TABLE I. Summary of data for the Hg-In alloys.

Metal	T_c	θ_D	γ (cal/mole-deg^2)	m^*/m
Hg	4.15	73[a]	$4.57^e\times10^{-4}$	1.9
$Hg_{0.20}In_{0.80}$	4.6	69.0[b]	3.85[d]	1.4
$Hg_{0.10}In_{0.90}$	3.2	83.5[b]	3.89[d]	1.4
In	3.4	111[c]	3.94[e]	1.4

[a] R. L. Douglass, R. G. Petersen, and N. E. Phillips, in *Proceedings of the Seventh International Conference on Low Temperature Physics*, edited by G. M. Graham and A. C. Hollis Hallett (University of Toronto Press, Toronto, Canada, 1961), p. 403.
[b] Lindemann melting rule. See text.
[c] B. S. Chandrasekar and J. A. Rayne, Phys. Rev. 124, 1011 (1961).
[d] Estimated on modified free-electron model. See text.
[e] J. E. Schirber and C. A. Swenson, Phys. Rev. 123, 1115 (1961).

with an effective mass m^*. In Eq. (A3), V_a is atomic volume and n the number of electrons/atom. For In, $n=3$, and the 80 and 90% In alloys $n=2.8$ and 2.9, respectively. Since N is related to the electronic specific heat, it can be determined calorimetrically. If this is done for In,[23] the value obtained satisfies Eq. (A3) for $m^*/m=1.4$. Consequently, we will use this value of m^* for the fcc solid solutions, obtaining the values of γ ($C_e=\gamma T$) shown in Table I.

We observe that, in going from 80 to 90% In, both γ, which is directly proportional to N ($\gamma=\frac{1}{3}\pi^2k^2N$), and θ_D increase with increasing indium content in the range 80–90% In, but that T_c decreases. Equation (1), therefore, does not give even a qualitative description of the situation, since it predicts an increase in T_c if θ_D and N both increase and V is approximately constant.

If we ask what variation in V is necessary to fit the data for T_c, we find

$$V(80\%\ \text{In})/V(90\%\ \text{In})=1.15. \qquad \text{(A4)}$$

Since use of the Lindemann rule to calculate θ_D is probably the least certain assumption in the above calculation, we verify the insensitivity of the conclusion to this result. If we assume, as an extreme case, $\theta_D(80\%\ \text{In})=\theta_D(90\%\ \text{In})=83.5°\text{K}$, we calculate the ratio (A4) to be 1.10 instead of 1.15.

It is difficult to understand a 15% variation in V over a 10% composition range in a single phase solid solution alloy where the lattice parameter does not change appreciably and the density of states presumably reflects only a 3% change in number of conduction electrons/atom.

We conclude that our results for compositions $Hg_{0.20}In_{0.80}$ to $Hg_{0.10}In_{0.90}$ are not well described by Eq. (A1).

[23] J. M. Ziman, *Electrons and Phonons* (Oxford University Press, New York, 1960), p. 117.

PHYSICAL REVIEW VOLUME 130, NUMBER 5 1 JUNE 1963

Neutron Diffraction Study of Short-Range Order in β-CuZn*

C. B. WALKER
Institute for the Study of Metals, University of Chicago, Chicago, Illinois
AND
D. T. KEATING
Brookhaven National Laboratory, Upton, New York
(Received 25 January 1963)

Neutron diffuse scattering measurements have been made on an isotopically enriched single crystal of β CuZn at a series of temperatures above T_c. The observed short-range order scattering exhibited the general characteristics of critical scattering, quite unlike the diffuse scattering reported for any other ordering alloy, and confirmed that the order-disorder transformation in this alloy is a phase transformation of second (or higher) order. No quantitative evaluation of the short-range order parameters from the measured scattering was possible. A comparison of the measured scattering with calculations based on the theories of Zernike, Cowley, and Elliott and Marshall showed rather good agreement, suggesting that these simple theories give a reasonable approximation to the actual short-range order correlations above T_c. From a consideration of the discrepancies between these theories and the experimental data, it appears that at temperatures above T_c the Ising model forms a surprisingly good model for this alloy.

INTRODUCTION

X-RAY diffuse scattering studies of short-range order in binary alloys have centered primarily on alloys with face-centered cubic lattices,[1] such as the well-known Cu_3Au. Only three such studies have been made on alloys of an equally interesting type, the equiatomic body-centered cubic alloys, and in two of these (LiMg [2] and MoTi [3]) the alloys do not order at any temperature, while in the third[4] (β-AgZn) a complex hexagonal

* Research supported in part by the Atomic Energy Commission and by the U. S. Army Research Office (Durham).
[1] See, for example, the review by B. E. Warren and B. L. Averbach, in *Modern Research Techniques in Physical Metallurgy* (American Society for Metals, Cleveland, 1953).
[2] F. H. Herbstein and B. L. Averbach, Acta Met. 4, 414 (1956).
[3] J. Dupouy and B. L. Averbach, Acta Met. 9, 755 (1961).
[4] E. Suoninen and B. E. Warren, Acta Met. 6, 172 (1958).

ζ phase intervenes between the ordered and disordered phases. No x-ray diffuse scattering study has been possible for an equiatomic bcc alloy that undergoes an order-disorder transformation free from complications, because in the few alloys that do meet these criteria (viz., β-CuZn, FeCo) the alloying elements are close neighbors in the periodic table, and the similarity of the two x-ray scattering factors makes the intensity of the diffuse scattering unobservable.

Neutron diffraction offered a possible technique for studying the short-range order scattering from these alloys. The average neutron scattering lengths differ appreciably for these particular pairs of atoms,[5] and this difference can be enhanced in some cases by using separated isotopes, so the short-range order diffuse scattering should be observable. Scattered intensities could be expected to be weak, because of the low intensity of available monochromatic neutron beams, but reliable measurements were thought to be possible. Thus, we decided to try this approach in a study of short-range order in β-CuZn.

