

Temperature Dependence of the Magnetization of an Amorphous Ferromagnet*

C. C. TSUEI, G. LONGWORTH, AND S. C. H. LIN
California Institute of Technology, Pasadena, California

(Received 10 January 1968)

An amorphous alloy $\text{Fe}_{80}\text{P}_{12.5}\text{C}_{7.5}$ obtained by rapid quenching from the liquid state has previously been shown to be ferromagnetic. We report here the results of bulk magnetization and magnetic hyperfine field measurements as a function of temperature. The Mössbauer spectrum of the alloy consists of broadened lines indicating a nonunique magnetic hyperfine field at the Fe^{57} nuclei. The average hyperfine field has the value 282 ± 1 kG at 4.2°K and is shown to vary with temperature essentially according to a Brillouin function with a Curie temperature of (586 ± 2) °K. Measurements of the bulk magnetization as a function of temperature agree with the hyperfine field variation and yield a value for the magnetic moment per iron atom of (2.10 ± 0.01) μ_B . A simple model of a disordered alloy with a spread in interatomic spacing is used to predict the shape of the Mössbauer spectra and also to explain the reduction in magnetic moment per iron atom compared with pure iron. Although the magnetic moment per iron atom in this amorphous alloy is only slightly smaller than that of pure iron, the Curie temperature is greatly reduced, possibly because of the lack of strict periodicity in the atomic arrangement.

I. INTRODUCTION

IT has been shown theoretically that the presence of strict periodicity in the atomic arrangement is not necessary for the existence of ferromagnetism since the range of exchange interaction is usually of the nearest-neighbor distance.¹ Recently, there have been several reports of evidence indicating the existence of amorphous ferromagnets.²⁻⁴ No investigation of the temperature dependence of the magnetic properties of an amorphous ferromagnet has been reported. This kind of study can be very significant in the sense that it may help to clarify the role of long-range crystalline order in ferromagnetism. It also can be useful to answer such questions as whether there is a unique magnetic hyperfine field at the nuclei of the ferromagnetic atoms and how well the Curie temperature is defined in a ferromagnetic material which does not have long-range crystalline order. We report here the results of bulk magnetization and magnetic hyperfine field measurements on an amorphous alloy,⁴ $\text{Fe}_{80}\text{P}_{12.5}\text{C}_{7.5}$, as a function of temperature.

II. EXPERIMENTAL PROCEDURES AND RESULTS

According to Cohen and Turnbull,⁵ a low eutectic point with respect to the melting point of the main constituent in the alloy is conducive to glass formation. The amorphous alloy studied in this investigation was produced by the rapid quenching⁶ of a molten alloy containing 80 at.% Fe, 12.5 at.% P, and 7.5 at.% C.

This particular alloy composition was chosen because the Fe-P system is known to have a low eutectic point⁷ (1323°K) at 17.5 at.% P as compared to the melting point of iron (1810°K). When binary Fe-P alloys around the eutectic composition were quenched, only a partially amorphous phase could be obtained. The addition of carbon enables an amorphous alloy to be formed possibly because carbon lowers the eutectic temperature. Details of the alloy preparation have been published elsewhere.⁴ The x-ray and electron diffraction patterns for this alloy showed only the diffuse rings characteristic of a liquid structure. In addition, no structure was revealed by transmission electron microscopy. Analysis of the x-ray diffraction pattern indicated that there are approximately seven nearest neighbors to a given iron atom, situated at a mean distance of 2.60 ± 0.01 Å.

In the present work, we have measured the temperature dependence of the bulk magnetization using a sensitive null-coil pendulum magnetometer.⁸ Measurements of bulk magnetization were made for temperatures between 1.8 and 300°K with an accuracy of $\pm 0.5\%$ (Fig. 1). The results of these measurements on the amorphous alloy extrapolated to 0°K gave a magnetic moment per iron atom of 2.10 ± 0.01 μ_B . The magnetic hyperfine field at the Fe^{57} nuclei has also been studied as a function of temperature by using the Mössbauer effect technique. The absorption spectra were obtained using a 10-mCi Co^{57} -in-Pd source and the amorphous sample in the form of a disk of 1.5-cm diam and 50- μ thickness as absorber for absorber temperatures between 4.2 and 800°K. For temperatures above room temperature, a vacuum furnace was used in which the absorber temperature could be controlled to better than 0.5°K. The absorption spectra at room temperature, 565 and 597°K, are shown in Figs. 2, 3,

* This work was performed under auspices of the U.S. Atomic Energy Commission. Prepared under Contract Nos. AEC AT(94-3)-63 and AT(94-3)-221, for the San Francisco Operations Office, U.S. Atomic Energy Commission.

