TEMPERATURE DEPENDENCE OF THE ISOMER SHIFT AND THE HYPERFINE FIELD NEAR THE CURIE POINT IN IRON

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Mössbauer measurements have been made on Fe^{57} in iron near the Curie temperature. The discontinuity in the isomer shift near T_C is found to take place within a temperature range of less than 0.3°C, which suggests that this magnetic transition could be of first order. The "critical index" β for the variation with temperature of the spontaneous magnetization in the range $0.98T_C < T < 0.9992T_C$ is found to be definitely greater than $\frac{1}{3}$.

This Letter reports the first results of a program of Mössbauer measurements on Fe^{57} in metallic iron near the Curie temperature T_C. Earlier measurements of the Mössbauer effect in iron[1] showed that the isomer shift undergoes a small but rather sharp change at the Curie temperature. The change appeared to occur over less than 3°C, a temperature range small enough to raise the possibility that there is really a finite discontinuity in the isomer shift at the Curie temperature. This, if true, might possibly be construed as evidence against the apparently well-established fact that the magnetic transition in iron is of higher than first order: None of the various mechanisms that have been proposed[1-5] to account for the change in the isomer shift at the Curie temperature would account for a finite discontinuity if the transition were not first order. Now, with improved temperature resolution, the discontinuity is seen to be an order of magnitude sharper than the earlier measurements indicated.

For the present measurements, the apparatus used in the earlier work was modified—particularly by improving the regulation of the oven that maintains the temperature of the Mössbauer absorber and by reducing the thermal gradients within the absorber. The temperature is measured and regulated with a Le Châtelier thermocouple to ±0.05°C. The thermocouple has not been calibrated; so no actual temperatures are reported in this Letter. However, according to the standard calibration tables, the transition temperature is within a few degrees of 760°C. The spectrometer now in use is a conventional system with a loudspeaker to drive the source and a multichannel analyzer to accumulate the velocity spectrum. The source is Co^{57} in Pd foil, and the source temperature is maintained constant to ±1°C.

One series of measurements has been made to observe the isomer shifts in the immediate vicinity of the transition temperature. The data, largely concentrated in a temperature span of 0.7°C, are shown in Fig. 1. In the figure, T_C represents the temperature at which the magnetic broadening goes to 0. It is obvious that there is a break in the isomer shift and that it occurs within a range of about 0.3°C. Imperfect temperature resolution could account for part of the observed span of 0.3°C. If so, the actual break in the isomer shift would be even sharper than it appears to be here. On the other hand, the sharpness of the break sets an upper limit of ~0.3°C on the temperature resolution since worse resolution would smear out the break over an even wider temperature range.

As further evidence of this break, Fig. 2 shows a spectrum taken while the absorber was held alternately at two temperatures which

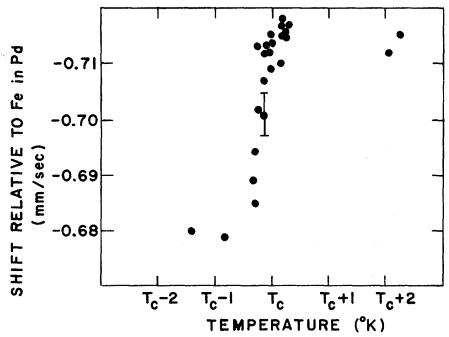

FIG. 1. Plot of isomer shift versus temperature near the Curie point.

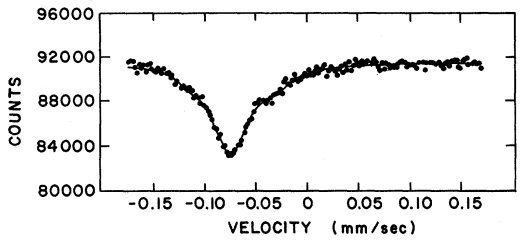

FIG. 2. Composite spectrum for two temperatures 0.5°C apart and bracketing the Curie temperature.

were 0.5°C apart and which bracketed T_C as determined by the disappearance of spectral broadening. During the running time of 24 h, the temperature was shifted from one of these temperatures to the other at 15-min intervals so that the two contributions to the composite spectrum would be equally affected by any spectrometer drifts. Upon careful inspection, it can be seen that the spectrum contains a shallow broad component as well as a deeper narrow component, and that the broad component is displaced to the right of the narrow component by a few hundreths of a millimeter per second.

Another series of measurements was made to determine the variation with temperature of the nuclear magnetic hyperfine field in the region just below T_C. According to the theory of critical-point phenomena, the spontaneous magnetization M of any magnetically ordered material should vary with temperature according to

$$M_T/M_0 = h(1-T/T_C)^{\beta} \qquad (1)$$

as $T \to T_C$. There are theoretical reasons to expect that in the limit $T = T_C$, β will be found to be the same number for all materials, possibly a simple fraction. The best experimental determinations[6] of β for various ferromagnets seem to cluster about $\frac{1}{3}$ and $\frac{1}{2}$. The magnetic hyperfine field H is closely proportional to the spontaneous magnetization, especially in pure materials and more especially at temperatures very near the Curie point. Thus, for pure metallic iron, a credible value of β can be obtained from the variation of the hyperfine field of Fe^{57} by substituting H_T/H_0 for M_T/M_0 in Eq. (1). This kind of procedure has already been used to determine β for a number of materials.[6] Of course, if this is not a second-order transition and the magnetization goes to zero discontinuously, then Eq. (1) is of doubtful validity.