The alloy β-CuZn occurs in a rather narrow composition range on the Cu-rich side of the 1:1 composition.[6] At room temperature, the atoms form an essentially perfectly ordered CsCl structure. As the temperature increases, the long-range order decreases continuously and goes to zero at the critical temperature, T_c, with effectively infinite slope.[7] Above the critical temperature, which varies from 468°C at the Zn-rich side to 454°C at the Cu-rich side, the structure is disordered body-centered cubic. This phase transformation is one of the classical examples of order-disorder transformations in alloys,[8] and it has been the object of many experimental and theoretical investigations.[8,9] It is also one of the few order-disorder transformations that are generally thought to be true second-order (or higher order) phase transformations,[9] so a knowledge of its short-range order correlations above the critical temperature should be of considerable interest.

EXPERIMENTAL PROCEDURE AND RESULTS

The theory of the diffuse scattering due to local ordering of the atoms in a binary alloy has recently been modified to include the effects of thermal vibrations[10] and of static displacements due to differing atomic sizes.[11,12] Using this, the differential cross section for neutron short-range order scattering by a single crystal can be written approximately as

$$(d\sigma/d\Omega)=x(1-x)(b_A-b_B)^2\sum_j\alpha(r_j)e^{-C_j|\mathbf{K}|^2}e^{i\mathbf{K}\cdot\mathbf{r}_j}, \quad (1)$$

where x is the atomic fraction of atoms of type A; b_A is the scattering length of an A atom; $\alpha(r_j)=1-P_{AB}(r_j)/x$, where $P_{AB}(r_j)$ is the probability of finding an A atom on a site a distance $\mathbf{r}_j$ from a site occupied by a B atom; and $\mathbf{K}=2\pi(\mathbf{S}-\mathbf{S}_0)/\lambda$, where λ is the neutron wavelength, and $\mathbf{S}$ and $\mathbf{S}_0$ are unit vectors parallel, respectively, to the diffracted and incident neutron beams. It is often more convenient to define this diffraction vector as $\mathbf{K}=2\pi(h_1\mathbf{b}_1+h_2\mathbf{b}_2+h_3\mathbf{b}_3)$, where the $\mathbf{b}_i$ are reciprocal lattice vectors and the h_i are continuous variables in reciprocal space. The attenuation factor, $\exp[-C_j|\mathbf{K}|^2]$, arises from thermal vibrations and static strains; the exponent can be written as two terms: $C_j|\mathbf{K}|^2=2M\gamma(r_j)+2M'\gamma'(r_j)$, where $2M$ is the usual Debye-Waller factor, $2M'$ is a similar static strain factor, and $\gamma(r_j)$ and $\gamma'(r_j)$ are displacement correlation functions that vary from zero at $r=0$ to unity for large r. At high temperatures, the term in $2M'$ can usually be neglected.

In an ordering alloy at a temperature above T_c, the short-range order parameters, $\alpha(r_j)$, are of such signs and magnitudes as to cause the diffuse scattering to peak at the same positions in reciprocal space at which superlattice reflections occur for an ordered crystal. If the intensity of this scattering (or differential cross section) can be measured at a given temperature for a number of positions of the diffraction vector, $\mathbf{K}$, in reciprocal space, using monochromatic neutrons and a single-crystal specimen, then by fitting these data to Eq. (1) by either a Fourier transform or a least-squares process one can obtain quantitative values for the short-range order parameters at that temperature. The neutron diffraction method differs from the standard x-ray approach only in some of the experimental details.

Measurements of the scattering lengths of the two stable copper isotopes[13] had shown that the intensity of the neutron short-range order diffuse scattering from β CuZn could be enhanced by a factor of seven if the copper atoms were isotopically pure Cu^{65}. We were able to borrow 27.4 g of copper enriched to 98.3% in Cu^{65} from the U. S. Atomic Energy Commission, and, using this copper with zinc of 99.99% purity, we grew a single crystal of β CuZn. This crystal, containing 53.2 at.% Cu, was shaped into a cylindrical specimen 0.979 in. in diameter and 0.327 in. thick.

The furnace and goniometer assembly built to hold this crystal at temperatures of the order of 550°C is shown in Fig. 1. Three rotational degrees of freedom gave sufficient orientation flexibility. An atmosphere of H_2 prevented sample oxidation. Triple sets of 0.001 in. Ni windows[14] contained this atmosphere, acted as a series of radiation shields, and transmitted the primary and scattered neutron beams. The innermost windows were only 0.1 in. from the surfaces of the crystal.

[5] G. E. Bacon, *Neutron Diffraction* (Oxford University Press, New York, 1962) 2nd ed., Table II.
[6] M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill Book Company, Inc., New York, 1958), 2nd ed.
[7] D. Chipman and B. E. Warren, J. Appl. Phys. **21**, 696 (1950).
[8] F. C. Nix and W. Shockley, Rev. Mod. Phys. **10**, 1 (1938).
[9] L. Guttman, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 3.
[10] C. B. Walker and D. T. Keating, Acta Cryst. **14**, 1170 (1961).
[11] B. Borie, Acta Cryst. **10**, 89 (1957).
[12] C. B. Walker and D. T. Keating (unpublished).
[13] D. T. Keating, W. J. Neidhardt, and A. N. Goland, Phys. Rev. **111**, 261 (1958).
[14] At the highest specimen temperature, 650°C, the outer Ni windows were replaced with 0.005 in. stainless steel.

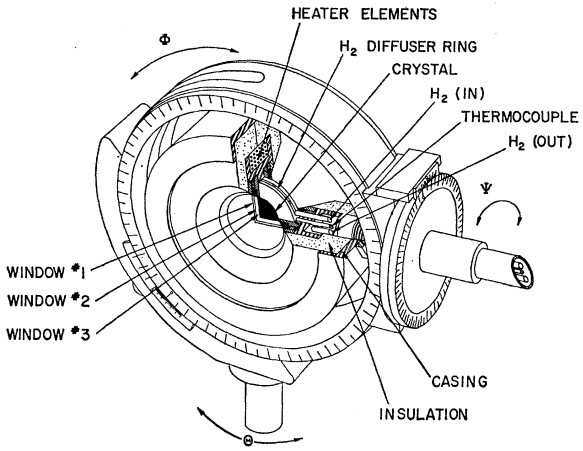

FIG. 1. Furnace cutaway.

