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Composition dependence of the order-disorder transition in iron-cobalt alloys

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The order-disorder phase transition in iron-cobalt alloys has been investigated by neutron-powder diffraction techniques for a composition range from 30- to 70-at.% cobalt. There appears to be a critical order-disorder phase transition throughout the composition range. The plot of the transition temperature against composition shows a peak at 47.9 ± 0.3-at.% cobalt; this is unexpected since simple theories predict a peak at the stoichiometric 50% composition and such a result is not compatible with our data. To within error, the critical index β of the order parameter is independent of composition; its weighted mean value is 0.303 ± 0.004.

I. INTRODUCTION

In recent years, there has been much interest in alloys which undergo a critical phase transition from ordered to disordered states. Such systems have a one-dimensional order parameter and would be expected to tie in with the general theory of critical phenomena in an interesting way. So long as the ordering interactions are of short range, the transition should follow the predictions of the Ising model. This model has been studied theoretically in a most extensive way because it is one of the simplest models which displays a critical phase transition.

Iron-cobalt is one of the few alloy systems which undergo a critical phase transition from ordered to disordered states. These alloys have a body-centered-cubic lattice at low temperatures from pure iron to about 75-at.% cobalt. The alloy shows an order-disorder transition into the cesium chloride structure for compositions which are close to 50%. It has been established that ordering occurs over the composition range 40–60-at.% cobalt and there is much indirect evidence that ordering occurs over a wider range of composition.[1,2]

A direct way of investigating the ordering is by neutron diffraction. In this method, long-range ordering manifests itself by the appearance of extra ("superlattice") lines in the diffraction pattern. The intensity of the superlattice lines depends on the degree of order and on the difference between the scattering lengths of the atoms involved. Neutron-scattering techniques are especially suitable for the iron-cobalt system because the neutron's scattering length from iron is nearly a factor of 4 larger than from cobalt.

The first aim of this investigation was to study the nature of the order-disorder transition at different compositions. The second aim was to study the composition dependence of the order-disorder transition temperature and to compare the results with predictions based on the Ising model.

In this paper we report our investigation of the order-disorder transition in FeCo in the composition range 30– 70-at.% cobalt. The results for stoichiometric 50-50 alloys have been previously presented elsewhere.[3]

II. EXPERIMENTAL

Twelve compositions were prepared separately from weighed amounts of Johnson-Mathey 99.99%-purity iron and cobalt. The materials were melted together and cast into the form of plates 4 mm thick. Each plate was annealed at a temperature 100 °C below its melting point and then ground down to a thickness of 2.0 mm. The 12 specimens were chemically analyzed after the experiment and found to contain 29.6-, 34.6-, 40.0-, 45.1-, 47.5-, 49.4-, 50.2-, 52.2-, 55.1-, 59.9-, 64.7-, and 69.5- (± 0.3) at.% cobalt, respectively. In every case these amounts were within 0.6% of the composition calculated from the weights of the starting ingredients.

The Powder patterns of the first set of samples to be investigated were taken with the spectrometer[4] at the McMaster University nuclear reactor. The compositions were 45.1-, 49.4-, 50.2-, and 55.1-at.% cobalt. The beam had a wavelength of 0.996 Å and the Bragg peaks had less than 0.1% contamination from half wavelengths. Because of the much higher neutron flux of the NRU reactor at the Chalk River Nuclear Laboratories, the powder patterns of the rest of the specimens were taken at that reactor using the McMaster University double axis spectrometer. The beam had a wavelength of 1.005 Å and the Bragg peaks again had less than 0.1% contamination from half wavelengths. The long-range order in each specimen was determined by measuring the intensity of the (110) superlattice peak. Relaxed collimation was employed through-

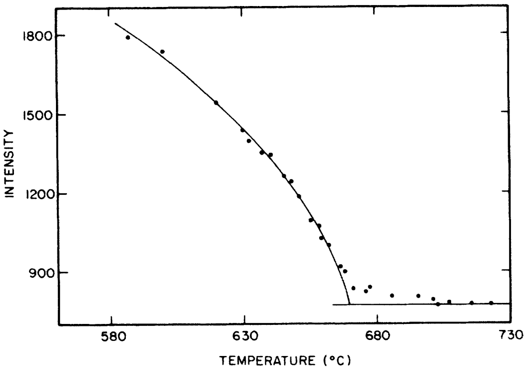

FIG. 1. Temperature dependence of the (100) superlattice peak intensity in FeCo, 34.6-at.% cobalt.

out. Powder specimens were used so extinction effects should not be important. The measurements were made while the specimen was maintained in the neutron beam at a controlled temperature by means of a vacuum furnace. The temperature was stable to better than 1 °C at around 725 °C.

