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Mössbauer study of the order-disorder and α-γ transitions in FeCo†

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A Mössbauer study of ^{57}Fe is used to measure the internal field (H_{int}) at the ^{57}Fe nucleus, Mössbauer spectral area, and the center shift for a nearly equiatomic FeCo alloy. Measurements were made between 297 and 1300 K with special attention to the region near the order-disorder (OD) transition (1006 K) and α-γ transition (1235 K). Near and above the OD transition, H_{int} changes slowly with temperature compared to the bulk magnetic moment. At the α-γ transition, H_{int} drops to zero abruptly. The Mössbauer spectral area shows a strong temperature dependence near the OD and α-γ transitions. In particular, an appreciable decrease in the spectral area is observed at the $\alpha \rightarrow \gamma$ transition. The Mössbauer spectral area is analyzed in correlation with the resistivity measurements of Seehra and Silinsky. Considerable deviations from the harmonic behavior near and above the OD transitions are evident. By contrast the center shift does not show any dramatic change near the OD and α-γ transitions.

I. INTRODUCTION

It is known that the FeCo alloy system undergoes an order-disorder (OD) transition for Co concentrations from about 40% to 60%.[1] A structural transition is also known to occur from the low-temperature α phase (bcc) to the high-temperature γ phase (fcc). In a recent paper, Seehra and Silinsky[2] have reported a detailed study of the OD and α-γ transition in a nearly equiatomic FeCo alloy (46.29 at.% of Co) using electrical-resistivity measurements. The OD transition is observed to occur at 1006 K. The α-γ transition occurs at 1235 K with nearly 12-K hysteresis and nearly 20% jump in resistivity with increasing temperatures.

In order to further explore the nature of these transitions, a Mössbauer study of the FeCo alloy covering the OD and α-γ transition region was undertaken. The results of this study are reported here. The Mössbauer spectroscopy is used to measure the temperature dependence of (i) the effective magnetic field at the iron nuclei, (ii) the Debye-Waller factor, and (iii) the center shift. These studies are correlated with the anomalies observed in the electrical-resistivity measurements.

II. EXPERIMENTAL

The sample of FeCo alloy used in these measurements was taken from the same batch on which electrical resistivity measurements have been reported earlier.[2] This sample was found to contain 46.29 at.% of Co. The spectrum was taken by bringing the sample to thermal equilibrium at each temperature. The sample was under vacuum (better than 10^{-4} Torr) inside a sealed quartz tube. Measurements taken with a vacuum of the order of a few Torrs showed the presence of oxides at high temperatures. It was therefore necessary to connect a liquid-nitrogen trap in between the high vacuum system and the furnace to avoid the formation of oxides. The temperature at the sample was measured using a chromel-alumel thermocouple. The sample thickness was about 0.001 in., so that the spectral area could be assumed proportional to the Debye-Waller factor. The sample was in the form of a thin foil and mounted in a lava sample holder. All measurements were taken with increasing temperatures. The radioactive source was 25-mCi Cu-^{57}Co at room temperature. A standard commercial spectrometer in the constant acceleration mode was used. The 14.4-keV detector consisted of a krypton-CO_2 proportional counter. A nonlinear least-squares-fitting program was used to fit the Mössbauer spectra and a Lorentzian line shape was assumed in the analysis. The system was calibrated using an iron metal foil, and all the center shifts are given with respect to iron metal. In Fig. 1, a Mössbauer spectrum of the FeCo alloy at 297 K is shown. The spectrum is typical of an ordered alloy with an internal field of 341 ± 2 kOe. In Fig. 2, a spectrum of the FeCo alloy at 1290 K, above the α-γ transition, is shown; a single line with a linewidth of 0.25 ± 0.03 mm/sec is observed.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Internal field at the ^{57}Fe nucleus

1. Previous work

For 3*d* transition metals and their alloys the internal field (H_{int}) at a particular atom arises mainly from core polarization (H_{cp}) and a contribution from 4*s*-like conduction-electron polari-

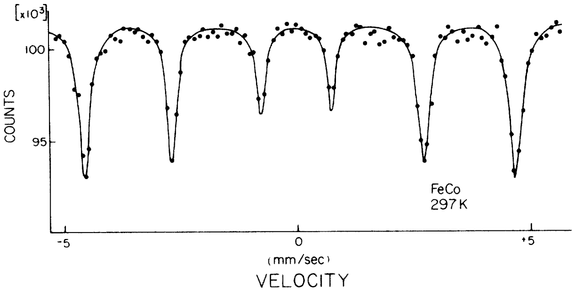

FIG. 1. Mössbauer spectrum of FeCo at 297 K.