Temperatures were maintained to ± 2°C by a Brown proportional controller.

The general experimental arrangement is outlined in Fig. 2. A beam of 1.059 Å neutrons from the Brookhaven reactor was diffracted by a Pb monochromator and passed through an evacuated collimator to strike the sample. Neutrons of wavelength $\lambda/2$ were eliminated by a filter containing 0.503 g/cm^2 of Pu^{239}, and neutrons of wavelength $\lambda/3$ were eliminated by an 0.0085 in. iridium foil. The final beam incident on the sample was of circular cross section 0.7 in. in diameter, with an average flux of 4×10^5 n/cm^2/min. Circular slits allowed divergences in the primary and scattered beams of approximately 1.5°. Fission counter No. 1 monitored the primary beam and controlled the counting periods. Fission counter No. 2 measured the sample transmission for correcting for absorption and extinction. The scattered radiation transmitted through the specimen was detected by a heavily shielded, high-pressure, enriched BF_3 proportional counter. Extra shielding, both around the beam port and also placed to isolate this apparatus from neighboring experiments, kept the background below 1 count/min. Parasitic scattering from the collimator, etc. was also quite low, ranging from 3 counts/min at a scattering angle $2\theta=5$°, to 1 count/min for $2\theta\geq 20$°.

The crystal and furnace were first oriented so that intensity measurements could be made along the [100] axis through the (100) superlattice reflection at room temperature and at a series of successively higher temperatures. The integrated intensity of the (100) superlattice reflection obtained from these measurements decreased continuously with increasing temperature and extrapolated to zero at the critical temperature with a very steep slope in accordance with the known temperature dependence of the long-range order.[7] The temperature indicated by the thermocouple at the critical temperature was 7°C higher than the true critical temperature, 468°C, so all indicated temperatures were corrected by this calibration factor to give mean sample temperatures.

Next a series of quick measurements were made of the diffuse scattering along the [100] axis near the (100) reciprocal lattice point at temperatures 5°, 15°, 25°, 35°, 45°, and 55°C above T_c. The results are plotted in Fig. 3. The total time spent on the measurements at any one temperature was only 90 min, so the data show considerable scatter, but diffuse scattering peaks due to the short-range order stand out clearly. These diffuse peaks exhibit two unusual characteristics: the peak height depends strongly on temperature, indicating a marked temperature dependence of the amount of local order, and the peak widths are all quite narrow, indicating that the short-range order correlations must extend over quite large distances in the crystal.

More accurate and extensive intensity measurements were made at 543°C, that is, T_c+75°C. Data were taken first along the [100] axis and then along the [111] axis. Scattered intensities were less than 1 count/sec, so for greater accuracy the measurements along each axis extended for $4\frac{3}{4}$ days. At the conclusion of the [111]-axis measurements, a recheck of the intensity at the diffuse peak on the [100] axis showed a decrease of $4\frac{1}{2}$%, indicating that zinc losses were becoming noticeable after $9\frac{1}{2}$ days at this temperature.

Finally, extensive measurements were made of the diffuse scattering along the [100] axis at two other temperatures, first at 643°C and then at 503°C. The measurements at each temperature extended for two days. Dezincification occurred at a rather high rate at 643°C, and at the conclusion of the measurements at this temperature the recheck of the diffuse [100] peak at 543°C showed a decrease of an additional $8\frac{1}{2}$% in the scattered intensity.

Systematic errors appear in these long sets of measurements because of two factors: zinc loss, and a drift in thermocouple calibration. The chromel-alumel ther-

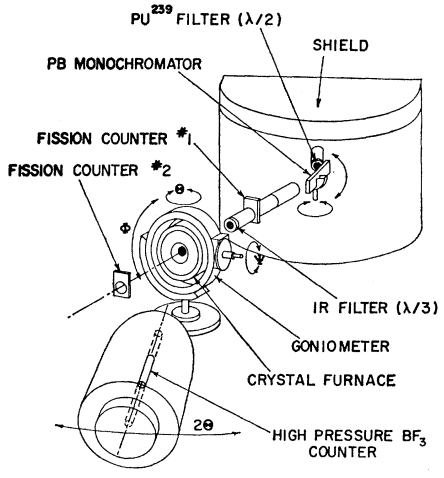

FIG. 2. Experimental layout.

mocouple used for the majority of the experiments reacted with the atmosphere of Zn and H_2, and at the end it was found to read 25°C too low at 550°C. The crystal lost 2.45 g from its original 33.38 g, causing the mean composition (assuming the loss to be only Zn) to change from 53.2 to 57.4 at.% Cu and, consequently, the critical temperature to change from 468 to 454°C. An approximate correction for the effects of these factors was developed that was based on the several experimental rechecks of the scattered intensity at the diffuse [100] peak at 543°C made during the course of the various sets of measurements. The net correction for the measurements at 543 and 643°C was rather reliable and not very large, ranging from 5% for the 543°C [100] data to 20% for the 643°C [100] data. The corrections for the final 503°C data were much larger and uncertain, because α-CuZn began to precipitate during this run, so these data were discarded.

The measured intensities of each run were corrected for background, absorption and secondary extinction, geometrical factors, and zinc loss and thermocouple drift, and the resulting data were converted to absolute units of barns per unit solid angle by comparison with the scattering from vanadium, including a correction for vanadium multiple scattering (reference 19). As an illustration, the results for the scattering along the [100] axis at 543°C are plotted in Fig. 4. One sees a sharp diffuse scattering peak due to the short-range order superimposed on a high background of scattering from other origins.

