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Theoretical Model for Tetragonal-to-Cubic Phase Transformations in Transition Metal Spinels*

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The origin of the large tetragonal distortions which occur in a number of transition metal oxides having the spinel structure has been examined recently by Dunitz and Orgel in terms of the crystal field theory. According to these authors the macroscopic distortions arise as a consequence of a Jahn-Teller type distortion in the immediate environment of certain transition metal ions. Thus, all the observed large distortions in spinels have been correlated with the results of this crystal field treatment on the basis of the spatial ordering of the local distortions.

In this communication we investigate the detailed properties of the transformations from tetragonal to cubic phases which are observed at elevated temperatures. An approximate model has been constructed which explicitly takes into account the interactions between local Jahn-Teller distortions about neighboring octahedral site cations. The configurational energy of the model has been derived in a completely general form in terms of occupation variables, and has been used to deduce the structure of the stable low-temperature phase. By the use of the usual methods of statistical mechanics it has proved possible to derive the thermodynamic behavior of the model, and hence to contribute to an understanding of the cooperative nature of these phase transformations. The temperature and composition dependence of the long-range order parameter, the thermodynamic functions, and the lattice parameters are calculated explicitly. The principal result of importance is the demonstration that the transformations from tetragonal to cubic spinel phases are thermodynamic transitions of the *first order* type. That is, a latent heat, a volume discontinuity, lattice parameter discontinuities, and a lambda anomaly in the heat capacity are to be observed at the transformation temperature. The available experimental evidence supports the conclusions drawn from the theoretical model. The agreement between theory and experiment is found to be semi-quantitative in most of the cases considered.

I. INTRODUCTION

THE origin of the large crystal distortions which occur in certain transition metal compounds has been examined by several investigators. Goodenough and Loeb[1] have discussed the large distortions from cubic to tetragonal symmetry in a number of spinels from the point of view of the ordering of square covalent bonds about the transition metal cations in octahedral sites. Goodenough[2] has also analyzed similar distortions occurring in the perovskite-type manganites in terms of the ordering of covalent and semicovalent bonds. Adopting the point of view of the crystal field theory,[3] McClure[4] has suggested that distortions from cubic symmetry will occur whenever there is a large Jahn-Teller distortion in the ligation of the transition metal cations. Dunitz and Orgel[5] have recently provided an exhaustive analysis of the distortions in transition metal oxides in terms of the crystal field theory. Emphasizing the role of the Jahn-Teller effect, they have constructed a table of the type and magnitude of distortions that can be expected in both the octahedral and tetrahedral ligations of all the transition metal cations. With these results Dunitz and Orgel have succeeded in correlating all the observed large distortions in transition metal oxides with the occurrence of the appropriate Jahn-Teller type distortion. In addition, they have shown the equivalence of the results of Goodenough and Loeb to the consequences of the more general crystal field theory.

Even though the origin of the crystal distortions is now clear, the work of the above authors does not explain the transformations from distorted to cubic phases which are observed in many transition metal compounds at elevated temperatures. Apart from the suggestion that covalent bonds or local Jahn-Teller distortions must order cooperatively below some transformation temperature to produce a noncubic phase, this aspect of the problem had not been treated in detail. Finch, Sinha, and Sinha,[6] on the other hand, recognized the resemblance of certain experimental lattice parameter curves on ferrite-manganite systems to those obtained in studies of the order-disorder and ferromagnetic problems. Following Goodenough and Loeb, they attempted a calculation of the temperature and composition dependence of the lattice distortions from a consideration of the number of covalent bonds oriented in "right" and "wrong" directions (by analogy with the order-disorder theory for binary alloys). It shall be shown in this paper, however, that the treatment of Finch *et al.* is inadequate, and that certain conclusions which can be drawn from their equations are in disagreement with the experimental results. Thus, an understanding of the variation of crystal distortion with temperature and composition has not yet been obtained.

In the present communication we wish to investigate the detailed properties of the transformations from the low-temperature distorted structures to the high-tem-

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* A short account of some of this work has already appeared: J. Appl. Phys. **30**, 30S (1959).

[1] J. B. Goodenough and A. L. Loeb, Phys. Rev. **98**, 391 (1955).

[2] J. B. Goodenough, Phys. Rev. **100**, 564 (1955).

[3] For a review of the crystal field theory see W. Moffitt and C. J. Ballhausen, *Annual Review of Physical Chemistry* (Annual Reviews, Inc., Palo Alto, 1956), Vol. 7.

[4] D. S. McClure, J. Phys. Chem. Solids **3**, 311 (1957).

[5] J. D. Dunitz and L. E. Orgel, J. Phys. Chem. Solids **3**, 20 (1957).