zation (CEP). The CEP contribution can be considered to be produced by two terms: self polarization of the s-like conduction electrons by the atom itself, H_s, and a contribution due to the neighboring atoms, H_Σ (using Stearns[3] notation $H_{\rm int} = H_{\rm cp}+H_s+H_\Sigma$). Since the orbital angular momentum is quenched to a large extent in transition metals, the orbital contribution to the internal field is expected to be small compared to the core polarization. Dipolar contributions are also small (and positive) and in general play a negligible role in transition metals. In pure iron the internal field is proportional to the saturation magnetization.[4] This results from the proportionality between the local moment and the core polarization.

Previous investigations of the FeCo alloys have shown that additions of cobalt to iron up to about 25-at.% cobalt, results in an increase in the effective magnetic field at the iron nuclei and increase in the local iron magnetic moment. Above 25-at.% cobalt, the iron magnetic moment continues to increase, saturating around 50-at.% cobalt[5]; however, the internal field at the iron nucleus decreases.[6,7] A very striking experimental result is the lack of proportionality between the magnetic moment at the Co atom, which stays essentially constant at 1.8 μ_B over the entire bcc composition region of 0.75-at.% cobalt,[5] and the continuous decrease of the internal field at the Co nucleus with decreasing iron concentration.[8] This lack of proportionality between the magnetic moment at the atom and the internal field suggests the importance of the neighbors CEP contribution to the internal field, H_Σ.

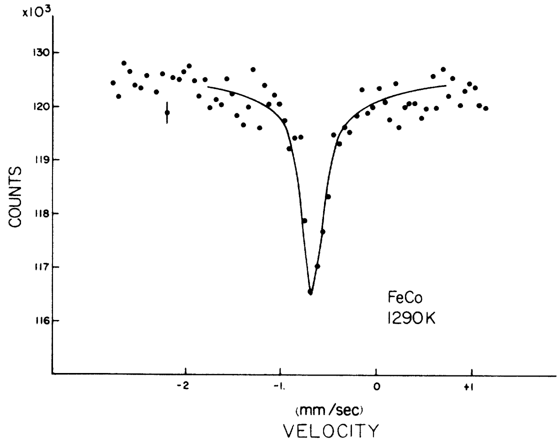

FIG. 2. Mössbauer spectrum of FeCo at 1290 K.

The magnetic moment at the iron atom decreases in going from the ordered to the disordered phase.[5] The largest difference, of about 3%, occurs in going from about 30- to 50-at.% cobalt. A decrease of the internal field upon ordering has been observed in the FeCo alloys.[7] The maximum decrease occurs at the equiatomic composition and is about 3%. It was observed that an increase in the number of cobalt neighbors to an iron atom, either by ordering or by increasing the cobalt concentration, decreases the internal field at the ^{57}Fe nucleus in the 25–75-at.% cobalt region. This change in the internal field is probably caused by the CEP, in particular for the term that depends on the neighbors H_Σ. This term will be the most affected by the order-disorder transformation.

2. *Present work (temperature dependence of* $H_{\rm int}$*)*

In Fig. 3, we have plotted the hyperfine magnetic splitting versus temperature for the FeCo alloy under study. The graph was normalized to the observed splitting at 297 K. The measured value of the hyperfine splitting at 297 K gives an internal field of 341 ± 2 kOe, in good agreement with the value reported in the literature for the ordered alloy.[7] The half-width of the outermost absorption lines are measured to be 0.35 ± 0.03 mm/sec, the same as the half-width obtained for a thin iron foil

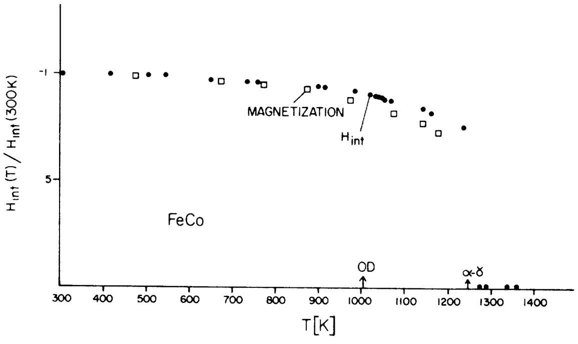

FIG. 3. Normalized internal field (full circles) and magnetization from Ref. 9 (squares) vs temperature for FeCo.