¹ A. I. Gubanov, *Fiz. Tverd. Tela* **2**, 502 (1960) [English transl.: *Soviet Phys.—Solid State* **2**, 468 (1961)].

² C. C. Tsuei and Pol Duwez, *J. Appl. Phys.* **37**, 435 (1965).

³ S. Mader and S. Nowick, *J. Appl. Phys. Letters* **7**, 57 (1965).

⁴ Pol Duwez and S. C. H. Lin, *J. Appl. Phys.* **38**, 4096 (1967).

⁵ M. H. Cohen and D. Turnbull, *Nature* **189**, 131 (1961); *D. Turnbull*, *Trans. AIME* **221**, 422 (1961).

⁶ Pol Duwez and R. H. Willens, *Trans. AIME* **227**, 362 (1962).

⁷ M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill Book Co., New York, 1958).

⁸ M. Weiner (to be published).

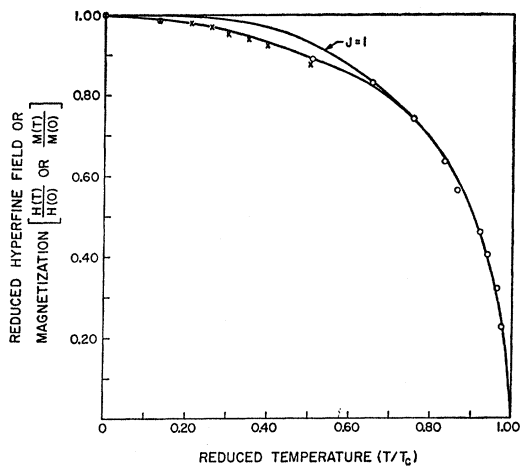


FIG. 1. Reduced hyperfine field (o) or magnetization (x) of the amorphous $\text{Fe}_{80}\text{P}_{12.5}\text{C}_{7.5}$ as a function of reduced temperature (T/T_c).

and 4, respectively. Low-temperature spectra which bore a close resemblance to the room-temperature spectrum are not shown here. The temperature variation of the Mössbauer spectra clearly indicated that there is a magnetic transition at about 596°K . Above this critical temperature, the spectrum consisted of a doublet presumably due to quadrupole splitting. Below this temperature the lines were considerably broadened over their natural width. In order to determine the Curie temperature more closely, the spectra obtained for temperatures between 560 and 590°K were fitted with a two-peak pattern and the splitting of the components, assumed to be proportional to the hyperfine field, was plotted as a function of temperature (Fig. 5). This indicated that the ferromagnetic transition was similar to that of a disordered alloy, and it is not as well defined as in, e.g., pure iron. The Curie temperature (T_c) of this amorphous alloy was thus determined to be $586 \pm 2^\circ\text{K}$. This agrees with the value $588 \pm 5^\circ\text{K}$ determined from induction measurements.⁴

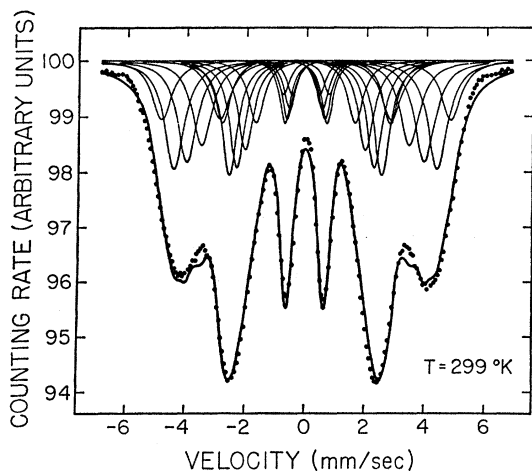


FIG. 2. Mössbauer spectrum of the amorphous $\text{Fe}_{80}\text{P}_{12.5}\text{C}_{7.5}$ at room temperature.

