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Pressure Dependence of the β-Brass Order-Disorder Critical Temperature*†

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The order-disorder critical temperatures T_c of β-brass samples of varying compositions were measured at pressures P of up to 10 kbar by the differential thermal analysis technique. T_c increases linearly with pressure, and $\delta T_c/\delta P$ varies with composition. The values of $\delta \ln T_c/\delta \ln a$, where a is the lattice constant, estimated from the measured $\delta T_c/\delta P$, vary by about 9% with 3% variation in composition. It is shown that this result implies that a single volume-dependent nearest-neighbor ordering interaction is insufficient to describe the order-disorder transition over the composition range in which it is observed. The comparison between these experimental results and various theories of the order-disorder interaction is presented.

I. INTRODUCTION

It is well known[1] that measurements of thermodynamic properties of alloy systems which exhibit order-disorder transitions show systematic disagreements with calculations based on the nearest-neighbor interaction model. It is difficult to determine if these disagreements indicate that the nearest-neighbor interaction model is inadequate because the mathematical approximations used to calculate the thermodynamic properties introduce systematic errors of a quite similar nature.[2]

Recently, the work of Dietrich and Als-Nielsen[3] has led many to believe that the nearest-neighbor interaction model is appropriate for β brass. These authors measured the temperature dependences of neutron diffraction intensities in a number of different important parts of reciprocal space and found, for the most part, good agreement with predictions made from recent sophisticated treatments of the nearest-neighbor Ising model.

Bienenstock and Lewis,[4] on the other hand, give some apparently, but not necessarily, contradictory evidence. Using the same sophisticated treatments of the nearest-neighbor Ising model, they calculate the composition dependence of the order-disorder critical temperature T_c and get results which do not agree with experiment. On the basis of this, they conclude that no single volume-dependent interaction energy can describe the interaction over the composition range in which the transition is observed.

Note, however, that this result does not necessarily imply that the range of the interaction is longer than nearest neighbor, since a nearest-neighbor interaction which varies with composition can be used to fit their results. Nevertheless, one would expect that a variation of the interaction with composition, at fixed lattice parameter, would result from a change in conduction-electron density. If this change in density is sufficiently important to alter the T_c versus composition curve markedly, it would be expected that the longer range of conduction-electron-type interactions would play an important role in the order-disorder process.

Hence, there is an apparent contradiction between the results of Bienenstock and Lewis and the common interpretation of Dietrich and Als-Nielsen results. It should also be noted, though, that there is always the possibility that the Bienenstock and Lewis calculation is not a sufficiently accurate representation of the Ising model to justify conclusions of this type.

Thus, the first aim of this investigation is to perform a direct experimental test of the validity of the nearest-neighbor Ising model. Such a test must be independent of any approximations used to evaluate the partition function. It is shown that the nearest-neighbor Ising model implies, without any approximation, that $\delta \ln T_c/\delta \ln a$ is independent of the composition of the sample. Here, a is the lattice constant, and the only assumption is that the interaction energies between the nearest-neighbor pairs are independent of composition.

To test this relation, measurements of the pressure dependence of T_c were made on samples of various compositions within the pure β-brass field. To convert the measured pressure dependences of T_c to volume dependences, it is necessary to know the compressibilities of the samples near T_c. The available experimental data on the compressibility and elastic constants of β brass are inadequate to give the complete composition dependence of the compressibility at T_c. Therefore, the discussions of the composition dependence of $\delta \ln T_c/\delta \ln a$ have to be based on the assumption that the change of compressibility between room temperature and T_c does not show an anomalously large composition dependence.

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[1] See, e.g., L. Guttman, Solid State Phys. **3**, 145 (1956).

[2] G. H. Wannier, Rev. Mod. Phys. **17**, 50 (1945).

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

[4] A. Bienenstock and J. Lewis, Phys. Rev. **160**, 393 (1967).

The second aim of this investigation is to test the validity of various theories of the origin of the ordering energy in β brass. Mott[5] suggested a model which includes both polar interactions and ion-core exchange. Recently, Harrison and Paskin[6] refined the calculations of the polar interaction. The observed pressure dependence of T_c and its variation with composition are compared with the predictions of these calculations.

Finally, it is suggested that the composition dependence of $\delta \ln T_c/\delta \ln a$ could be explained by the composition dependence of the geometrical factor relating T_c with the next-nearest-neighbor interaction energy.

