[6]R. V. D'Aiello and S. J. Freedman, Bull. Am. Phys. Soc. 13, 1742 (1968), and to be published.
[7]D. C. Mattis and J. Bardeen, Phys. Rev. 111, 412 (1958).
[8]B. Abeles, R. W. Cohen, and W. R. Stowell, Phys. Rev. Letters 18, 902 (1967).
[9]R. E. Glover and M. Tinkham, Phys. Rev. 108, 243 (1957).

VARIATION OF LONG-RANGE ORDER IN Fe_3Al NEAR ITS TRANSITION TEMPERATURE*

L. Guttman, H. C. Schnyders, and G. J. Arai†
Argonne National Laboratory, Argonne, Illinois
(Received 20 November 1968)

The long-range order parameter of the fcc ordered Fe_3Al structure, as measured by x-ray scattering, varies as $(T_C-T)^\beta$, with $\beta=0.307$, in the range between 1 and about 10 K below T_C (823 K).

Of the many order-disorder transformations in binary metallic solid solutions, only a handful appear to be other than first order in the thermodynamic sense. These are the transitions from the $L2_0$ structure to $A2$ in CuZn, FeCo, and FeAl, and that from $D0_3$ to $L2_0$ in Fe_3Al. The scanty evidence for this classification has been reviewed[1] by one of us. In the light of a possible connection between the crystal structure and the order of the transformation, it seemed desirable to verify that some order-disorder transformations do take place without any isothermal discontinuity in long-range order and, therefore, presumably without a latent heat. For such transformations, it also seemed desirable to study the behavior of the pair-correlation function in detail near the transition temperature. An x-ray investigation of Fe-Al alloys was begun because the components of this system differ far more in x-ray scattering amplitude than do those of either of the other two systems mentioned above. In this Letter, we are presenting our results on the variation of the long-range order parameter with temperature near the $D0_3 \rightarrow L2_0$ transition ($T_C \cong 823$ K). We have also measured the "critical" diffuse scattering above T_C, but interpretation of these data is strongly dependent on corrections for instrumental resolution, and is reported in the following Letter.[2]

The starting material for the sample was an ingot containing 29.2-at.% aluminum, made by the Hamilton Watch Company. A 5-kg piece of this ingot, after annealing for 40 h just below its melting point, had substantially one orientation. A slab with faces parallel to (111) was cut from this crystal, and annealed at 1375°C for 48 h in hydrogen to reduce composition variations. The final specimen was a disk about 1 cm in diameter and 1 mm thick. The face exposed to the x-ray beam was polished metallographically, last with 1-μ diamond powder, and was lightly etched to remove traces of cold work. The opposite face was brazed to the end of a copper cylinder, on whose lateral surface was wound a Nichrome wire heater insulated with MgO from its stainless steel sheath. The furnace, with surrounding radiation shields, was supported on a goniometer of the "Eulerian cradle" type, in an evacuated chamber mounted on the spindle of a commercial x-ray diffractometer.

Temperatures constant to about ±0.02°C for many hours were achieved by proportional control of the heating power, the controlling signal being the difference between a fixed emf and that from a Chromel-Alumel thermocouple attached to the furnace. A very low-noise, commercial breaker amplifier provided the necessary gain of about 6000 between the error signal and the input to the controller.

The x rays were the chromium $K\alpha$ radiation from a tube operated at 50 kV and 30 mA, selected by diffraction from (200) "planes" of a lithium fluoride crystal plastically bent to a toroidal form. The detection system, using a xenon proportional counter and pulse-height selection, was of standard commercial design, except that the incident beam was continually monitored. For this purpose, the beam passed through a thin, uniform titanium foil, the fluorescence from which was counted and used to drive the electronic timer. All intensity measurements were thus automatically normalized to constant incident flux.