[6] Finch, Sinha, and Sinha, Proc. Roy. Soc. (London) **A242**, 28 (1957).

perature cubic phases. Concluding with Dunitz and Orgel, and McClure that the origin of the distorted structures is the Jahn-Teller effect, we have constructed an approximate model for the system which takes into account the interaction between local distortions about neighboring transition metal cations. By the use of the usual methods of statistical mechanics it has proved possible to derive the thermodynamic behavior of this model, and hence to contribute to an understanding of the cooperative nature of these crystal transformations. This paper treats the model for the spinel structure, while that required for the perovskites will be described separately.[7] Furthermore, we are concerned here only with those spinels having distorting cations on the octahedral sites alone (e.g., Mn_3O_4, $ZnMn_2O_4$, $CuFe_2O_4$, etc.); the more general case will form the subject of a separate investigation.

Section II is devoted to a brief review of the Jahn-Teller effect followed by a detailed description of the model for the spinels. In Sec. III, the Hamiltonian of the system is derived, and from it is deduced the structure of the distorted phase which may exist at low temperatures. Section IV contains a mathematical treatment of the thermodynamic properties of the model by the general methods employed in the study of cooperative phenomena. Explicit consideration is given to the temperature dependence of the free energy, entropy, internal energy, heat capacity, and lattice parameters. Section V outlines the calculation of Sec. IV for the case where nondistorting cations dilute the active compound; the composition dependence of the transformation is thus obtained. A comparison of the theoretical results with the experiments to which they apply is presented in Sec. VI.

The principal result of importance in this investigation is the demonstration that the transformations from tetragonal to cubic spinel phases are thermodynamically of the *first order*. That is a latent heat, a volume discontinuity, lattice parameter discontinuities, and a lambda anomaly in the heat capacity are to be observed at the transformation temperature.

II. THEORETICAL MODEL

To begin, we review the action of the Jahn-Teller effect in causing the large crystal distortions by summarizing the main conclusions presented by Dunitz and Orgel.[5] According to the theorem of Jahn and Teller,[8] molecules with orbitally degenerate electronic ground states are unstable in the symmetric configuration. The molecule will always find at least one vibrational coordinate along which it can distort to split the degeneracy and lower its energy. In the octahedral transition metal complexes, those cations having one, two, four, six, seven, and nine $3d$ electrons will have orbitally degenerate ground states. It is only for the $3d^4$ (Cr^{2+}, Mn^{3+}, Fe^{4+}) and $3d^9$ (Cu^{2+}) configurations where the degeneracy occurs in the strongly antibonding orbitals, that the distortions are large, however. For these two cases the commonly observed distortions are of the prolate tetragonal type; the octahedron is elongated so that now four ligands lie close to the cation while two are farther removed. The opposite distortion, giving two close and four distant ligands is also possible, but does not seem to occur (in spinels, at any rate). Öpik and Pryce[9] have ascribed the greater stability of the prolate tetragonal distortion to the anharmonic nature of the electrostatic forces acting between the central cation and the ligands. In a more complete analysis Liehr and Ballhausen[10] have shown that either distortion may occur depending on the exact nature of the cation-ligand interaction. In this paper, we shall consider only the elongated distortion, the generalization to the other case being straight forward if required. Furthermore, there are three equivalent tetragonal distortions, one along each of the cubic axes, and in the isolated complex each will occur with equal probability.

In a crystalline material the situation is made complicated by the interaction of neighboring distortions, and it becomes necessary to examine the problem in terms of the details of specific lattice structures. In the ideal cubic AB_2O_4 spinel structure[11] the oxygen ions form a cubic close-packed lattice with the A and B cations occupying, respectively, the tetrahedrally and octahedrally coordinated interstices. The octahedral sites may be subdivided into four interpenetrating nonequivalent face centered cubic lattices, and a B cation in any one such sublattice has six B neighbors, two from each of the other sublattices. For the purposes of this investigation it is convenient to view the spinel lattice simply as a collection of octahedral transition metal complexes centered on the B ion sites, the apexes falling on the cubic close-packed anion positions. The octahedra are then seen to pack in such a way that each complex shares two oxygen ions with each of its six neighboring complexes.

Now, in such a cubic system, each B transition metal ion will be subject to a crystalline electric field of octahedral symmetry, and those whose electronic configurations were listed above will possess orbitally degenerate ground states. To satisfy the Jahn-Teller theorem each such cation must distort its immediate environment, the distortions presumably being of the same type as in the free complexes. Since the octahedra about the cations share ligands at their edges, the distortions in neighboring complexes must interfere with each other. At high temperatures, where this interaction

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[7] P. J. Wojtowicz, Bull. Am. Phys. Soc. **4**, 63 (1959).