II. EXPERIMENTAL TECHNIQUES

T_c's of β brass samples under pressure were detected by the differential thermal analysis (DTA) technique using a furnace placed inside the pressure vessel. Argon gas was used as the pressure medium. The pressure generating system, which consists of a separator, intensifier, and the "upper cylinder," is a standard one used in this laboratory. The wall thickness of the sample vessel and the length of the threaded parts for the drive plugs were made large because of the danger in using a gas system at high temperature. Electrical and thermocouple wires were introduced continuously into the pressure vessel by the technique utilizing swaged metallic-sheathed wires and epoxy liquid reported by Yoon.[7]

DTA involves the use of a "dummy" or neutral body as a comparison standard of temperature. The heat supplied to the sample and standard is increased at the same rate, while the temperature difference ΔT between the sample and the standard is measured along with the temperature of the sample. ΔT will show a sharp peak when the sample goes through a transformation at T_c. This technique is particularly suitable for the accurate determination of T_c in β brass because the equilibrium state is maintained throughout the transition in this system.

A cylindrical electrical resistance furnace containing the sample was placed inside the pressure vessel. The heating wires were wound more closely spaced at the ends to obtain a uniform temperature zone at the center. The effect of the temperature gradient on the measured T_c was systematically investigated in furnaces of varying temperature gradients. The uncertainty in T_c caused by the temperature gradients in the furnaces used for actual measurements is estimated to be less than 0.1°C.

The standard dummy was placed in another furnace outside of the pressure system. The temperature of the sample and the standard were kept almost equal by adjusting variable resistors connected with the furnaces.

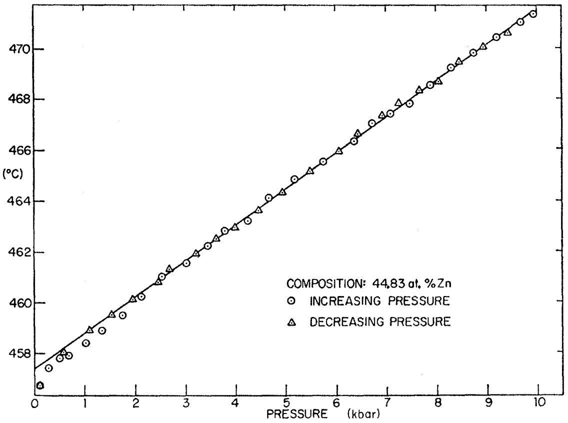

FIG. 1. Critical temperature as a function of pressure for the sample containing 44.83 at% Zn. The circles and triangles represent data taken with pressure increasing and decreasing, respectively. The effect of pressure on the thermocouple readings is not taken into account.

The rate of temperature increase through T_c was about 10°C per min. The temperature of the sample and ΔT were recorded on a two-pen recorder with 1-mV range. T_c's were sometimes determined as the temperature was being decreased through the critical temperature. These were identical to the T_c's measured with increasing temperature, in spite of the asymmetry of the specific heat versus temperature curve around T_c. This observation shows that the DTA peaks do correspond to T_c's defined by sharp maxima in the specific heats.

The samples were cylindrical with about $\frac{1}{4}$-in. diam and $\frac{3}{8}$-in. length. They were mounted on the thermocouples by tightly fitting the thermocouple tip into small holes along the center axes of the samples. The thermocouple tip and the hole were first made wet with sauereisen cement. Great care was taken to obtain good thermal contacts between the thermocouples and the samples, because they were found to have large effects on the accuracy of measured T_c's. The samples were grown by the Bridgman technique. Most of them consisted of several large single crystals. They were annealed at 800°C for 48 h to increase composition homogeneity, and were chemically analyzed after the measurements were completed.

III. EXPERIMENTAL RESULTS AND ANALYSIS OF DATA

A. Observed Pressure Dependence of T_c

Figure 1 shows a typical experimental result of the observed T_c's, corresponding to direct thermocouple readings, at pressures from 0 to 10 kbar. The anomalous sharp increase of T_c in the low-pressure region is due to a systematic experimental error. The correct behavior is given by extrapolating the straight line in the high-pressure region. This anomaly became smaller as the contact between the sample and the thermocouple was improved. Moreover, the zero pressure T_c determined

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[5] N. F. Mott, Proc. Phys. Soc. (London) **49**, 258 (1937).

[6] R. J. Harrison and A. Paskin, J. Phys. Radium **23**, 613 (1962); J. Phys. Soc. Japan **15**, 1902 (1960).

[7] D. Yoon, Rev. Sci. Instr. **37**, 1611 (1966).