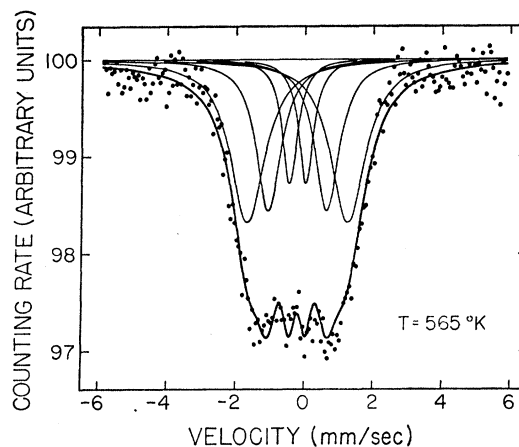


FIG. 3. Mössbauer spectrum of the amorphous $\text{Fe}_{80}\text{P}_{12.5}\text{C}_{7.5}$ at $T = 565^\circ\text{K}$ (about 20° below the Curie temperature).

The amorphous alloy rapidly transformed to its crystalline state at about 690°K . The Mössbauer spectrum of this transformed sample (heated at $T = 1000^\circ\text{K}$ for 48 h) consisted of four or five six-line patterns with the prominent set of lines having a hyperfine magnetic splitting equal to that of pure iron (330 kG) (Fig. 6). No attempts were made to single out the remaining components of this composite spectrum. X-ray analysis revealed the presence of $\alpha\text{-Fe}$, Fe_3P , and possibly Fe_3C in the transformed alloy; Fe_3C is known to have a field of 210 kG ,⁹ whereas one expects three fields in Fe_3P arising from iron atoms at different crystal sites.

III. DISCUSSION

A. Mössbauer Effect

The fact that below T_c the lines were symmetrically spaced in the presence of a combined magnetic and

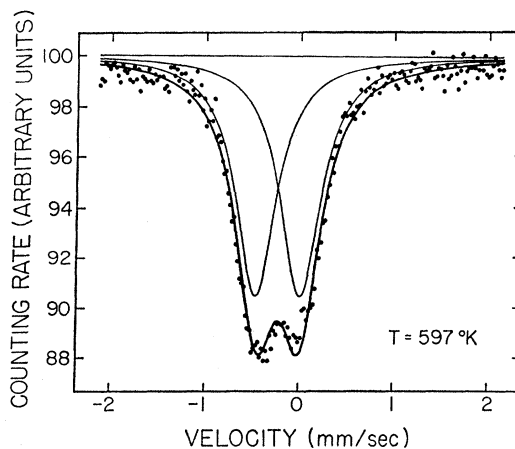


FIG. 4. Mössbauer spectrum of the amorphous $\text{Fe}_{80}\text{P}_{12.5}\text{C}_{7.5}$ at $T = 597^\circ\text{K}$ (about 10° above the Curie temperature).

⁹ T. Shinjo, F. Itoh, H. Takaki, Y. Nakamura, and N. Shikazono, J. Phys. Soc. Japan 19, 1252 (1964).

electric quadrupole interaction could be explained if there exists a range of electric field gradients which give rise to a broadening rather than a shift in the lines. This would also explain why the components of the doublet above T_c had a width (0.47 ± 0.01 mm/sec) greater than the natural linewidth.

The observed broadening of the hyperfine components at temperatures below the transition temperature could be due to (1) the effects of electronic relaxation and (2) the existence of a nonunique hyperfine field. Van der Woude and Dekker¹⁰ have shown for $S = \frac{1}{2}$ that when the electronic relaxation time (τ_e) is of the same order as the nuclear Larmor precession period (ω_L), the hyperfine components may be considerably broadened. We have, however, analyzed the spectra in terms of a nonunique hyperfine field and no attempt was made to fit the spectra using a relaxation model. Although we cannot rule out relaxation effects, the fact that the linewidths were independent of temperature between 4.2 and 800°K implies that any relaxation mechanism must be also independent of temperature.

The lack of structure in the observed components means that it is unlikely that a unique fit to the spectra can be obtained. It was not possible to obtain a good fit to the room-temperature spectrum based on the assumption of a Lorentzian distribution of field. This suggests that a model with unique fields would be more appropriate. One model would be that of a disordered alloy in which the interatomic distance has a spread in value. In some alloys, as for example FeAl alloys,^{11,12} different fields arise from the effects of different number of non-iron atoms in the first-neighbor shell via a transfer of electrons to the $3d$ band of iron. An attempt was made to fit the spectrum at room temperature using this hypothesis, assuming that the probability $P(H)$ of having a given number of iron atoms in the

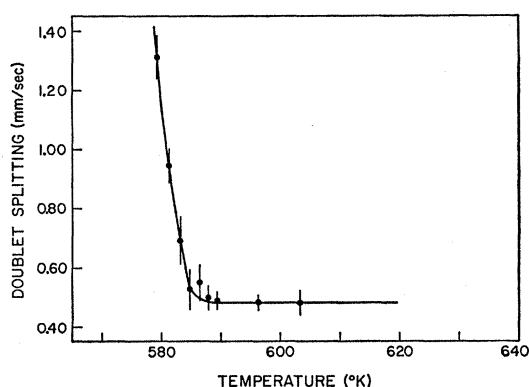


FIG. 5. Doublet splitting of the Mössbauer spectra of the amorphous $\text{Fe}_{80}\text{P}_{12.5}\text{C}_{7.5}$ at temperatures near the Curie point.