in the center of the furnace. The broadening of the line is mainly caused by the geometry of the experiment. In Fig. 3 we have also plotted the magnetic moment per atom for an equiatomic alloy of FeCo taken from reference.[9] Below about 700 K, the internal field and magnetization have a similar temperature dependence. Above 700 K there is an increasing difference between the temperature dependence of the magnetic moment and the internal field at the ^{57}Fe nucleus. The difference increases gradually and becomes about 7% near the OD transition temperature. This observation can be understood as follows. In going from the ordered to disordered phase the magnetic moment *decreases* by about 3%,[5] whereas the internal field *increases* by nearly 3%.[7] Therefore, in the disordered phase H_{int} should exceed the magnetic moment by about 6%, in good agreement with the observations reported in this work. Because of the second order nature of the OD transition the difference between H_{int} and magnetic moment develops over a large temperature range (Fig. 3). Using $H_{\text{int}} = H_s + H_{\text{cp}} + H_\Sigma$, some additional comments can be made about changes in different contributions to H_{int}, although we do not know the exact magnitude of H_s, H_{cp}, and H_Σ. First H_{cp} should decrease by about 3% in going through the OD transition since core polarization is proportional to the magnetic moment. This suggests that H_Σ should be considerably larger in the disordered phase (since H_s is not expected to change appreciably) to compensate for the decrease in H_{cp} and to explain the observations in Fig. 3. A change in H_Σ upon ordering is not unexpected because of the change in the environment. In the ordered phase all the Fe are surrounded by Co atoms (CsCl structure), whereas in the disordered phase on the average only 50% of the iron nearest neighbors will be Co atoms. Consequently, the nearest-neighbor CEP contribution to the internal field in FeCo plays a fundamental role in causing the difference between the internal fields in the ordered and disordered phases.

B. Debye-Waller factor

In order to analyze our experimental results correctly, it is important to take into consideration all the factors that affect the Mössbauer spectral area. In the experiments reported here we used a transmission geometry and several runs with different sample thicknesses gave reproducible results. The average effective thickness (t) of the sample is given by $t = n\sigma_0 f_a$, where n is the number of resonant nuclei per cm^2, σ_0 the absorption cross section at resonance, and f_a the Debye-Waller factor (DWF) of the absorber. For our experiment $t \simeq 1.5$, therefore the total spectral area will be proportional to f_a. The scattering of the γ-ray by the furnace walls makes the calculation of the background correction extremely uncertain. Therefore we will not try to evaluate the absolute value of the DWF, but only to measure its temperature dependence, in particular around the OD and α-γ transition temperatures.

The DWF in the harmonic approximation is given by[10]

$$f(T) = \exp\left\{-\frac{R}{N}\sum_{\lambda}\left[\frac{[\vec{K}\cdot\vec{e}(\lambda)]^2}{\hbar\omega_\lambda}\coth\left(\frac{\hbar\omega_\lambda}{2k_BT}\right)\right]\right\}, \tag{1}$$

where $\vec{K}$ is the unit vector along the direction of the γ rays, R is the recoil energy, $\vec{e}(\lambda)$ is the polarization vector of the lattice, and ω_λ are the normal frequencies of the lattice. One can use the Thirring expansion for the exponent of the DWF. For $\hbar\omega_{\max}/k_BT < 2\pi$, the component along the γ-ray direction is given by[10]

$$-\ln f(T) = 2Rk_BT\left(\sum_{\lambda}\frac{[e(\lambda)]^2}{N(\hbar\omega_\lambda)^2} + \frac{1}{12(k_BT)^2} - \cdots\right). \tag{2}$$

Using the frequency density and the moments of the frequency spectrum

$$\langle\omega^n\rangle = \int_0^\infty g(\omega)\omega^n\,d\omega\,, \tag{3}$$

one can then write for the isotropic case

$$-\ln f(T) = 2Rk_BT\left[\langle(\hbar\omega)^{-2}\rangle + \frac{1}{12}\,\frac{1}{(k_BT)^2} - \frac{1}{720}\left(\frac{\hbar}{(k_BT)^2}\right)^2\langle\omega^2\rangle + \cdots\right]. \tag{4}$$