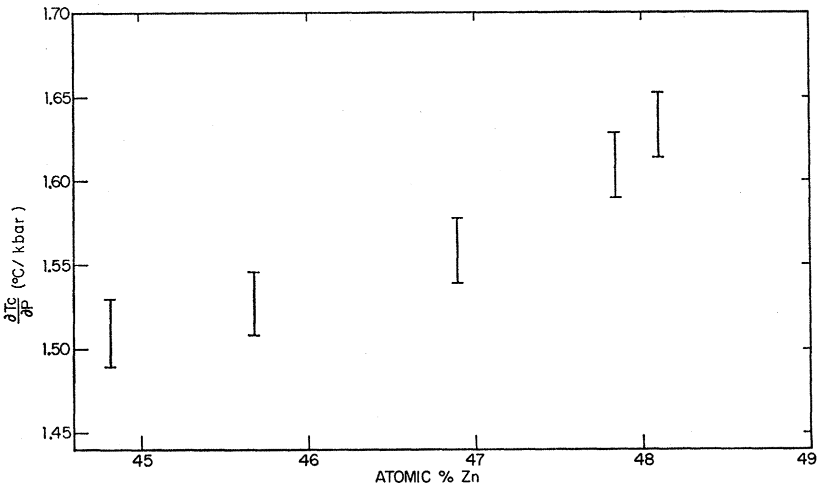

FIG. 2. Observed variation of $\delta T_c/\delta P$ with composition.

by extrapolating the straight line coincided with that measured in a longer furnace outside the pressure vessel with a good contact between the sample and the thermocouple. These observations indicate that the anomaly is caused by the thermal gradient along the thermocouple between the pressure plug and sample. As the furnace surrounding is filled with hot gas of higher pressures the temperature gradient decreases and the correct sample temperature is detected.

A straight line was drawn through the data points by least-square fit, excluding the data below 3 kbar. To obtain the true values of T_c, corrections should be made for the effect of pressure on the thermocouple voltage. Fortunately, pressure has a small effect on the chromel-alumel thermocouples used in this experiment. According to the best available data by Hanneman and Strong,[8] the true temperature will be obtained by adding 0.1°C per kbar to the observed T_c. This correction was included in the final analysis of the data. Although this correction introduces some uncertainty, it is still small compared to the total change of T_c with pressure, and cannot alter any conclusions based on the composition dependence of the T_c increase with pressure.

Figure 2 shows the composition dependence of the increase of T_c per unit pressure, $\delta T_c/\delta P$. The indicated errors include the random errors of about 1% determined by the standard deviation in the least-square fitting of T_c versus pressure curves, and also an uncertainty of about 1% determined by several measurements of $\delta T_c/\delta P$ on the same sample using different furnaces and sample positions in the furnace. $\delta T_c/\delta P$ increases by about 9% with 3% increase of Zn content from 45 to 48 at.% Zn. In this composition range CuZn alloys consist of pure β phase near T_c.

B. Conversion to Volume Dependence

The observed pressure dependences of T_c need to be converted to volume dependences to make them amenable to theoretical analysis. The relevant volume changes in β-brass samples under compression are determined mainly by the compressibility K at T_c. K can be evaluated from the elastic stiffness constants C_{11} and C_{12} by the usual relation,

$$K=3/(3C_{11}-4C'),$$

where C' is given by

$$C'=\tfrac{1}{2}(C_{11}-C_{12}).$$

McManus[9] measured C's of β brass as a function of composition at room temperature, and on a sample with 50-50 atomic composition, as a function of temperature up to T_c. Yoon and Bienenstock[10] suggested, however, that the presence of γ phase in the samples near the 50-50 composition probably caused some peculiar composition and temperature dependences of the elastic constants in McManus's measurements. Therefore, there appears to be no reliable data of the independent set of elastic constants up to T_c. Rough estimates can, however, be made of the compressibility at T_c, $K(T_c)$, from the measurements of elastic constants by McManus and the Young's modulii measurements of Artman.[11] One estimate was obtained from McManus's measurements using the relation $K=3/(3C_{11}-4C')$. The resulting K increases by approximately 15% between room temperature and T_c. Since C' is about $\frac{1}{10}$ of C_{11}, most of the error in the estimate is caused by uncertainties in C_{11}, which is probably least affected by the phase uncertainties discussed by Yoon and Bienenstock. A second estimate was obtained using Artman's measurements of E_{111} and McManus's measurements of C_{44} in the relation $K=9/E_{111}-3/C_{44}$. The resulting K increases by 30% between room temperature and T_c. Since the second estimate depends more strongly on the more uncertain C_{44}, we have assumed that the increase in K between room temperature and T_c is 20±10%. Adding

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[8] R. R. Hanneman and H. M. Strong, J. Appl. Phys. **36**, 523 (1965).