[8] H. A. Jahn and E. Teller, Proc. Roy. Soc. (London) **A161**, 220 (1937).

[9] U. Öpik and M. H. L. Pryce, Proc. Roy. Soc. (London) **A238**, 425 (1957).

[10] A. D. Liehr and C. J. Ballhausen, Ann. Phys. **3**, 304 (1958).

[11] The geometry of the spinel lattice has been described in detail by E. W. Gorter, Philips Research Repts. **9**, 295 (1954).

is of little importance, each complex will distort independently, all three equivalent tetragonal distortions again occurring with equal probability. Furthermore, the orientations of the distortions are rapidly interchanged by means of the lattice vibrations, and at any instant an equal number of complexes are distorted in the three cubic directions. The structure is described as being statistically cubic; to a diffraction experiment the crystal will indeed appear to be cubic, although requiring an abnormally large vibrational correction. Upon lowering the temperature, the interactions between distortions begin to dominate, and the probability of a given distorted complex being oriented in a certain direction now depends on the orientations of at least those neighboring complexes with which ligands are shared. A short-ranged ordering of distortions may then occur. Finally a temperature is reached, below which minimization of the free energy is accomplished by minimizing the interaction energy between local distortions rather than by a maximization of the entropy (disorder). The distortions will form a superlattice, ordering in such a way as to provide the least interference between neighboring complexes. A macroscopically distorted phase thereby results. The exact nature of such a transformation cannot, of course, be inferred from these and previous considerations. In this paper these heretofore lacking details will be derived from our model, a description of which now follows.

The basic unit of the model, chosen to represent the complex formed by a transition metal cation and its six ligands, is the simple rigid octahedron. Because of the Jahn-Teller effect each octahedron is given a prolate tetragonal distortion so that there will be one long and two short axes. The magnitude of the distortion is assumed to be a constant independent of the temperature and the orientation of neighboring distortions. The model for the spinel (A ions not included) may now be constructed by centering these basic units on the points of the four B-ion fcc lattices with the axes of the octahedra directed along the cubic directions. Each octahedron shares an edge with six neighboring octahedra. If the octahedra were undistorted a cubic structure would result. Since the octahedra are distorted, this structure will not, in general, possess cubic symmetry. It is convenient, however, to define a set of pseudo-cubic axes with respect to which it will be possible to specify the orientation of the octahedral axes. Within this framework it is easily seen that the octahedra are constrained to only three approximately definite orientations. The long axes of the octahedra may be directed (exactly, or very nearly so) in the x, the y, or the z directions of the pseudocubic coordinate system defined by the stacking of our basic units.

The essential feature of the model is the pairwise interaction of neighboring Jahn-Teller distortions. Assuming that only nearest neighbors interact appreciably, we find that there are four different pair potentials depending on the relative orientation of the octahedra involved. The possibilities, along with the resulting pair interaction potentials are depicted in Fig. 1 where the octahedra are schematically represented by drawing their three mutually perpendicular axes (these are equivalently the six cation-ligand bonds, four short and two long). The magnitudes of the potentials V_{11} and V_{12} should be small as the Jahn-Teller distortions do not interfere with each other in these configurations. In the configurations leading to the potentials V_{21} and V_{22}, the distortions do interfere with each other, and considerable strains are induced in the structure about the two cations involved. The potentials V_{21} and V_{22} are therefore larger in magnitude, and it is reasonable to order the pair potentials as follows: $V_{12} < V_{11} \ll V_{22} < V_{21}$. We shall further assume that the pair potentials are constants, independent of the temperature and the orientations of other octahedra in the neighborhood of the pair in question. Moreover, an analysis of the detailed nature of these interactions in terms of more basic principles shall not be undertaken at this time.

In addition to the assumptions already discussed, it is important to indicate several other approximations made in the construction of this model. For simplicity the influence of the lattice vibrations is completely neglected. It is known,[12,13] however, that although the lattice vibrations may contribute profoundly to cooperative phenomena, the effect is not such as to alter the qualitative character of the transformation. Thus this theory would predict a first order transformation even if the lattice vibrations were included; the exact values of the derived thermodynamic functions would, of course, be changed. The interaction between the octahedra and the tetrahedrally coordinated A ions is also neglected. But since these will be nondistorting cations in the systems of interest, it is reasonable to suppose that these interactions will depend little on the orientations of the octahedra. Also ignored are the small trigonal distortions induced in the octahedra by deviations of the oxygen parameter, u from the ideal value of 0.375.