Each term in the above expression can be described by an equivalent Debye distribution with[10]

$$\Theta_D(n) = (\hbar/k_B)\left[\tfrac{1}{3}(n+3)\langle\omega^n\rangle\right]^{1/n}. \tag{5}$$

In Fig. 4, the normalized area versus temperature is plotted on a semilog scale. One observes a change in the DWF near the OD transition temperature. The normalized resistivity measurements from Seehra and Silinsky[2] are also included in the figure. The FeCo alloy cannot be described by a simple Debye model above 1050 K since the DWF is changing too fast with temperature. If one uses Eqs. (4) and (5), one obtains an equivalent Debye temperature $\Theta_D = 190 \pm 20$ K. By contrast, between room temperature and 970 K, the system can be described by an equivalent Θ_D of 470 ± 20 K. It is questionable that the Debye approach will be applicable in the OD region, since anharmonicities should play an important role. We use the equi-

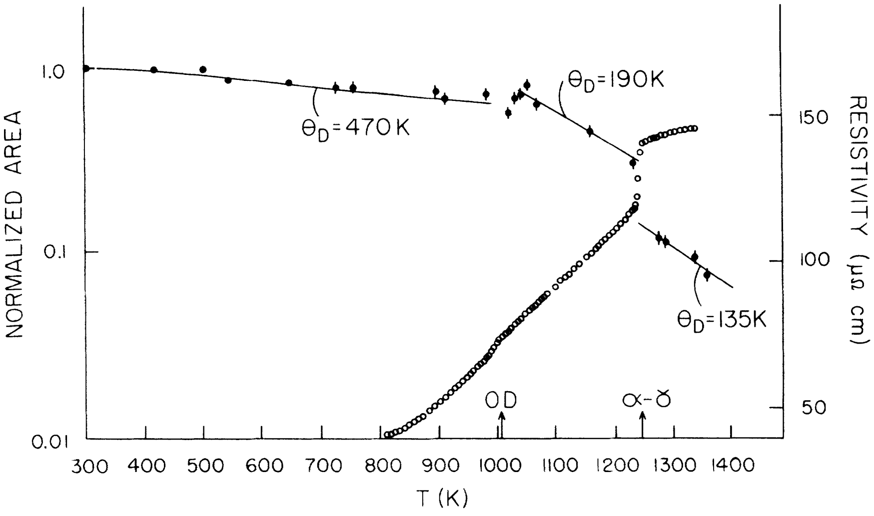

FIG. 4. Normalized Mössbauer spectral area versus temperature in FeCo (full circles). Resistivity measurements from Ref. 2 (open circles).

valent Debye temperature as a parametrization of the experimental results which gives a measure of the hardness or softness of the lattice. In Fig. 2 a typical Mössbauer spectrum above the α-γ transition is shown. There is a considerable drop in the spectral area in going from the α to the γ phase. The equivalent Debye temperature in the γ phase ($1240 < T < 1360$ K) is 135 ± 10 K. The drop in the DWF and the increase in ρ observed at the α-γ transition are in good qualitative agreement ($\ln f_\gamma / \ln f_\alpha \simeq 1.6$, $\rho_\gamma / \rho_\alpha \simeq 1.2$).[11] The above results are in contrast with the Mössbauer[12] and resistance measurements[13] of the α-γ transition in pure iron. In this case ρ decreases and the DWF increases in going from the α to the γ phase. A quantitative evaluation of the effective Debye temperature from the slope of the resistivity measurements versus temperature is not likely to be accurate. Also it is unreasonable to believe that the harmonic approximation could describe the phonon spectrum at such high temperatures. A marked difference between FeCo and pure iron is the presence of two dissimilar atoms in the primitive cell, which consequently produces optical modes. If one of these modes goes soft at the α-γ transition, then appreciable change in ρ and the DWF will be observed. Our experimental results strongly indicate the active role played by the lattice modes in the dynamics of the OD and α-γ transitions.