[9] G. M. McManus, Phys. Rev. **129**, 2004 (1963).

[10] D. Yoon and A. Bienenstock, J. Appl. Phys. **39**, 356 (1968).

[11] R. A. Artman, J. Appl. Phys. **23**, 475 (1952).

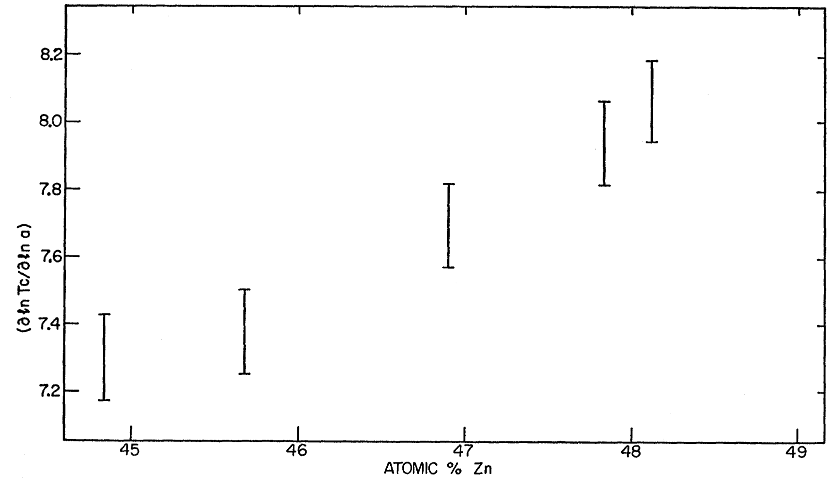

FIG. 3. Estimated variation of $\delta \ln T_c/\delta \ln a$ with composition.

this increase to the room-temperature compressibility, which is known fairly accurately, K of β brass near T_c was estimated to be $11 \pm 1 \times 10^{-7}$/bar.

Although no experimental data on the composition dependence of K near T_c is available, McManus's room-temperature data indicates that at room temperature K changes by about 3% with composition in the pure β-phase range. It was assumed, therefore, that the increase of K between room temperature and T_c does not show an anomalously large composition dependence. Thus, the volume dependence, $\delta \ln T_c/\delta \ln a$ was obtained from the observed $\delta T_c/\delta P$ with the assumption that the composition dependence of K near T_c is the same as at room temperature. If the variation of $\delta T_c/\delta P$ with composition is caused by the variation of K with composition near T_c, then K near T_c should vary by about 10% with 3% increase in Zn content. This means that the increase of K from room temperature to region just below T_c of a sample with 48% Zn should be twice as large as the increase for a sample with 45% Zn.

Further uncertainties in the volume changes are introduced by Garland's[12] suggestion that K should show peaking in the immediate vicinity of T_c. This effect has not been dealt with seriously in this work because the volume changes associated with it and the associated peaking of the thermal expansion coefficient are expected to be small compared to the abovementioned uncertainties.

The effects of the change of compressibility with pressure and thermal expansion due to increasing T_c were included in converting the pressure to volume dependence. These effects are quite small, however, and any inaccuracies in including these effects is expected to cause negligible errors in estimating the volume dependence of T_c.

For discussions which follow, the important quantity is $(\delta \ln T_c/\delta \ln a)_{a_0}$ evaluated at the same lattice constant a_0 for all compositions. Therefore, the variation of the lattice constant with composition should be included in evaluating this quantity. The overlap between the variation of a with composition and that with pressure is sufficient, however, so that for samples of increasing Zn content, a_0 corresponds to a value of a under higher pressures. Therefore, T_c versus a curves for all compositions have a common point a_0, where the slope is evaluated. T_c versus a curves are linear anyway, so that $\delta \ln T_c/\delta \ln a$ is independent of a for a given composition. This shows that the variation of $\delta \ln T_c/\delta \ln a$ with composition is not caused by the variation of a with composition.

Figure 3 shows the estimated variation of $\delta \ln T_c/\delta \ln a$ with composition. The shape and percentage variations in this figure are only slightly changed from the $\delta T_c/\delta P$ versus composition curve in Fig. 2 because only small changes were introduced by the variation of T_c, lattice constant, and compressibility with composition in the conversion from $\delta T_c/\delta P$ to $(\delta \ln T_c/\delta \ln a)_{a_0}$. The quantity $-(\delta \ln T_c/\delta \ln a)$ increases by approximately 9% with a 3% Zn concentration increase. The indicated errors represent the random and systematic errors in the T_c versus pressure curves and the uncertainties in the composition dependence of the compressibility at room temperature given by McManus.[9] They do not include the absolute errors of compressibility estimated earlier to be about 10% because only the composition dependence of $\delta \ln T_c/\delta \ln a$ is of interest here.