¹⁰ F. Van der Woude and A. J. Dekker, Phys. Status Solidi **9**, 775 (1965).

¹¹ P. A. Flinn and S. L. Ruby, Phys. Rev. **124**, 34 (1961).

¹² G. K. Wertheim, V. Jaccarino, J. H. Wernick, and D. N. E. Buchanan, Phys. Rev. **12**, 24 (1964).

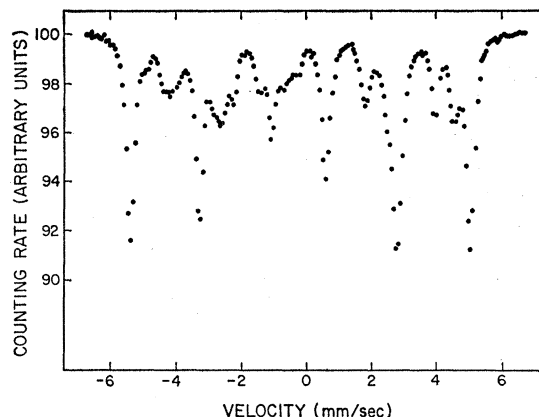


FIG. 6. The room-temperature Mössbauer spectrum of transformed $\text{Fe}_{80}\text{P}_{12.5}\text{C}_{7.5}$ (the amorphous sample was heated at 1000°K for 2 days).

first-neighbor shell is given by a binomial expansion. This leads to eight field values for a bcc structure, but in the computer fits only the five most prominent field values were used. Using such a distribution, however, it was not possible to obtain a good fit, but the fit was greatly improved by allowing each field to have a small Lorentzian distribution of values. Such an effect could arise physically (1) from the effect of iron atoms in the more distant shells and (2) from the fact that there is a spread (~ 0.5 Å) in the interatomic distance (2.6 Å). A reasonable fit was obtained with five fields of 175.4 ± 1.5 , 213.8 ± 1.0 , 244.3 ± 0.8 , 270.8 ± 0.7 , and 297.4 ± 1.6 kG (Fig. 2). The weighting factors $P(H)$ for each field determined from the fit (14.4, 20.5, 24.5, 26.5, and 14.4%) agree reasonably well with those predicted by the binomial expansion (10, 27, 30, 20, and 9%). The width of the inner component 0.394 ± 0.012 mm/sec is broader than the natural linewidth probably because of quadrupole broadening as discussed previously. The discrepancy on the outer limbs of the outer components could be explained if the individual lines are Gaussian in shape and not Lorentzian as assumed. Although the numerical results are model-dependent, such a fit does give us confidence that the disordered alloy model is a good one.

No attempt was made to fit the spectra for all temperatures according to the above hypothesis because of poorer counting statistics and lack of resolution in the spectra at higher temperatures. Instead, an average hyperfine field value was obtained for each temperature by fitting the spectra to a six-line pattern, allowing the heights and widths of the lines to vary independently with the restriction that heights and widths of corresponding lines (i.e., 1 and 6, 2 and 5, etc.) should be equal. The widths of the lines 0.47, 1.18, 1.38 mm/sec were practically independent of temperature. The ratios of their areas varied from 1:4:3 to 1:2:3 after prolonged heating, suggesting that there was an initial preferred orientation of the magnetic structure produced in the process of the rapid quenching from the liquid state.

B. Bulk Magnetization

As shown in Fig. 1, the average magnetic hyperfine field varies with temperatures above $T/T_c \approx 0.65$ according to a Brillouin function with $J=1$. The results obtained from the measurements of the bulk magnetization as a function of temperature agree with the hyperfine field variation between room temperature and liquid-helium temperature. With the experimental information available now, it is not clear how much significance should be attached to the fact that the experimental curve follows $J=1$ curve at temperatures not far from the Curie point.