In each specimen, the measured width [full width at half maximum (F.W.H.M.)] of the (100) superlattice peak was the same at low temperatures and close to T_c, to within experimental error. As this width of 0.80° was equal to the instrumental resolution width, it can be concluded that the samples had long-range order. To determine the order parameter it is necessary to measure the intensity of the superlattice peak as a function of temperature. Strictly we need to measure the integrated intensity of the peak, but since the peak widths (and shapes) were found to be independent of temperature at a few trial temperatures, measurements were just made of the peak height at most temperatures. If the order was of long range, theory would predict sharp peaks with width independent of temperature. With the coarse resolution used, there was no detectable shift of the peak center with temperature for either the fundamental or the superlattice line over the temperature range used.

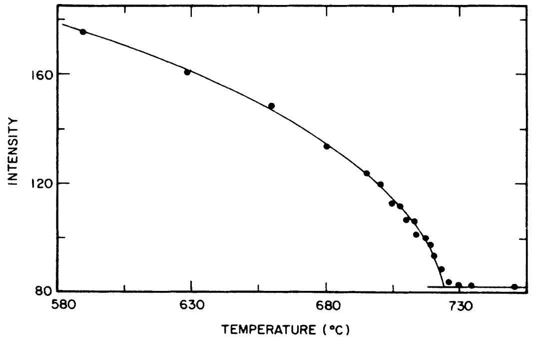

FIG. 2. Temperature dependence of the (100) superlattice peak intensity in FeCo, 50.2-at.% cobalt.

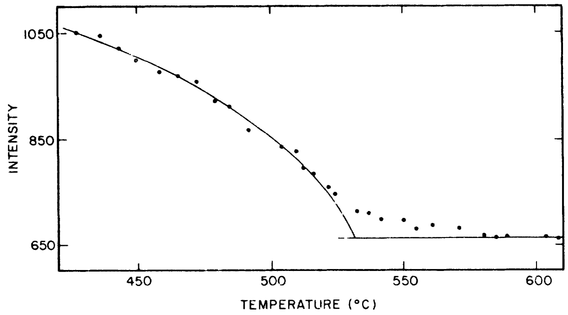

FIG. 3. Temperature dependence of the (100) superlattice peak intensity in FeCo, 69.5-at.% cobalt.

This method of collecting and interpreting data is bound to run into difficulties very close to T_c where there is critical scattering as well as scattering due to long-range order. To calculate properly the magnitude of the critical scattering, it would be necessary to know more about the system than is currently known. However, an estimate of the effect can be made by examining the apparent rounding of the data at the critical temperature for the stoichiometric alloy. The peak intensity varies with reduced temperature according to a simple power law except for a rounding within 2 °C of T_c. This observation and the temperature independence of the scattering at the superlattice position at higher temperatures indicates that the measurements can be interpreted as giving the superlattice peak intensity except within about 2 °C of T_c.

The variation of the intensity of the (100) superlattice peak with temperature for 34.6-, 50.2-, and 69.5-at.% cobalt is shown in Figs. 1–3, respectively. The behavior is qualitatively what is expected for a critical phase transition at temperatures of about 669, 724, and 532 °C, respectively. The measurements were repeatable and showed no hysterisis effects; the results are analogous to those obtained in the remaining samples. There was no anomaly in the intensity versus temperature curve of any of the samples at about 550 °C in contrast to some authors[5,6] who have reported such an anomaly in the specific heat versus temperature curve. There is a rounding of T_c in all the samples. The magnitude of this rounding increases as the alloy composition becomes further from the stoichiometric 50% composition. It is likely that this effect is due to microscopic inhomogeneities in the specimen, since, as will be demonstrated later, T_c varies rapidly with composition for alloys far from stoichiometry.

Just below T_c, the superlattice peak appeared to change intensity to its new equilibrium value immediately as the temperature was changed. Below about 450 °C the intensity ceased to vary appreciably with temperature; this is presumed to have happened because diffusion becomes too slow at these temperatures to bring the specimen into equilibrium during the course of the measurements.[7]

III. RESULTS AND DISCUSSION

The intensity of the superlattice peak I, is given by

$$I \propto S^2[(b_{\mathrm{Fe}}\, e^{-W_{\mathrm{Fe}}} - b_{\mathrm{Co}}\, e^{-W_{\mathrm{Co}}})^2 + q^2(p_{\mathrm{Fe}}\, e^{-W_{\mathrm{Fe}}} - p_{\mathrm{Co}} e^{-W_{\mathrm{Co}}})^2],$$