IV. COMPARISON WITH THEORIES

A. Ising Model with Nearest-Neighbor Interaction

It will now be shown that the nearest-neighbor Ising model implies that, at fixed a, $\delta \ln T_c/\delta \ln a$ is independent of composition for an AB alloy. In this model the energy of any configuration of A and B atoms can be written as[13]

$$W_c = Q_{AB}V + \tfrac{1}{2}z(Q_A V_{AA} + Q_B V_{BB}), \quad (1)$$

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[12] C. W. Garland, Phys. Rev. **135**, 1696 (1964).

[13] See, e.g., F. C. Nix and W. Shockley, Rev. Mod. Phys. **10**, 63 (1938).

where Q_A and Q_B are the numbers of A and B atoms, respectively, Q_{AB} is the number of nearest-neighbor A-B pairs, z is the number of nearest neighbors, and the ordering energy is

$$V=V_{AB}-\tfrac{1}{2}(V_{AA}+V_{BB}). \qquad (2)$$

If attention is restricted to an ensemble of systems with fixed Q_A Q_B, the last term of Eq. (1) is independent of configuration and may be neglected. The partition function may be written as

$$\Lambda(x,Q_A)=\sum\nolimits_{c(Q_A)}\exp(-Q_{AB}x). \qquad (3)$$

Here,

$$x=V/kT \qquad (4)$$

and the summation is over only those configurations, $c(Q_A)$, consistent with a fixed composition. Since the Q_{AB} are numbers, it follows that this canonical ensemble partition function is a function of the variable x only, with composition being represented only in the functional form. Thus, for each composition there is an $x_c(Q_A)$ which defines $T_c(Q_A)$ in terms of V, i.e.,

$$T_c(Q_A)=V/kx_c(Q_A), \qquad (5)$$

where $x_c(Q_A)$ is a number for each composition. It follows that

$$\delta \ln T_c(Q_A)/\delta \ln a=\delta \ln V/\delta \ln a \qquad (6)$$

is independent of composition when evaluated at some fixed lattice parameter, if V is independent of composition.

In contrast to this prediction, the experimentally estimated $\delta \ln T_c/\delta \ln a$ varies by about 9% with 3% change in Zn content. Therefore, under the assumption that the compressibility does not show an anomalously large composition dependence near T_c, it can be concluded that a single volume-dependent nearest-neighbor ordering energy is insufficient to describe the ordering energy in β brass over the composition range in which it is observed.

Such an insufficiency can arise in two ways. The first is that there is a predominately nearest-neighbor interaction which varies with composition. The second is that longer-range interactions are playing a significant role in the determination of T_c, and that the contribution of these interactions relative to the nearest-neighbor interaction changes with composition even when the interaction energies themselves are fixed. The remainder of this section describes studies designed to determine which of these two effects is more important. At the same time, models for the origin of the ordering energy are discussed in terms of their volume dependences.

B. Theories of the Nature of the Ordering Energy

In his original discussion of this problem Mott[5] discussed two sources of the ordering energy. One, called the polar model interaction, is a Coulomb interaction between partially screened ions. The other arises from the core overlap exchange interaction between copper nearest-neighbor pairs in the disordered or partially ordered states. Later, Harrison and Paskin[6] calculated the ordering energy in β brass using Mott's polar model and the results of more recent theoretical treatments of electron screening in alloys. The order of magnitude of the ordering energy predicted by these theories agreed with the value estimated from experimental data. The present experimental results on the pressure dependence of T_c and its variation with composition provide more stringent tests of the validity of these calculations.

Now, it should be noted that the polar model interactions are essentially of longer than nearest-neighbor range. Nevertheless, it is quite possible that the combination of copper core-core repulsion and the polar interaction lead to nearest-neighbor predominance, while the polar interaction itself leads to the variation of the interaction with composition. This is the hypothesis to be tested. To be consistent with this hypothesis, it will be necessary for us to make some assumptions.

The first is that T_c is primarily determined by a linear combination of the interaction energies. There are several reasons for believing this is the case. They are: (1) T_c must be a homogeneous function of first order in these energies. (2) The Cowley theory[14] predicts a linear dependence. (3) Dalton and Wood's[15] Padé approximant analysis of the Heisenberg ferromagnet with nearest and next-nearest interactions yields a linear dependence of T_c on the exchange interactions. With this assumption, the possibility that terms of high power in a strongly volume-dependent interaction divided by one lower power in a more weakly volume-dependent interaction control the volume dependence, is neglected. Such an assumption is also the only one consistent with the hypothesis that the interaction is predominately nearest neighbor, but varies with composition. This hypothesis is, of course, one to be tested in these analyses.