The square of the long-range order parameter of the $D0_3$ structure is proportional to the intensity of any Bragg reflection with all odd indices, referred to the fcc unit cell containing 16 atoms. We measured the first and most intense of these, (111), in several series. The goniometer was set at the orientation giving maximum intensity,

and the counts were taken point by point, in the radial direction in reciprocal space (θ-2θ scan). The angular steps were small enough that integration by the trapezoidal rule and by Simpson's rule agreed to better than 0.1%, and the latter value was chosen to be the integrated intensity.

We have deliberately subjected the sample to a complex thermal treatment in order to reveal hysteresis. The sample has been heated and cooled repeatedly over the range $T_c \pm 50$ K, and the intensity has been measured at constant temperature after waiting times between 15 min and 15 h. We find that the (111) integrated intensity shows no isothermal discontinuities, and that it is quite reversible (but see below for qualifications). These measurements were made during two main periods of time, the first of which was terminated by a failure of the furnace heater. We used this interruption to realign the apparatus and to improve the method of attaching the thermocouples to the furnace. During the second period, the sample cooled accidentally when a vacuum pump failed. These incidents preclude a unified analysis of all our data. We have divided the measurements into series taken generally at temperatures in a rising or falling sequence. To each series we have fitted an equation of the form

$$I_{111} = A\left(\frac{T_c - T}{T_c}\right)^{2\beta} \qquad (1)$$

by a weighted least-squares method, and in the following, we discuss the representation of our results by the parameters β, A, and T_c.

Of these parameters, only β has any general significance. It was sufficient for our purposes to measure relative intensities on an arbitrary scale; moreover, we have relied for the temperature of the sample on the stability of the emf-temperature relation of the thermocouple and on the constancy of thermal contact between the two. The parameters A and, to a lesser extent, T_c are therefore particular to our experimental arrangement. However, some indication of the precision of our measurements of β can be obtained from the variations of A and T_c between series.

A crucial point in the least-squares procedure is the choice of weights.[3] We have used the logarithmic form of Eq. (1) with weights, w, given by

$$\frac{1}{w} \propto (\delta \ln I)^2 + \left(\frac{2\beta \delta T}{T_c - T}\right)^2, \qquad (2)$$

where $\delta \ln I$ is the fractional error of the intensity, and δT is the error of the temperature. From numerous measurements of the (222) integrated intensity, which is nearly temperature independent, we estimate that $\delta \ln I$ is about 1%, and not at all limited by the counting statistics. The temperature error is somewhat harder to estimate, but is only important very close to T_c; we have chosen the constant value 0.02 K. Preliminary estimates of β and T_c are accurate enough for the weighting, and the solution of the three simultaneous least-squares equations is easily carried out by algebraic elimination of the two parameters that appear linearly (β and $\ln A$), after which T_c is found by Newton's method as the root of a transcendental equation. The errors of the parameters were estimated from the external consistency[3] of the data.

We were troubled, during the second main period, by occasional abrupt changes in the (111) intensity, amounting to several percent. These changes could not be traced to any purely instrumental cause, either in the counting system or in the temperature measuring apparatus, and their occurrence was not correlated with the thermal history of the sample. We have eliminated from our analysis only data that could not (because of an obvious intensity discontinuity) be grouped into series taken in a monotonic sequence of temperatures covering a wide temperature range, from about 1 to about 10 K below T_c. We estimate that the diffuse scattering contributes less than 1% to the integrated intensity at 1 K below T_c, from our measurements[2] above T_c, and the Ising-model result[4] that the ratio of the peak intensities at equal intervals above and below T_c is about 5:1. A few measurements extending to 22 K below T_c show no significant deviations from Eq. (1), so we feel that our choice of the lower temperature limit ($T_c - 10$ K) is conservative.

We have made about 500 individual intensity measurements, nearly equally divided between the two periods, that can be grouped into 13 heating series and 15 cooling series. We find that the weighted mean of $\ln A$ in the heating series differs from that in the cooling series by -0.010 ± 0.008, the error being obtained from the observed variance of A. This is not significantly different from zero, as would be expected. On the other hand, the critical temperature estimated from heating series is greater than that from cooling series by 0.14 ± 0.02 K. This suggests that complete equilibrium was not attained, although it should be pointed out that this is not at all evident from a direct comparison of indivi-

dual intensity measurements, or even of individual series. Ordering is probably slower than disordering[1]; so the heating series are probably closer to equilibrium.