where b and p are the nuclear and magnetic scattering lengths. q, W, and S are, respectively, the magnetic interaction vector, the Debye-Waller factor, and the order parameter. The alloys remain ferromagnetic at temperatures well above the critical ordering temperature so that it seems reasonable to neglect the temperature dependence of p over small ranges of temperature just below T_c. The Debye-Waller factors are near to unity for the first superlattice peak, but they may make an important contribution to the intensity and its temperature dependence if the scattering lengths of the constituents are almost the same. This was demonstrated by Chipman and Walker[8] for the interpretation of x-ray data from CuZn where the x-ray form factors are close to being equal. The effect is less important but still significant for the neutron data in CuZn because the scattering lengths are close to being equal with $(b_{\mathrm{Cu}} - b_{\mathrm{Zn}}) / (b_{\mathrm{Cu}} + b_{\mathrm{Zn}}) = 0.14$. In FeCo the scattering lengths are much less similar with a corresponding factor of 0.55. This reduces substantially the influence of the Debye-Waller factor. Further, the physical properties of iron and cobalt are more similar than those of copper and zinc so one might expect their Debye-Waller factors to be more nearly equal. In view of these points we have neglected the temperature dependence of W near to T_c, so that the intensity of the superlattice line is taken to vary with temperature in the same way as the square of the order parameter near to T_c.

A log-log plot of the intensity versus the reduced temperature $(1 - T/T_c)$ for 29.6-, 50.2-, and 69.5-at.% cobalt is shown in Fig. 4. All the plots fit straight lines over a considerable range of reduced temperature. For these plots T_c was selected so as to make the graph most nearly linear at small values of reduced temperature. The fits go to within about 10, 2, and 15 K of the critical temperature, showing how there is a much larger amount of apparent rounding of T_c for the most nonstoichiometric alloys.

To estimate the errors in T_c and in the slope of the plots, similar plots were made with slightly different values of T_c. For the 50.2%-alloy, plots for $T_c = 999$, 997, and 995 K gave linear fits to within 6, 2, and 5 K of their assumed critical temperatures with fitted slopes of 0.655, 0.615, and 0.545, respectively. We arbitrarily defined the error in T_c and in the slope as the difference between the best-fit values and the (interpolated) values where the departures from the linear plot commence twice as far from T_c as for the best fits. For the 50.2%-alloy case quoted above this corresponds to an error in the slope of 0.02 on the high-temperature side and 0.04 on the low-temperature side.

The slopes in Fig. 4 are 0.600, 0.615, and 0.605 for the three alloys, respectively; since the intensity is proportional to S^2, the critical index β is therefore 0.300, 0.308, and 0.303 for the three specimens. Values of β for the other specimens were obtained in a similar manner; and these are given in Table I. There is no discernible composition dependence of β and a weighted mean value of the results gives $\beta = 0.303 \pm 0.004$.

The best theoretical estimate of the critical exponent β for an Ising model is 0.312 ± 0.005.[9] As found in other experiments, the experimental value obtained for β is slightly lower than the theoretical estimate. In β-brass, Norvell and

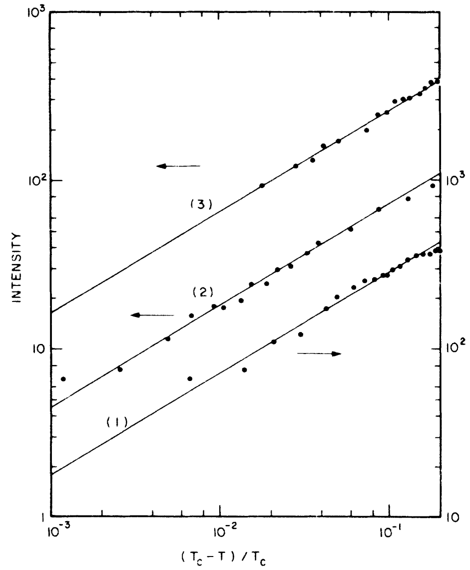

FIG. 4. Log-log plot of the (100) superlattice peak intensity against the reduced temperature in 29.6-at.% cobalt (1) 50.2-at.% cobalt (2), and 69.5-at.% cobalt (3). The slopes of the lines are 0.600, 0.615, and 0.605, respectively.

TABLE I. Order-disorder critical temperature T_c and exponent β as measured in each specimen. The errors in the composition and transition temperature are of the order 0.3 and 2 K, respectively.

Composition (at. % Co)	Transition temperature T_c (K)	Critical exponent β
29.6	865	0.300 ± 0.014
34.6	942	0.315 ± 0.014
40.0	980	0.300 ± 0.011
45.1	993	0.302 ± 0.011
47.5	998.5	0.293 ± 0.008
49.4	995	0.295 ± 0.010
50.2	997	0.308 ± 0.014
52.2	989	0.300 ± 0.010
55.1	975	0.308 ± 0.007
59.9	946	0.319 ± 0.018
64.7	892	0.321 ± 0.018
69.5	805	0.303 ± 0.018

Als-Nielson[10] find $\beta = 0.304 \pm 0.007$ and in Fe_3Al, Guttman *et al.*[11] find $\beta = 0.307 \pm 0.011$. Baker and Essam[12] have suggested that lattice compressibility may reduce the critical index slightly. Within the limit of errors our values of β are comparable with the experimental results for other alloy systems.