At the same time, it will be assumed that the relative contributions of fixed interaction energies to T_c are independent of composition. When, for example, the ordering energy is determined by nearest- and next-nearest-neighbor interaction energies, V and V', respectively, it is assumed that T_c can be written as

$$kT_c=\mu(c)(V-\nu V'),$$

where ν is composition-independent. With this assumption, the possibility that the composition dependence of ν leads to the composition dependence of $\delta \ln T_c/\delta \ln a$ is ignored. In the present case, the composition dependence of $\delta \ln T_c/\delta \ln a$ arising from the explicit composition dependence of the interaction energies is of main interest. With these assumptions, $\delta \ln T_c/\delta \ln a$ becomes equivalent to $\delta \ln E/\delta \ln a$, where E is the total difference in energy between the ordered and disordered state.

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[14] J. M. Cowley, Phys. Rev. **120**, 1648 (1960).

[15] N. W. Dalton and D. W. Wood, Phys. Rev. **138**, 779 (1965).

Since E is the quantity most frequently calculated in the theories to be considered, we will speak of $\delta \ln T_c/\delta \ln a$ when it is actually $\delta \ln E/\delta \ln a$ which has been calculated.

In Mott's[5] polar model the ordering energy is represented by the electrostatic energy of a point charge distribution of a net positive charge located at the Zn sites and a negative charge located at the Cu sites. The total energy of these charges in the disordered state is zero, but in the ordered state it is, per atom,

$$-(\alpha/2a)(\Delta Q)^2, \tag{7}$$

where a is the lattice constant, ΔQ is the net charge on either Zn or Cu site, and α $(=2.0354)$ is the Madelung constant for the CsCl structure. Using the Thomas-Fermi approximation Mott obtained

$$\Delta Q=\pm eqr_0 \operatorname{csch}\tfrac{1}{2}(qr_0), \tag{8}$$

where r_0 is the radius of the spherical Wigner-Sietz cell and q is the screening constant. In the Thomas-Fermi approximation, q is given by the relation

$$q^2=(4me^2/\hbar^2)(3N/\pi)^{1/3}, \tag{9}$$

where N is the average density of conduction electrons. The volume dependence of Mott's polar energy is determined therefore by a and q.

In his calculation, Mott used an "experimental" value of q obtained from the measured changes with composition of resistivity in dilute alloys of Zn in Cu, assuming that the q of β brass is equal to that of the dilute alloy. In doing this, he felt, presumably, that the most important determinant of q is the difference in the effective one-electron potentials of Cu and Zn. Thus, he ignored the changes in q which come through changes of the N of Eq. (9) with composition. These changes would result from the change of electron to atom ratio and the changes of average atomic volume. Hence, in examining the volume dependences of $\delta \ln T_c/\delta \ln a$ predicted by the model, it seems most reasonable to assume that q is independent of volume and composition. The resulting $\delta \ln T_c/\delta \ln a$ calculated from his model is -7.0. This is in good agreement with the measured values, when the uncertainty in the absolute value of the compressibility is considered. Unfortunately, the Mott model, with q independent of N, predicts no composition variation of $\delta \ln T_c/\delta \ln a$ under the basic assumptions cited above. This is in marked contrast to the variations obtained in these experiments. Since the additional core-core interactions may be expected to have an extremely small composition dependence, there would appear to be no means of bringing the theory into accord with experiment.

One temptation is to keep the order of magnitude of q which Mott found, but to allow q to vary as $N^{1/6}$ as indicated in Eq. (9). This gives a $\delta \ln T_c/\delta \ln a=-4.0$. Although this value seems small compared to experiment, it may not be unreasonable because the core-core interactions increase the volume dependence. This expedient is insufficient to bring the predicted composition dependence of $\delta \ln T_c/\delta \ln a$ into accord with experiment. The calculated variation of this quantity over the 3% composition range is less than 0.5% compared to the measured change of 9%. Thus, we conclude that the Mott model, in its original form, was not sufficiently developed to deal with these experiments.