The results for the exponent β are given in some detail in Table I. It is clear that the average exponent on heating is somewhat greater than that on cooling, and the large values of χ^2 show that the error limits set by external consistency are rather optimistic. The mean of the values in Table I, weighted inversely as χ^2, is $\beta = 0.307$, with standard error 0.003. The limits ± 0.011, which include 21 of our 28 measurements of β, would be at least 5σ for the mean. However, since there is manifestly some irreversibility, the error in β may be somewhat greater than that given by purely statistical arguments.

We may now rather confidently assert that the long-range order parameter for the $D0_3$ structure varies as $(T_C - T)^\beta$, β having the value given above. The other sources of variation of the (111) intensity are (a) the temperature dependence of the thermal diffuse scattering; to a good approximation, this is also proportional to S^2, over this short temperature interval, and it is always a small fraction of the total; (b) the Debye-Waller factor, which we estimate to vary less than 0.1% over the relevant range; and (c) extinction, which we estimate to be small even at much lower temperatures.

The observed continuity of S shows that this transformation is not first order. We may therefore compare the exponent β with the values predicted from the phenomenological theory of second-order phase transitions[5] and with the numerical estimates for the Ising model for cubic crystals.[4,6] If the transition were truly of second order (no latent heat, but a finite jump in heat capacity), β would have the value $\frac{1}{2}$, and the (111) intensity would vanish linearly with $T_C - T$, with a finite slope at T_C. This it clearly does not do. On the other hand, the Ising-model prediction[4] is that $0.303 \leq \beta \leq 0.318$, or more narrowly,[6] that $0.307 \leq \beta \leq 0.314$. Our result is within these limits, although somewhat below the conjectured "exact value," $\frac{5}{16} = 0.3125$. The Ising model is therefore in quantitative agreement with this aspect of the transformation, as was found[7] for the analogous transformation in β brass.

Table I. Mean values of exponent β.

Main period		Number of series	β	σ[a]	χ^2
I	Heating	7	0.3073	0.001	5
	Cooling	7	0.3005	0.005	63
II	Heating	6	0.3145	0.002	26
	Cooling	8	0.2978	0.002	14

[a]Standard deviation estimated from observed variance.

We are indebted to R. D. Lowde, for the suggestion that order-disorder transformations might exhibit "critical" behavior. This work was begun at the General Electric Research Laboratory. At Argonne National Laboratory, we have had much able assistance, particularly from Nicholas J. Gaspar, Edward Edwards, and Carl A. Feickert.

*Based on work performed under the auspices of the U. S. Atomic Energy Commission.

†Present address: Zenith Radio Corporation, Chicago, Ill.

[1]L. Guttman, Solid State Phys. 3, 146 (1956).

[2]L. Guttman and H. C. Schnyders, following paper [Phys. Rev. Letters 22, 520 (1968)].

[3]W. E. Deming, Statistical Adjustment of Data (John Wiley & Sons, Inc., New York, 1943).

[4]J. W. Essam and M. E. Fisher, J. Chem. Phys. 38, 802 (1963).

[5]L. Landau, Phys. Z. Sowjetunion 12, 123 (1937); L. Landau and E. M. Lifshitz, Statistical Physics (Addison-Wesley, Inc., Reading, Mass., 1958), Chaps. XII and XIV, and references cited therein.

[6]G. A. Baker, Jr., and D. S. Gaunt, Phys. Rev. 155, 545 (1967); the quantity actually treated here and in Ref. 4 is the spontaneous magnetization, but this is isomorphous to the long-range order.

[7]J. Als-Nielsen and O. W. Dietrich, Phys. Rev. 153, 706, 711, 717 (1967).