The scattering due to the short-range order must be separated from the scattering from the other origins before detailed information about the short-range order correlations can be obtained. The methods used to subtract the extraneous scattering were only approximate, but the height and shape of the sharp short-range order diffuse peaks were relatively insensitive to the inaccuracies of the approximations. The methods were as follows:

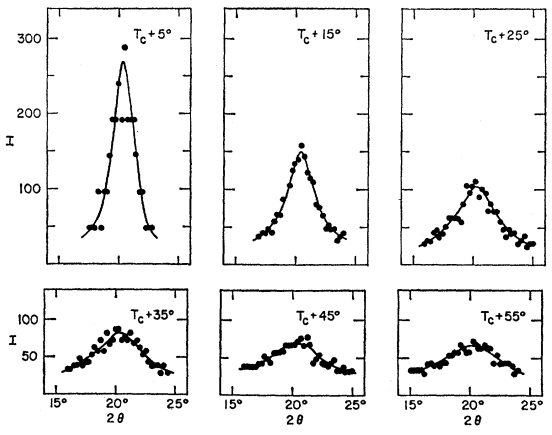

FIG. 3. Diffuse scattering in arbitrary units measured along the [100] axis through the (100) reciprocal lattice point at a series of temperatures above T_c.

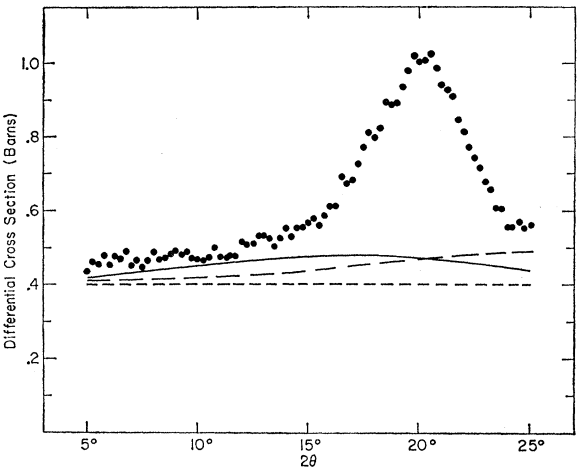

FIG. 4. Differential cross section for scattering along the [100] axis at 543°C. The solid circles represent the experimental values. The short dashes represent the background level due to incoherent and multiple scattering. The long dashes represent the sum of the background and the thermal diffuse scattering. The solid line gives the total extraneous scattering, i.e., background plus thermal diffuse scattering plus size-effect scattering.

(1) The scattering due to thermal vibrations was calculated from an expression that neglects neutron wavelength changes and is the exact analog of the equation for single phonon x-ray scattering. Phonon dispersion curves were taken from Cole and Warren,[15] adjusted to the different temperatures using the elastic constant temperature dependence given by Rinehart and Good,[16] and Debye temperatures were taken from Chipman.[17] This scattering was rather weak at our low angles of measurement, as is illustrated in Fig. 4.

(2) The scattering due to strains from differing atomic sizes appears as an asymmetry in the scattering about the short-range order diffuse peak.[18] The parameters defining this scattering were evaluated from the 543°C [100] and [111] data, corrected for thermal diffuse scattering, by varying their values until the remaining scattering was approximately symmetrical. The values obtained ($\beta_1=-0.04$, $\beta_2=+0.01$, $\beta_3=0.00$) were quite reasonable in view of the differences in atomic radii and scattering lengths of the two atoms. These values were then used to calculate the size-effect scattering at all temperatures. This scattering also was relatively weak, as is shown in Fig. 4.

(3) Other extraneous scattering included the weak isotope, spin, and hydrogen incoherent scattering and a large amount of multiple scattering.[19] We assumed that all this other extraneous scattering formed a con-

[15] H. Cole and B. E. Warren, J. Appl. Phys. **23**, 335 (1952).
[16] P. R. Rinehart, Phys. Rev. **58**, 365 (1940); W. Good, *ibid.* **60**, 605 (1941).
[17] D. R. Chipman, J. Appl. Phys. **31**, 2012 (1960).
[18] B. E. Warren, B. L. Averbach, and B. W. Roberts, J. Appl. Phys. **22**, 1493 (1951).
[19] G. H. Vineyard, Phys. Rev. **96**, 93 (1954).

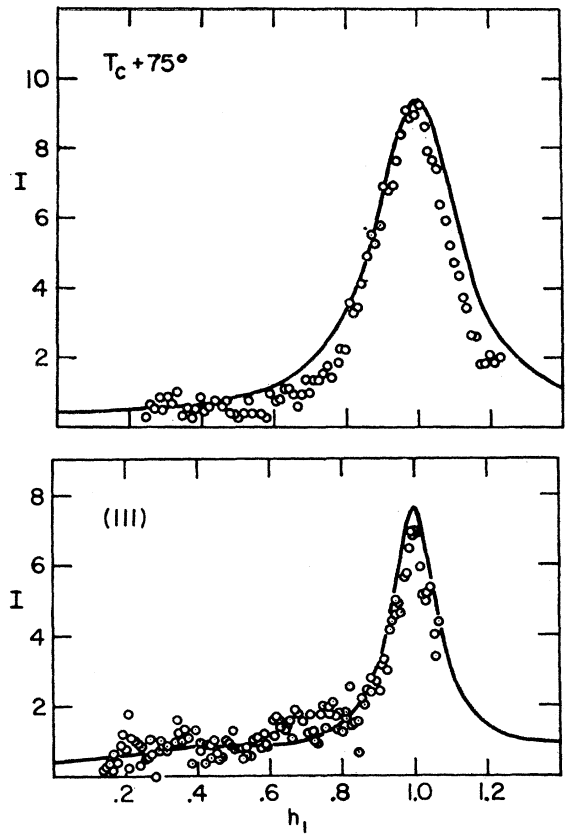

FIG. 5. Short-range order scattering, in Laue monotonic units, along the [100] and [111] axes of β-CuZn at 543°C. The circles represent the experimental values, and the smooth curves give the broadened, calculated scattering curves derived from the Zernike order-disorder theory.

stant background[20] of uncertain magnitude. The experimental data for any set of measurements, after correction for thermal diffuse scattering and size-effect scattering, then consisted of short-range order scattering superimposed on this constant background. The magnitude of this background was determined by requiring the experimental short-range order scattering to match a calculated short-range order scattering at *very low angles* ($5° \leq 2\theta \leq 7\frac{1}{2}°$) where the calculated scattering is weak and insensitive to the model of short-range order used in the calculation. Details of the calculation are given in a later section. The magnitude of this background was found to be quite large, as is shown in Fig. 4. This background is within the range to be expected from the multiple scattering theory.[19]

Experimental values for the short-range order scattering were determined from each of the sets of measurements by the methods outlined above. The results for the short-range order scattering along the [100] and [111] axes at 543°C (T_c+75°C) are shown in Fig. 5. The scattered intensity is plotted for convenience in units of the Laue monotonic scattering[21] as a function of the reciprocal space variable h_1 defined earlier. The 24% difference in the heights of the two peaks is due almost entirely to the exponential thermal attenuation. The unusual sharpness of the diffuse peaks is quite striking.