More recently, Harrison and Paskin[6] have developed the polar model in an attempt to bring it into accord with developments in the theory of the screening of impurities in metals. Their theory yields, as the interaction energy of a pair of ions, separated by a distance r_{mn},

$$E_{nm}=eZ_nV(r_{mn};Z_m), \tag{10}$$

where $V(r_{nm};Z_m)$ is the potential at site n of the screened charge at m, and Z_m is the difference between the ionic charge and the average number of conduction electrons per atomic polyhedron. Z_m is plus or minus one-half for Zn and Cu, respectively, in stoichiometric β-CuZn. $V(r_{mn};Z_m)$ is given by the expression

$$V(r_{mn};Z_m)=\frac{-eZ_m\alpha^2\cos(2k_Fr_{mn}+\phi)}{(2k_F)^2r^3{}_{mn}(1+\frac{1}{2}\alpha^2)^2}. \tag{11}$$

Here, k_F is the magnitude of the Bloch vector at spherical Fermi surface, q is the Thomas-Fermi screening parameter,

$$\alpha=q/2k_F,$$

and ϕ is a phase factor associated with the effective one-electron potential.

Harrison and Paskin used this interaction to calculate the difference in energy between the ordered and disordered states, $E_{o\text{-}d}$, by summing the interaction out to nineteenth neighbors. The resulting expression is

$$E_{o\text{-}d}=-0.39\sin(\phi-0.28)\text{ eV/atom}. \tag{12}$$

Paskin[16] later pointed out that the ϕ obtained by equating the $E_{o\text{-}d}$ of Eq. (12) with experimentally determined estimates of it agrees well with the value for dilute solutions of Zn in Cu obtained by Blandin and Friedel.[17] This agreement implies that the bulk of the ordering energy can be ascribed to the polar interactions, and that ϕ is independent, roughly, of composition and interatomic distance.

If ϕ is assumed to be independent of volume, the volume dependence of the Harrison and Paskin interactions are determined by the volume dependences of r_{mn}, q, and k_F. It should be noted, in this regard that $\delta \ln V(r_{mn};Z_n)/\delta a$ is independent of m and n, since (k_Fr_{mn}) is independent of volume. Thus we calculate $\delta \ln V(r_{mn};Z_n)/\delta \ln a=-0.3$. This shows quite clearly, and not unexpectedly, that the Harrison and Paskin

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[16] A. Paskin, Phys. Rev. **134**, A246 (1964).

[17] A. Blandin and J. Friedel, J. Phys. Radium **21**, 689 (1960); J. Phys. Chem. Solids **17**, 170 (1960).

interaction is insufficient, in itself, to determine the β-brass order-disorder interaction energy.

One might hope, however, that the Harrison and Paskin interaction shows sufficient variation with composition so that it would, in combination with core-core interactions, explain the composition dependence of $\delta \ln T_c/\delta \ln a$. Unfortunately, detailed calculations indicate that this is not the case.

We conclude, then, that there exists no model for a conduction electron induced ordering interaction which is known to have a sufficiently large composition dependence so that the composition dependence of $\delta \ln T_c/\delta \ln a$ can be attributed to a primarily nearest-neighbor interaction which is a combination of it and core-core interactions.

C. Composition Dependence of T_c with Second-Neighbor Interactions

It has been assumed thusfar that the experimentally estimated composition dependence of $\delta \ln T_c/\delta \ln a$ represents the explicit composition dependence of the volume dependence of the ordering energy. It is possible, however, that such an effect can arise from the composition dependence of geometrical factors relating T_c with interaction energies which extend beyond the nearest neighbors. A simple statistical calculation was performed to investigate such a possibility. Assuming that the ordering energy can be represented by the nearest- and next-nearest-neighbor interactions and that T_c is a linear function of these energies, T_c can be written as

$$kT_c=\mu(c)[V-\nu(c)V'], \tag{13}$$

where $\mu(c)$ is a proportionality factor representing the dependence of T_c on nearest-neighbor ordering energy V alone, and the composition dependence of T_c due to the introduction of the next-nearest-neighbor (NNN) ordering energy V' is represented by $\nu(c)$. Then Eq. (13) gives the change of $\delta \ln T_c/\delta \ln a$ due to the composition change ΔC,

$$\frac{\Delta(\delta \ln T_c/\delta \ln a)/\Delta C}{(\delta \ln T_c/\delta \ln a)} =\frac{\Delta\nu(c)}{\Delta C}\left[\frac{-dV'/da}{dV/da-\nu(c)dV'/da}+\frac{V'}{V-\nu(c)V'}\right]. \tag{14}$$

Therefore, the variation of $\delta \ln T_c/\delta \ln a$ with composition could arise from the variation of $\nu(c)$ with composition.

