange field because each site has a different environment. As the temperature is raised two things happen: the spins acquire a smaller alignment along their local exchange field and this changes the geometrical effect; also the fluctuations in the spins from one orientation to another introduce a time-varying field at each site. This time-varying field at a site occurs at frequencies such that the spin at the site can respond to the field, and so when discussing the energy in the electron spin system, it is reasonable to include the effects of both geometrical disorder and spin disorder in the $p(H)$ curve. The

spin disorder acts qualitatively very much as though it were at zero frequency. But the fluctuating fields due to spin disorder occur at frequencies comparable to J/h , where J is a characteristic exchange coupling, and for this system we can take J to be of the order of 6°K (the specific-heat results of Franck, Manchester, and Martin show a maximum at this temperature for the three alloys they studied). The fluctuation time is therefore of the order of 10^{-10} sec, and this is too short for the nucleus to respond effectively. Therefore, if this rough estimate is correct, the Mössbauer experiment should see only the distribution of fields due to the geometrical effect.

We are unable to give any plausible explanation of why the width of our $p(H)$ curves increases with increasing temperature. However, it is worth noting that in our alloys the nearest-neighbor exchange interaction is playing a more important role than in

the alloys where the specific-heat anomalies have been observed. For example, in the 2.6% alloy there is a 30% chance that an Fe atom has a nearest neighbor which is also Fe. Assuming this nearest-neighbor interaction is antiferromagnetic and stronger than the more distant interactions, it seems likely that our samples must contain a good deal of zero-point motion in the spin system. This qualitative idea is supported by the observation that the entropy deduced from the specific-heat results on an 0.2% alloy showed that the spins at 1.3°K were almost completely aligned, whereas our Mössbauer measurements on higher concentrations show that, at the same temperature, the majority of the spins are only partially aligned. We believe the present results indicate that the experiments could be profitably pursued at lower concentrations and lower temperatures.

CONTRIBUTED PAPERS FOR SESSION V

Magnetic Shielding and Local Moments of Fe⁵⁷ Impurities*

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The hyperfine field of Fe⁵⁷ has been studied as a function of temperature and external magnetic field for sources composed of Co⁵⁷ diffused into such host metals as Cu, Ti, Nb, Au, Pd, and Pt. In zero external field all of the sources, except Ti, showed a single narrow Mössbauer line at all temperatures from 300 to 4°K. Titanium, not being cubic, gave a broader line. At room temperature these sources showed little, if any, shielding of the Fe⁵⁷ from the external field, i.e., the observed partially resolved Mössbauer hyperfine spectrum directly corresponded to the applied field. At 4°K a remarkable magnetic shielding is apparent for Cu, Ti, and Au, while little shielding was found for Nb, Pd, and Pt.

We define the shielding constant $a = (H - H_{\text{eff}} + H_i)/H$, where H is the applied field, H_{eff} is the field at the Fe⁵⁷ impurity deduced from the Mössbauer spectrum, and, where present, H_i is the internal field. We find a (4°K) is 0.45 ± 0.04 for Cu, 0.23 ± 0.05 for Ti, and 1.0 ± 0.1 for Au. The value of a for a given source at 4°K is nearly constant, independent of H , up to 60 kOe, the maximum field used. For Cu, a was studied in detail as a function of temperature with $H = 60$ kOe. A reasonable fit to the data is given by $a = 8.1/(T + 13)$. Circular polarization measurements showed H_{eff} for Cu to be positive with respect to H .

Previous studies of the localized moment of Fe⁵⁷ in Pd and Pt¹ assumed zero shielding of the impurity from the external field. A somewhat improved fit of the data is possible if one allows a to be 0.05 and 0.11, respectively. A similar treatment of new data on Fe⁵⁷ in Au requires a to be 1.0 ± 0.1 . The local moment observed is 2.0 ± 0.2 Bohr magnetons if $J = 1$ is assumed and the saturation internal field is -120 ± 2 kOe.

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¹ P. P. Craig, D. E. Nagle, W. A. Steyert, and R. D. Taylor. *Phys. Rev. Letters* **9**, 12 (1962).

High Field Studies of Localized Moments in Metals

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In this paper we report on a series of Mössbauer experiments in high external magnetic fields. Such measurements have been shown to give new information concerning localized magnetic moment distributions in metals and alloys.¹⁻³

The hyperfine field at the Fe⁵⁷ nucleus in a number of alloys of the $3d$ and $4d$ transition metals was measured as a function to temperature and applied magnetic field over the range 1.5 to 300°K and up to 110 000 Oe in both longitudinal and transverse field geometries using high current Bitter solenoids. The spectrometer, which is similar to those described elsewhere,⁴ uses a constant acceleration drive system to produce a linear velocity spectrum, and a multi-channel analyzer for handling and storing the data. Results for 1% Fe⁵⁷ in Ti and Sc are given; these show no additional contributions to the hyperfine field at any temperature studied. Alloys with 1% Fe⁵⁷ in Mo and Rh exhibit large negative temperature-dependent contributions to the hyperfine field at low temperatures. These results contrast with recent experiments using Co⁵⁷ in Mo and Rh as sources,² where no anomalous contributions to the hyperfine field were observed. Experiments using Co⁵⁷ in Cu as a source also exhibit large temperature-dependent negative contributions to the hyperfine field at low temperatures. Details of the results are given, and the data are analyzed and discussed in terms of current theoretical views on localized magnetic distributions in metals.

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¹ N. Blum and L. Grodzins, *Bull. Am. Phys. Soc.* **7**, 39 (1962).