ANALYSIS

The sharpness of the diffuse peaks shows unambiguously that the short-range order correlations in this alloy actually extend for quite a long distance. A rough measure of the range of this short-range order can be obtained from a Fourier transform of a diffuse peak. That is, the short-range order scattering along the [100] axis, neglecting the exponential attenuation factors of Eq. (1), can be written in the simple form

$$(d\sigma/d\Omega) \sim \sum_n A_n \cos n\pi h_1, \qquad (2)$$

where the A_n's are linear combinations of the short-range order parameters, $\alpha(r)$, such that the larger the value of n, the more distant are the neighbors that are predominant in A_n. Now the observed diffuse [100] peak at 543°C is so sharp that, if it is to be described by Eq. (2), the coefficients A_n must be non-negligible at least through A_6. But

$$A_6 = 2\alpha_{13} + 8\alpha_{14} + 8\alpha_{16} + \cdots,$$

where the subscript to a short-range order parameter indicates the shell of neighboring atoms that is involved. We conclude that the short-range order correlations at this temperature must be significant at least out through 13th neighbors. This is a longer range than has been reported for any other ordering alloy.

We are not able to determine quantitative values for the short-range order parameters from these limited scattering measurements. A least-squares analysis of the data along the two axes, [100] and [111], is capable of yielding solutions for the short-range order parameters if the short-range order does not extend beyond 7th neighbors, but if the order extends farther than this, then essentially the number of unknown short-range order parameters to be determined exceeds the number of *independent* measured quantities [viz., the A_n's of Eq. (2)] and no unique solution is possible. The exponential attenuation factors cannot be depended on to remove this restriction, since the coefficients in the exponents are only calculated from a simple model and are not known to the necessary accuracy. Then, because of the observed long-range nature of the short-range order in this alloy, a direct determination of the short-

[20] The spin, isotope, and hydrogen incoherent scattering all give a constant background. The multiple scattering also will form a constant background, provided that the Vineyard quasi-isotropic approximation (reference 19) is applicable. Given the high temperature of the crystal, the wavelength spread of the incident neutrons, and the fact that only occasionally could small, specific extinctions be observed in the measured transmission, this is believed to be a reasonable approximation in the present experiment.

[21] The Laue monotonic scattering for this alloy is $x(1-x) \times (b_{Cu}-b_{Zn})^2 = 0.0604$ b.

range order parameters from our scattering data is impossible.

COMPARISON WITH THEORY

As an alternative procedure, we have compared the measured scattering with scattering curves calculated from various theoretical approaches. The five theories of order, or of the scattering due to order, that we have investigated differ considerably in their development. Landau[22] and Krivoglaz[23] derived scattering theories from a consideration of fluctuations in order expressed in terms of a macroscopic thermodynamic potential. Zernike,[24] Cowley,[25] and Elliott and Marshall[26] derived microscopic theories of order using specific models of atomic interactions and quite different methematical formulations.

Despite these differences, all five of these theories predict the same qualitative behavior for the short-range order diffuse scattering: At the critical temperature the diffuse peak is extremely intense and very narrow; as the temperature increases above T_c the diffuse peaks broaden and decrease rapidly in intensity, varying approximately as $(1-T_c/T)^{-1}$; and as the temperature drops below T_c the diffuse peaks, coexisting with the crystalline superlattice reflections, again broaden and decrease rapidly in intensity. This diffuse scattering has been called "critical scattering,"[26] by analogy with the critical opalescence in light scattering from liquids or dense gases near their critical points. It is directly analogous to the critical magnetic scattering of neutrons from magnetic materials near their Curie points.[27]

A quantitative comparison of the three microscopic theories for $T>T_c$ shows only small differences. The basic equation of each, to a first approximation,[28] is a linear difference equation in the α's, and these lead to very similar values for the α's and, hence, to similar scattering curves. For example, at $T/T_c=1.101$ the values of α_1 calculated from the theories of Zernike, Cowley, and Elliott-Marshall[29,30] are, respectively, -0.180, -0.171, and -0.182. These theories then must each represent effectively the same degree of approximation to the basic Ising model order-disorder theory.

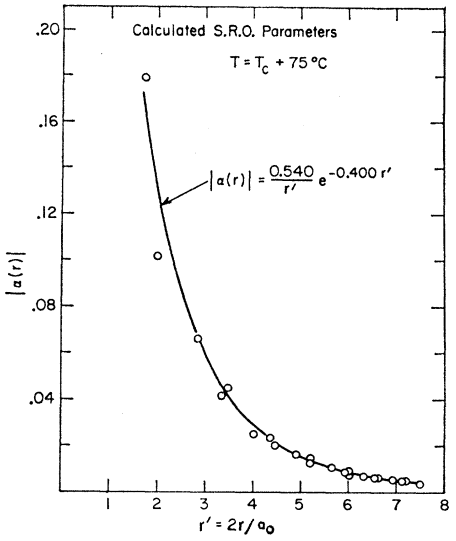

FIG. 6. Short-range order parameters for β-CuZn at 543°C as calculated from the Zernike theory. The circles give the actual calculated values for the different shells of neighbors. The smooth curve shows the asymptotic dependence on r to be expected at large r if $(T-T_c)\ll T_c$.