C. Center shift (CS)

The shift of the Mössbauer centroid is given by the isomer shift (IS) and the second-order Doppler shift (SODS). The IS is given by[14]

$$\delta V_{\mathrm{IS}} = 6.105\,(Z/E_\gamma)\Delta\langle r^2\rangle\,\Delta\rho(0)\,, \tag{6}$$

where δV_{IS} is the IS in mm/sec, $\Delta\langle r^2\rangle$ is the change in mean-square nuclear radius ($\Delta\langle r^2\rangle = \langle r^2\rangle_{\mathrm{excited}} - \langle r^2\rangle_{\mathrm{ground}}$ and is given in units of fm^2), $\Delta\rho(0)$ is the difference between electron densities due to excited and ground states at the nucleus (units of a_0^{-3}); E_γ is the transition energy in keV, and Z is the atomic number. The shift due to SODS is given[15] by

$$\delta E = -\,(E_\gamma/2)\frac{\langle v^2\rangle_T}{c^2}\,, \tag{7}$$

where $\langle v^2\rangle_T$ is the thermal average of the square of the velocity of the vibrating atom, and c is the velocity of light. For high temperatures and using the effective weighted Debye temperature for the isotropic case, one has[10]

$$-\frac{\delta E}{E_\gamma} = \frac{3}{2}\,\frac{k_B T}{Mc^2} + \frac{3}{40}\,\frac{k_B\Theta_D^2(2)}{Mc^2 T} + \cdots\,, \tag{8}$$

where M is the mass of the Mössbauer atom. It is evident that the SODS is strongly temperature dependent. On the other hand, the IS depends very weakly on temperature, mainly through lattice expansion. One expects in general to observe a discontinuity in the IS at a first-order phase transition.

In Fig. 5 we have plotted the CS versus temperature for $297 < T < 1360$ K. For $500 < T < 900$ K the temperature dependence of the CS can be explained by the SODS alone, i.e., the leading term of Eq. (8), since we are already in the high-temperature limit. Near the OD transition temperature there is a small indication of a change in the CS. This could be produced by a change in the phonon spectrum, since one does not expect any appreciable difference in the IS. At the α-γ transition the slope of the CS vs T is given by the classical limit, but a small discontinuity in the centroid is necessary

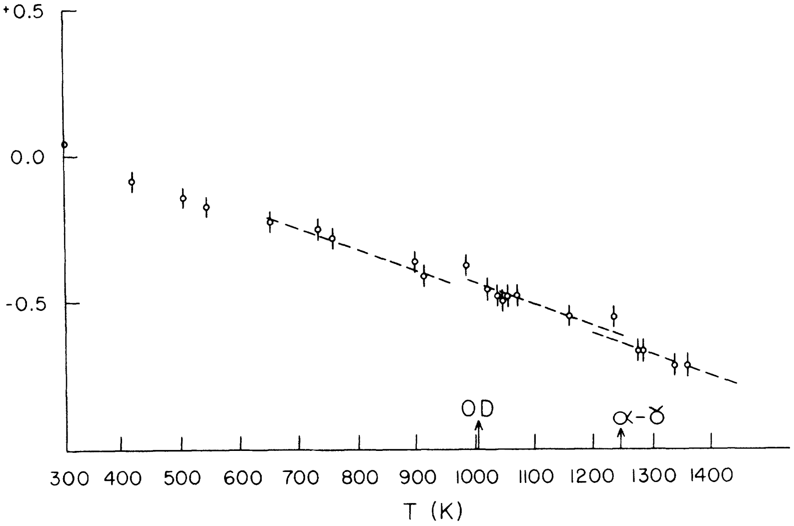

FIG. 5. Center shift in mm/sec vs temperature of FeCo. Dashed line is the high-temperature limit.

to fit all the points. The discontinuity, of 0.04 mm/sec., is about the same magnitude as the experimental error. The above change is equivalent to an increase in the 4*s* electron density of around 2%. The change in the IS at the α-γ transition in FeCo is much smaller than the one observed in pure iron.[4,12] In summary, the IS does not show dramatic changes at the OD and α-γ transitions in the nearly equiatomic FeCo alloy.

IV. CONCLUDING REMARKS

Measurements reported here show that at the $\alpha \rightarrow \gamma$ transition, a considerable softening of the lattice occurs. This results confirms the suggestion made earlier from the electrical resistivity measurements.[2] Elastic constant and neutron scattering measurements in single crystals are needed to gain insight as to which phonon modes are responsible for this transition. Another important result of this study is the lack of proportionality between the internal field at ^{57}Fe nucleus and the bulk magnetic moment near and above the order-disorder transition. Our analysis shows that the nearest-neighbor conduction-electron polarization contribution to the internal field in FeCo is primarily responsible for this difference. Further theoretical work in this area is clearly needed.

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