Figure 5 shows the composition dependence of T_c. There is a well-defined maximum in T_c and it is quite clear that this occurs at a cobalt concentration which is less than the stoichiometric value of 50%.

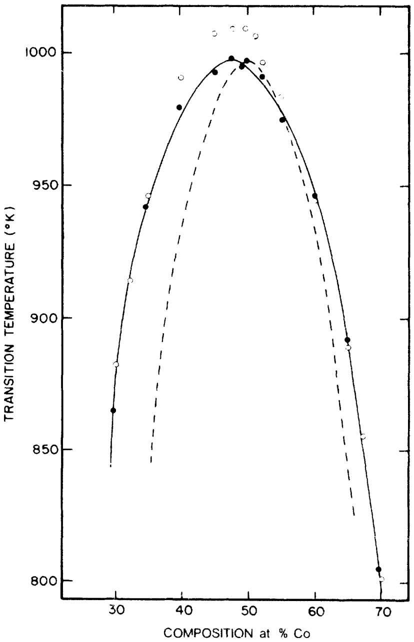

FIG. 5. Composition dependence of the order-disorder transition temperature of FeCo. The solid points are our data and the open circles are those of Asano *et al.* (Ref. 6). The solid line is the nonlinear least-squares fitting of our data and the dashed line gives the calculated values of Bienenstock and Lewis (Ref. 15).

Figure 5 also shows the specific-heat data of Asano *et al.*[6] Our results agree with those of Asano *et al.* at compositions away from the peak of the curve but not around the peak. A more recent specific-heat measurement on the 50-50 alloy by Orehotsky *et al.*[13] gave a critical temperature of 995 K in good agreement with our value of 996 ± 1 K and significantly lower than the value of 1009 K given by Asano *et al.*[6] We should also note that the specific-heat data of Asano *et al.*[6] indicated an anomaly at around 820 K for equiatomic alloys; our measurements indicate that this effect is not connected with the order-disorder process.

Whatever the source may be of the discrepancy in values of T_c, it is interesting to note that the measurements of Asano *et al.* give a shift in the position of the peak by about the same amount as is given by our data. This shift is surprising, as for a first guess one might expect the peak to be at the stoichiometric composition.

Since it is assumed in the Ising model that the transition occurs at a constant volume—because the interaction energies can be expected to vary with composition if the lattice parameter changes—a better comparison of the observed composition dependence of T_c with the predictions based on the Ising model could be made by converting the values of the observed T_c's to values corresponding to constant lattice parameter. Yoon and Jeffery[14] have made such correction by combining their data of the pressure dependence of T_c with the T_c's measured by Asano *et al.* in the composition range 40–60-at.% cobalt. The resulting composition dependence of T_c is only slightly different and the asymmetry about the stoichiometric composition remains.

Bienenstock and Lewis[15] have calculated the critical temperature as a function of composition using the low-temperature series-expansion treatment of the Ising model and the Padé-approximant techniques. For the bcc lattice, they predicted a quadratic variation of the form

$$T_c(c)/T_c(0.5) = [1 - 9.007(c - 0.5)^2]^{0.739};$$

T_c and c are, respectively, the critical temperature and atomic composition. The predicted variation is quite different from the observed variation as shown in Fig. 5, assuming $T_c\ (0.5) = 997$ K. Since the observed composition dependence of T_c is not symmetric about the 50-50 composition, we tried a least-squares fit to

$$T_c(\mathrm{max}) - T_c = A[c - c(\mathrm{max})]^2,$$

where T_c (max) is the maximum T_c and $C(\mathrm{max})$ is the composition for which it was observed. The fit is not satisfactory. The data was then least-squares fitted to an expression like that of Bienenstock and Lewis, viz.,

$$T_c/T_c(\mathrm{max}) = \{1 - p[c - c(\mathrm{max})]^2\}^q .$$

The result is shown in Fig. 5. The values obtained for $T_c(\mathrm{max})$, $c(\mathrm{max})$, p, and q are 997.4 ± 1.6 K, 0.479 ± 0.003, 10.8 ± 1.6, and 0.306 ± 0.061, respectively. It has also been observed in β-brass that the composition dependence of T_c predicted by Bienenstock and Lewis does not agree with experimental results. Yoon and Bienenstock[16] have shown that the Ising model with a single volume-dependent ordering interaction is insufficient to describe the order-disorder transition in β-brass over the composition range in which it is observed.

We must conclude that the order-disorder transition in iron-cobalt alloys cannot be interpreted in terms of a simple Ising model with nearest-neighbor interactions.

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