We chose to use the Zernike theory for a detailed comparison with our measured short-range order scattering. For $T>T_c$ the basic equation of this theory can be written approximately as

$$\sum_k \alpha_k + n\alpha_j = P_j, \tag{3}$$

where the index k denotes the eight sites that are first neighbors of site j. At the origin site ($j=0$) $\alpha_0\equiv 1$ and $P_0=n+8\alpha_1$; for all other sites ($j\neq 0$) P_j represents terms of order α^3 that can generally be neglected.[31] The coefficient n is defined by a cumbersome expression which, for $(T-T_c)\ll T_c$, can be approximated by

$$n=8+6.280(T-T_c)/T_c.$$

Equation (3), neglecting P_j for $j\neq 0$, forms a set of linear difference equations in the α's. These can be solved with no further approximations by the Laplace transform method suggested by Zernike. Values of α_1 can be determined from tabulated complete elliptic integrals, while values of α_j ($j>1$) require a numerical integration of functions of elliptic integrals. We have used this procedure to calculate the α's for β CuZn at $T=T_c+75$°C ($T/T_c=1.101$). The results are shown in Fig. 6. The smooth curve represents the asymptotic behavior expected for large r if $(T-T_c)\ll T_c$ and gives a reasonably good fit over the entire range. The long-range nature of the predicted short-range order is quite evident.

[22] L. Landau, Physik Z. (Sowjetunion) **12**, 123 (1937).
[23] M. A. Krivoglaz, Zh. Eksperim. i Teor. Fiz. **31**, 625 (1956) [translation: Soviet Phys.—JETP **4**, 293 (1957)]; Zh. Eksperim. i Teor. Fiz. **32**, 1368 (1957) [translation: Soviet Phys.—JETP **5**, 1115 (1957)].
[24] F. Zernike, Physica **7**, 565 (1940).
[25] J. M. Cowley, Phys. Rev. **77**, 669 (1950); **120**, 1648 (1960).
[26] R. J. Elliott and W. Marshall, Rev. Mod. Phys. **30**, 75 (1958). The reader is warned that this article contains a number of typographical errors.
[27] M. K. Wilkinson and C. G. Shull, Phys. Rev. **103**, 516 (1956); H. A. Gersch, C. G. Shull, and M. K. Wilkinson, *ibid.* **103**, 525 (1956); R. D. Lowde, Rev. Mod. Phys. **30**, 69 (1958); M. Ericson and B. Jacrot, J. Phys. Chem. Solids **13**, 235 (1960); T. Riste, *ibid.* **17**, 308 (1961).
[28] Considering only first neighbor interactions, and neglecting terms in α^3.
[29] The Elliott-Marshall difference equations give solutions that are quite different from those predicted by the "parent" Bethe first approximation (reference 30), due to a propagation-of-order effect. For comparison, this Bethe theory at $T/T_c=1.101$ predicts that $\alpha_1=-0.130$.
[30] H. A. Bethe, Proc. Roy. Soc. (London) **A154**, 552 (1935).
[31] A calculation for $T/T_c=1.101$ showed that inclusion of these terms changed the values of the α's by less than 1%.

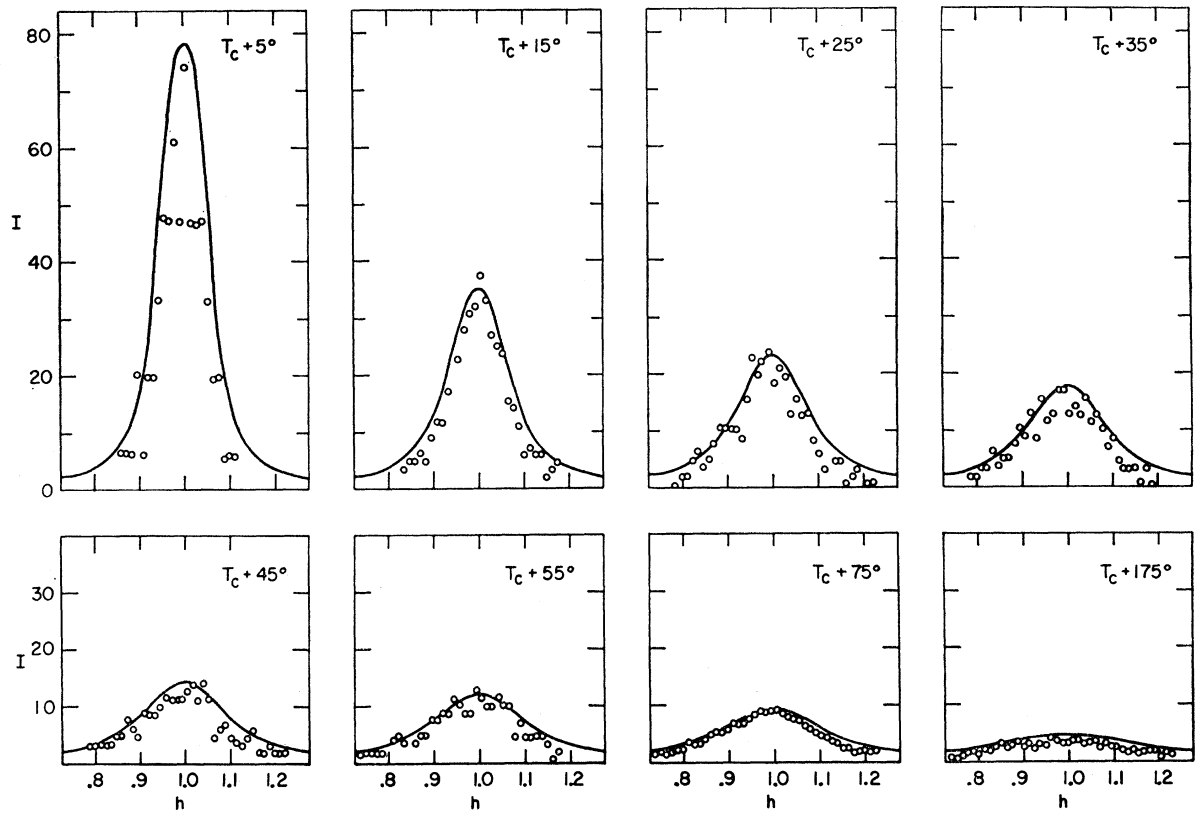

FIG. 7. Short-range order scattering, in Laue monotonic units, along the [100] axis of β-CuZn at a series of temperatures above T_c. The circles represent the experimental values. The smooth curves give the broadened, calculated scattering curves derived from the Zernike theory.