The slight reduction in magnetic moment compared to pure iron ($2.22\mu_B$) can be explained in terms of addition of electrons from the phosphorus and carbon atoms to the $3d$ band in iron. This is also the model used to explain the nonunique hyperfine field. It is known that the addition of both carbon and phosphorus to iron reduces the magnetic moment per iron atom, e.g., Fe_3P has a moment of $1.84\mu_B$ /iron atom and Fe_2P , FeP , and Fe_3C have moments of 1.32, 0.36, and $2.015\mu_B$ /iron atom, respectively.¹³ The observed positive

isomer shift (0.19 mm/sec) with respect to pure iron is consistent with the explanation just proposed.

The Curie temperature of the amorphous $\text{Fe}_{80}\text{P}_{12.5}\text{C}_{7.5}$ is about 60% lower than that of pure iron, indicating that the size of the exchange integral must be considerably reduced. Although the average nearest-neighbor distance (2.6 Å) is about the same as in iron (2.48 Å), it is known from the radial distribution function that there is a spread of about ± 0.5 Å in its value which might give rise to a net reduced exchange integral.

In summary, the results of magnetization and hyperfine field measurements definitely indicate that the amorphous alloy $\text{Fe}_{80}\text{P}_{12.5}\text{C}_{7.5}$ is ferromagnetic. The magnetization of such an alloy varies with temperature in the same way as that of a crystalline ferromagnet, i.e., essentially according to a Brillouin function with a relatively well-defined Curie temperature. Although the magnetic moment is only slightly smaller than that of pure iron, the Curie temperature is greatly reduced, possibly because of the lack of strict periodicity in the atomic arrangement.

ACKNOWLEDGMENTS

We wish to thank Professor F. Boehm and Professor P. Duwez for their advice and encouragement and M. F. Bent for his help in the computational analysis.

¹³ A. J. P. Meyer and M. C. Cadeville, J. Phys. Soc. Japan 17, Suppl. B-I, 223 (1962).

Errata

Electron Paramagnetic Resonance of Gd^{3+} in YVO_4 , JACK ROSENTHAL [Phys. Rev. 164, 363 (1967)]. The expression for $H_{1/2}$ in Eq. (2) should be corrected. The coefficient of Q^2 in braces which has the form $[\] - [\]^{-1}$ should be $[\]^{-1} + [\]^{-1}$. Also the crystal-field parameters in Eq. (2) are shown in magnetic field units, while in Eq. (3) energy units are used. The connection, of course, is the factor $g\beta$. We are grateful to Dr. J. Bronstein for pointing this out and also for the information that the errors in his paper (Refs. 6 and 7) had already been corrected in Phys. Rev. 139, AB1 (1965).

Anisotropic Lattice Dynamic Studies and Line Asymmetries in Mössbauer-Effect Doublet Spectra, H. A. STÖCKLER AND H. SANO [Phys. Rev. 165, 406 (1968)]. In Eq. (1), λ_{\pm} should read

$$\lambda_{\pm} = [(3)^{1/2} \pm (3 + \eta^2)^{1/2}] / \eta.$$

In the last paragraph of the paper the typographical error $d(I_2/I_1)/dR$ should be corrected to read $d(I_2/I_1)/dT$.

Stress Effects on the Paramagnetic Resonance of Yb^{3+} in ThO_2 and Ho^{2+} in CaF_2 , Z. SROUBEK, M. TACHIKI, P. H. ZIMMERMANN, AND R. ORBACF [Phys. Rev. 165, 435 (1968)]. Recently we were able to measure the Δg_{\perp} of Yb^{3+} in ThO_2 stressed along the [001] axis. The experimental value $\Delta g_{\perp} = -(1.1 \pm 0.3) \times 10^{-6}$ per kg/cm^2 agrees in sign and roughly in magnitude with the calculated value shown in (39). The Δg_{\perp} in (39) was calculated from (36) without any covalency (overlap) enhancement of the crystalline field terms. Such an enhancement was formally introduced in the case of Ho^{2+} stressed along [111] by multiplying the fourth-order term by factor of 3. The same correction applied to (36) yields $\Delta g_{\perp} = -1.2 \times 10^{-6}$ per kg/cm^2 , giving much better agreement with experiment.

Dynamic Polarization of Na^{23} and F^{19} in NaF Containing F_2^- Molecular Ions, J. J. HILL [Phys. Rev. 157, 204 (1967)]. In Fig. 3, replace a by c . In Fig. 7, replace Eq. (23) by Eq. (32). The last line of Sec. VII D should read "Fig. 7" instead of "Fig. 8."