The simplest method of calculating T_c including the next-nearest-neighbor interaction is by extending the Bragg-Williams approximation. It gives the relation,

$$kT_c=2F_AZV(1-F_A)(1-Z'V'/Z), \tag{15}$$

where F_A is the fraction of A atoms, Z and Z' are the coordination numbers for the nearest and next nearest neighbors, respectively. Therefore, in this approximation the parameter $\nu(c)$ is independent of composition.

The next improvement can be obtained by extending Bethe's[18] first approximation or the equivalent quasichemical model of Fowler and Guggenheim.[19] The simplest quasichemical model which includes NNN interactions is obtained by initially assuming that the number of configurations with a certain number of NNN pairs is independent of the number of configurations with a specified number of NN pairs. With this assumption the calculation of the composition dependence of T_c follows, in a straightforward way, Fowler and Guggenheim's treatment of quasichemical model with NN interactions only.

The results of this calculation show that $\nu(c)$ is approximately positive unity and increases by about 0.5% from 45 to 48 at.% Zn. Therefore, according to Eq. (14), a large composition dependence of $\delta \ln T_c/\delta \ln a$ could occur from this effect if the NNN interactions tend to disorder the system, so that V and V' have the same sign. Since the actual values of V, V', dV/da, and dV'/da are quite uncertain at this stage, no quantitative comparisons can be made. It was merely demonstrated from a crude approximate calculation that such an effect is a possibility. A more exact treatment of the Ising model with NNN interactions may indeed show a larger composition dependence of $\nu(c)$ than does the calculation presented here.

V. CONCLUSIONS

It is important in a work of this sort, to distinguish between what is reliable and new and that which is not. Thus, let us point out that we consider the basic contributions of this paper to be the measurement of the *pressure* dependence of T_c as a function of composition and the proof that, for a nearest-neighbor interaction model, where the interaction is volume-dependent, but independent of composition, $\delta \ln T_c/\delta \ln a$ is independent of composition for a fixed a.

All other parts of the paper are less reliable in the following sense. Both the conclusion that a single volume-dependent interaction is insufficient to describe the ordering process and the discussion of the validities of the various theories of the ordering energy depend strongly on a knowledge of the variation with composition of the compressibility near T_c. There is always the possibility that the critical phenomenon under discussion leads to variations of the compressibility with composition near T_c which can account for the large variation of $\delta \ln T_c/\delta P$. It might be this large variation which, when converted into $\delta \ln T_c/\delta \ln a$ through the use of the uncertain compressibilities, causes all the theories to disagree with experiment.

We believe that a large variation of the compressibility with composition is unlikely, since such a varia-

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[18] H. Bethe, Proc. Roy. Soc. (London) **A150**, 552 (1935).

[19] R. W. Fowler and E. A. Guggenheim, Proc. Roy. Soc. (London) **A174**, 189 (1940).

tion would require the change of the compressibility from room temperature to T_c to vary by a factor of 2 over a 3% composition range.

On the basis of this belief, then, we conclude that $\delta \ln T_c / \delta \ln a$ is varying appreciably with composition. Our brief investigation of various proposed conduction electron motivated polar interactions indicates that these do not vary sufficiently with composition to explain the observed variation. On the other hand, the investigation of the variation of T_c with composition indicates that the introduction of second-neighbor interactions can lead to a variation of $\delta \ln T_c / \delta \ln a$ with composition even if the interactions themselves do not vary with composition. Hence, we conclude that interactions of longer than nearest-neighbor range play an important role in the order-disorder transformation. Such interactions may be describable by the Harrison and Paskin theory, but may also be core-core or other interactions. The work presented here is insufficient to distinguish between them because no reliable statistical calculation of the variation of T_c with composition with longer-range interactions has been presented.

It should also be noted that the conclusions presented here are not in conflict with the findings of Dietrich and Als-Nielsen.[3] These authors measured the critical exponents associated with the divergence of the diffuse neutron-scattering intensity as T_c is approached from above and the vanishing of the superlattice reflection intensity as T_c is approached from below. Their results were in good agreement with Baker's[20] predictions based on Padé-approximant analyses of appropriate nearest-neighbor Ising model series expansions. It has since been demonstrated by Domb and Dalton[21] that longer-range interaction Ising models yield the same high-temperature exponent. There is no reason to believe that the low-temperature exponent will be different when longer-range interactions are included. Thus, agreement between theoretical predictions and experimental measurements are not sufficient justification for the conclusion that only nearest-neighbor interactions are important.

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[20] G. A. Baker, Jr., Phys. Rev. **124**, 768 (1961).

[21] C. Domb and N. W. Dalton, Proc. Phys. Soc. (London) **89**, 859 (1966).