The short-range order scattering could now be calculated directly by substituting these calculated values of the α_j into Eq. (1), but such a method converges very slowly. A much simpler form for the scattering equation is obtained, following Elliott and Marshall, by multiplying Eq. (3) by the product, $\{\exp[-C_j|\mathbf{K}|^2]\exp[i\mathbf{K}\cdot\mathbf{r}_j]\}$, and then summing over all sites j. By comparing with Eq. (1) one finds after some manipulation that the short-range order scattering, in Laue monotonic units, can be written

$$\left(\frac{d\sigma}{d\Omega}\right)=\frac{\sum_j[P_j+E_j]e^{-C_j|\mathbf{K}|^2}e^{i\mathbf{K}\cdot\mathbf{r}_j}}{8[1+\cos\pi h_1\cos\pi h_2\cos\pi h_3]+(n-8)}, \quad (4)$$

where

$$E_j=-\sum_k\alpha_k\{1-e^{-[C_k-C_j]|\mathbf{K}|^2}\}. \quad (5)$$

The index k refers as before to sites that are first neighbors of site j; the h_i are the reciprocal space variables; and the P_j are defined by Eq. (3).

Using Eq. (4), we have calculated the short-range order scattering predicted for β-CuZn at the various temperatures of our measurements. The dominant factors P_0, E_0, and n were calculated directly for each temperature. The small terms E_1, E_2, and E_3 were calculated directly for $T=T_c+75$°C and their values at the other temperatures derived by an approximate extrapolation. All other P_j and E_j were less than 0.001 P_0 and could be neglected. The coefficients, C_j, in the attenuation factors were evaluated using Chipman's Debye temperatures and assuming that only thermal effects were significant.

The scattering curves calculated in this manner then had to be folded with a function representing the experimental instrumental resolution before they could be compared with the measured scattering. We approximated these broadening functions by normalized experimental profiles of the appropriate room-temperature superlattice reflections. The numerical calculations were done on an IBM 1620 computer. As could be expected, this broadening had an important effect on the shapes of the scattering curves at temperatures near T_c, but at higher temperatures the effect became much less significant. For example, at $T=T_c+5$°C this broadening reduced the height of the diffuse [100] peak by 38%, but at $T=T_c+75$°C the corresponding peak reduction was only 5%.

The calculated, broadened scattering curves along the [100] and [111] axes at $T=T_c+75$°C are plotted as the smooth curves in Fig. 5, where they are compared with the corresponding experimental scattering data. The theoretical curves have no adjustable parameters.

The experimental data have been adjusted only in subtracting off the background scattering by fitting the data to the curves *at the low angles* (near $h_1=0.2$) along each axis. The agreement between theory and experiment is really quite good.

The calculated, broadened scattering curves along the [100] axis for all the various temperatures are compared with the corresponding experimental scattering data in Fig. 7. Again the only adjustment has been in the subtraction of background scattering from the experimental data.[32] At the lower temperatures the data show considerable scatter and the uncertainties in specimen temperature and in the instrumental broadening correction offer sources of serious error, so the accuracy of these results is poor. Nonetheless, there is surprisingly close agreement between theory and experiment over the entire range of temperatures.

Although the over-all agreement between theory and experiment is good, a few small discrepancies can be observed. These are better demonstrated in Fig. 8, where we compare the theory with the more accurate and extensive [100] measurements at the two higher temperatures. The observed diffuse peaks are seen to be somewhat sharper than the calculated peaks and displaced slightly to smaller angles, and the observed peak intensity decreases more rapidly with increasing temperature than is predicted by the theory. The first two are evident in all the sets of measurements. The third, the discrepancy in the temperature dependence of the peak height, can be seen only in the measurements at the higher temperatures, where the data are more accurate and where the combined systematic uncertainty due to the various corrections is less dependent on temperature. The discrepancy in peak widths indicates an underestimation of the short-range order, which might be due either to the neglect in the theory of all except first-neighbor interactions or to the oversimplified approximation adopted as a substitute for the exact Ising model.[33] The reason for the peak displacement is not known; similar displacements have been observed in several x-ray short-range order studies,[1] but the mechanism usually suggested, the presence of ordered nuclei above T_c, cannot be the explanation in the present case, since it would produce a shift in the opposite direction.

The discrepancy in the temperature dependence of the peak height seems to be due primarily to the oversimplified approximation to the exact Ising model adopted in the Zernike theory. Domb and Sykes,[34] working with an exact series expansion of the reduced magnetic susceptibility for a bcc Ising model of a ferromagnet, have recently shown that this reduced susceptibility at temperatures near T_c should be given approximately by the asymptotic form,

$$\chi\sim(1-T_c/T)^{-5/4},$$

rather than by the $(1-T_c/T)^{-1}$ dependence given by the usual theories. A bcc Ising model short-range order calculation is mathematically equivalent to this Ising model magnetic order calculation, with the height of a short-range order diffuse peak (neglecting attenuation effects) being the analog of this reduced susceptibility, so one can expect that an exact Ising model short-range order calculation should lead to diffuse peaks showing this same temperature dependence. Using this, and including thermal attenuation effects approximately, we calculate that the (100) diffuse peak for β-CuZn at $T=T_c+75$°C should be 2.52 times higher than the peak at $T=T_c+175$°C, while the Zernike theory predicts this ratio to be only 2.05. The observed value for this ratio is 2.53, in very good agreement with the Domb and Sykes calculation.