At each temperature the value of H_T was determined from a least-squares fit of the Mössbauer spectrum to a standard Fe^{57} spectrum. With the help of a computer program developed by Ridout,[7] the experimental values of T and H_T were then fitted by an expression of the form of Eq. (1) with h, T_C, and β as the parameters adjusted for a least-squares fit. In Fig. 3 the solid line represents the best fit to the first six points on the left; its slope is $\beta = 0.349$ over the range $8\times10^{-4} \leq (1-T/T_C) \leq 2\times10^{-2}$. The

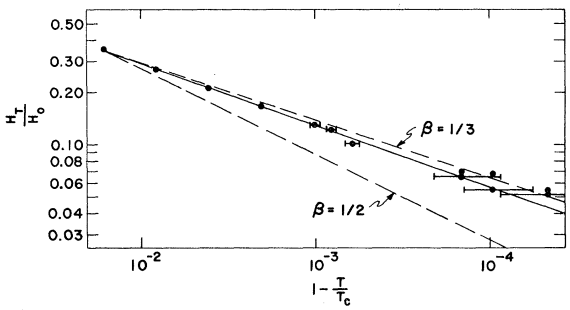

FIG. 3. Temperature dependence of the hyperfine field. The solid line is a least-squares fit to the first six points on the left. Representative horizontal error bars are shown. The horizontal error bars for the data points on the left are smaller than the dots that represent the points. All the vertical error bars are smaller than the dots.

best previous value of β for iron[2] was determined from measurements at temperatures farther from T_C and, because of the estimated probable error, was not inconsistent with $\beta = \frac{1}{3}$. The probable error for the present value of $\beta = 0.349$ has not yet been calculated. However, dashed lines with slopes of $\frac{1}{3}$ and $\frac{1}{2}$ are shown in Fig. 3 for comparison, and it is clear that neither of these simple fractions fits the data. In the region $4\times10^{-5} \leq (1-T/T_C) \leq 8\times10^{-4}$, the scatter of the points is too large for a meaningful least-squares fit.

Finally, it should be noted that the value of T_C determined from the least-squares fit lies within the temperature region where the sharp change in the isomer shift occurs. The highest temperatures shown in Fig. 3 are just at the beginning of the break in the isomer shift.

A real discontinuity in the isomer shift might be interpreted as evidence for a first-order transition. However, none of the existing data on the thermodynamics of this transition would support such an interpretation. The measurements are being continued in order to gain more precise data near the transition temperature.

I am grateful to all the members of the Mössbauer experimental group at Harwell for their assistance and encouragement in carrying out the measurements, and to Dr. E. Bradford and Dr. W. Marshall for discussions of the significance of this type of experiment for the theory of phase transitions.

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SUPERCONDUCTIVITY IN THE PRESENCE OF MAGNETIC EXCHANGE FIELDS*

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The upper-critical-field behavior of type-II superconductors in the presence of strong magnetic exchange fields is reported. In regimes where the exchange fields are temperature dependent the critical-field displays a nonmonotonic dependence on temperature as predicted by de Gennes and Sarma.

Conduction-electron polarization is detrimental to superconductivity. It was first pointed out by Clogston[1] and by Chandrasekhar[2] that this effect can be important in high-kappa, type-II materials in which superconductivity extends to high magnetic fields. In a more quantitative treatment Maki[3] considered the effect of conduction-electron spin paramagnetism on the second-order transition at the upper critical field H_{c2} of a superconductor in the vortex state. Subsequent work[4,5] included the effect of spin-orbit scattering, which strongly mediates the spin susceptibility of the superconducting state. Numerous studies[6] have demonstrated the lowering of H_{c2} due to spin polarization in high-kappa bulk materials. The effect of spin polarization on the parallel critical field of thin Al films has been demonstrated by Strongin and Kammerer.[7]

In the work discussed above, the only case considered is that in which the electron spins are polarized by an externally applied field which penetrates the sample. A second method of obtaining electron polarization in superconductors is by utilizing the internal exchange fields which result from the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction[8] in superconductors with polarized magnetic impurities. Two cases may be considered. The first is the case in which the sample is magnetically ordered, wherein the exchange fields seen by the conduction electrons are independent of temperature and the applied magnetic field. This case was considered first by Gor'kov and Rusinov[9] and later by Fulde and Maki[10] and Bennemann.[11] Bennemann's extension of the existing theories qualitatively explained the anomalous dependence[12] of the superconducting-transition temperature on spin-impurity concentration in the $La_{3-x}Gd_xIn$ system, reported by Crow and Parks.[13] The second case is that in which the impurity spins are disordered in zero magnetic field but are polarized according to the Brillouin function in the presence of an externally applied field. This case has been considered by de Gennes and Sarma,[14] who demonstrated that in this regime it is possible to have a nonmonotonic temperature dependence of the upper critical field[15] because of the temperature dependence of the Brillouin function. We have made critical-field measurements on the $La_{3-x}Gd_xIn$ system both in the Gor'kov-Rusinov and de Gennes-Sarma regimes.

The samples of $La_{3-x}Gd_xIn$ were prepared by melting the constituents under argon in a conventional arc furnace. The disk-shaped ingots were turned over and remelted ten times to ensure spatial homogeneity of the Gd impurity. In addition to the previously mentioned x-ray measurements,[13] we have made electron-microprobe and metallographic studies on the $La_{3-x}Gd_xIn$ samples. The electron-microprobe study showed that for samples with Gd concentrations less than 2.5 at.% the Gd was dispersed uniformly. This was determined by scanning separate regions over distances of the order of 200 μ (approximately 5-7 times the average grain size[16]) with a 2-μ-diam probe. The noise level of the probe corresponded typically to