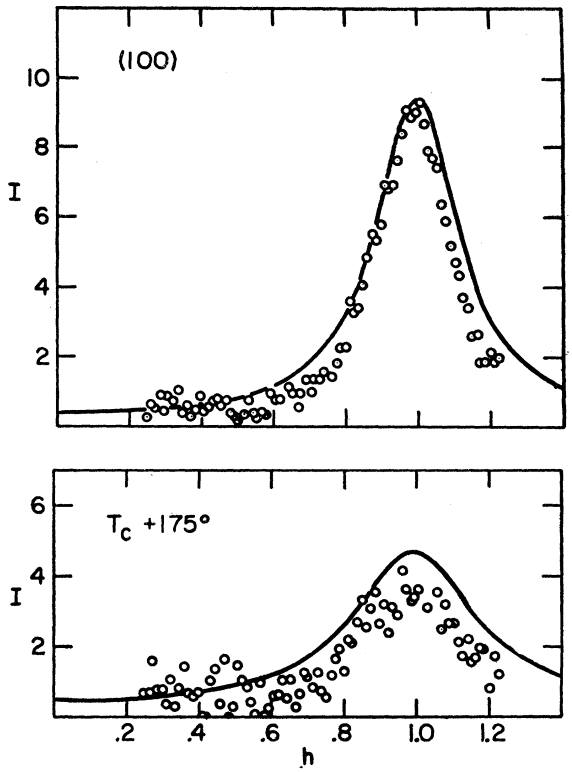

FIG. 8. Short-range order scattering, in Laue monotonic units, along the [100] axis of β-CuZn at 543 and 643°C. The circles represent the experimental values. The smooth curves give the broadened, calculated scattering curves derived from the Zernike theory.

SUMMARY AND DISCUSSION

Neutron diffraction measurements made on an isotopically enriched single crystal of β-CuZn at a series

[32] At the six lower temperatures, where measurements did not extend to low angles, the background was assumed to be the same as at $T=T_c+75$°C.

[33] For a discussion of the Ising model and the problems of its solution, see reference 9.

[34] C. Domb and M. F. Sykes, Proc. Roy. Soc. (London) **A240**, 214 (1957); J. Math. Phys. **2**, 63 (1961). See also G. A. Baker, Phys. Rev. **124**, 768 (1961).

of temperatures above T_c have clearly shown diffuse scattering peaks due to short-range order in the alloy. These diffuse peaks exhibit characteristics that have not been observed in short-range order studies of any other alloy: at the temperature nearest T_c the diffuse peak is very intense and quite narrow, and at successively higher temperatures the peak intensity decreases, first rapidly, and then more and more slowly, while the peak width increases slowly. From these general characteristics one can immediately draw several conclusions about the short-range order in this alloy: the amount of short-range order must be very large at T_c and strongly temperature dependent, and the short-range order must be unusually long-range in nature throughout the temperature range investigated. A simple peak shape analysis makes this last conclusion more quantitative, showing that at $T=T_c+75°C$, for example, the short-range order must be significant at least out through the 13th neighbors.

Diffuse scattering with just these general characteristics has been predicted for this alloy by both macroscopic and microscopic theories. It has been called "critical scattering," by analogy with the phenomenon of critical opalescence in light scattering, and is directly analogous to the critical magnetic scattering of neutrons from magnetic materials near their Curie points. It is just short-range order scattering from an alloy whose order-disorder transformation is a phase transformation of second (or higher) order, and it will occur for any such alloy, regardless of its crystal structure. The unusual scattering characteristics arise because of the large fluctuations in atomic order that are possible near the critical temperature for such high order transformations.

The general characteristics of the observed diffuse scattering thus give a direct confirmation that the order-disorder transformation in β CuZn is a phase transformation of second (or higher) order. Furthermore, since no short-range order diffuse scattering study of any other alloy has reported diffuse scattering with similar characteristics, then these other order-disorder transformations that have been studied in this way must have all been first-order phase transformations. This conclusion had already been advanced for many of these transformations[9,35] from other evidence, so the scattering characteristics only offer further corroboration.

It has not been possible to analyze our scattering data to obtain experimental values for the short-range order parameters in β CuZn at any temperature because of the observed long-range nature of the short-range order; there are not enough independent measured quantities to allow the evaluation of so many unknowns. As an alternative, we have made a comparison of the experimental short-range order scattering with calculated scattering curves based on the Zernike theory of order-disorder in alloys. The agreement between theory and experiment is found to be rather good over the entire range of temperatures investigated. The Elliott-Marshall theory and the Cowley theory are not very different from the Zernike theory, and they also will give acceptable agreement with the measured scattering. We then conclude that these theories, despite their approximations, do give a reasonable first approximation to the actual short-range order correlations in β CuZn above T_c.

There are a few discrepancies between the experimental and calculated scattering curves, and most of these can be attributed to the known approximations and restrictions of the theories. In particular, the discrepancy in the temperature dependence of the peak height appears to be due to the way in which the bcc Ising model has been approximated and is not an intrinsic defect of the Ising model itself, for a calculation based on the Domb and Sykes asymptotic form for an exact Ising solution gives excellent agreement with the observed temperature dependence of the more accurate data. The discrepancy in peak widths might be due to the same approximation or to the neglect of all but first neighbor interactions. The Ising model, thus, appears to be a surprisingly good model for describing the short-range order correlations in this alloy at temperatures above T_c.

Short-range order diffuse scattering studies have been made on only one other equiatomic body-centered cubic alloy that undergoes an order-disorder transformation, the alloy β AgZn. The results found for that alloy are not similar to those found in this investigation: for example, the width of the diffuse peak found in that investigation (where $T/T_c\simeq 1.1$) is twice that found for comparable conditions in the present study, so the range of the short-range order must be much smaller in that alloy. This Ag-Zn alloy does not show a normal order-disorder transformation, however, but instead a complex ζ-phase intervenes between the disordered and ordered phases, so the difference in the short-range order correlations probably just reflects this difference in the stability of the various phases.

ACKNOWLEDGMENTS

During the course of this experiment we have benefited greatly from the advice and help of numerous colleagues. Particular thanks are due M. H. Cohen and J. C. Phillips for their suggestions and comments concerning the critical scattering theory and to C. S. Barrett and L. Guttman for frequent discussions. The support of the Brookhaven National Laboratory, which allowed one of us to spend several months there as a visitor, is also gratefully acknowledged.

[35] F. Rhines and J. B. Newkirk, Trans. Am. Soc. Metals **45**, 1029 (1945).