III. THE HAMILTONIAN

The Hamiltonian for a particular configuration of the crystal is the sum of all the nearest neighbor pair

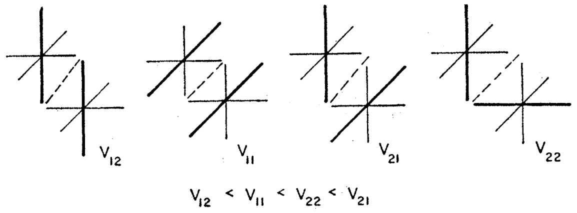

FIG. 1. The four possible pair interactions between octahedra in the spinel. The octahedra are schematically represented by their axes, one long (heavy) and two short. The dashed lines are the shared octahedral edges.

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[12] K. F. Stripp and J. G. Kirkwood, J. Chem. Phys. **22**, 1579 (1954).

[13] P. J. Wojtowicz, thesis, Yale University, 1956 (unpublished).

interaction potentials appropriate to that configuration. The enumeration of the pair potentials is facilitated by the division of the system of octahedra into the four face-centered *B*-ion sublattices of the spinel structure. The four sublattices may be classified according to the (110) directions along which the lines of centers between neighboring octahedra are found to fall. Figure 2 shows the arrangement of nearest neighbors about a site of sublattice 1, while Table I gives the directions of the lines of centers for neighbors between all pairs of sublattices. The directions are labeled both by the usual Miller indexes and in the more convenient (μ,μ') notation. The (μ,μ') direction is defined to be the direction of the sum of unit vectors pointing in the μ and μ' cubic directions. We note that the lines of centers between a given site and the two nearest neighbors from the same neighboring sublattice are collinear. Furthermore, there will be $N/2$ sites in each sublattice so that we treat a mole of transition metal spinel, AB_2O_4 (N is Avagadro's number).

The many possible configurations of the system may be completely specified by the use of a set of occupation variables defined as follows:

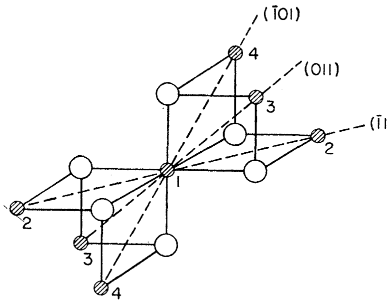

FIG. 2. The arrangement of nearest neighbor *B* sites about a *B* site of sublattice 1. The open circles are the oxygens while the hatched circles represent cations. Each cation is labeled according to the sublattice on which it resides.

$$\rho_i^s(\nu)=\begin{cases}1, & \text{if site } i \text{ on sublattice } s \text{ is occupied by an octahedron distorted in the } \nu\text{-direction,}\\ 0, & \text{otherwise,}\end{cases}$$

where $i=1, \cdots, N/2$; $s=1, 2, 3, 4$; and $\nu=x, y, z$. From their definition, it is seen that the occupation variables must satisfy the relation:

$$\textstyle\sum_\nu \rho_i^s(\nu)=1, \quad (s=1, 2, 3, 4), \quad (i=1, \cdots, N/2), \tag{1}$$

since an octahedron in any one site must have a single definite orientation with respect to the pseudocubic axes. Further,

$$\textstyle\sum_i \rho_i^s(\nu)=N_s^\nu, \quad (\nu=x, y, z), \quad (s=1, 2, 3, 4), \tag{2}$$

where N_s^ν is the number of octahedra on sublattice s with long axis oriented in the ν-direction. A specification of the values of the $6N$ occupation variables completely determines the configuration of the system.

To obtain the Hamiltonian function which determines the energies of these configurations, it is necessary to introduce another set of two-valued variables, the nearest neighbor selector factors which are defined by

TABLE I. Directions of lines-of-centers of neighboring octahedra between all pairs of sublattices.

Sub-lattice	1	2	3	4
1	None	$(\bar{1}10)$ $(-x, y)$	(011) (y, z)	$(\bar{1}01)$ $(-x, z)$
2	$(\bar{1}10)$ $(-x, y)$	None	(101) (x, z)	$(0\bar{1}1)$ $(-y, z)$
3	(011) (y, z)	(101) (x, z)	None	(110) (x, y)
4	$(\bar{1}01)$ $(-x, z)$	$(0\bar{1}1)$ $(-y, z)$	(110) (x, y)	None

$$\lambda_{ij}^{st}=\begin{cases}1, & \text{if site } i \text{ on sublattice } s \text{ is a nearest neighbor to site } j \text{ on sublattice } t.\\ 0, & \text{otherwise.}\end{cases}$$

These satisfy the relations:

$$\textstyle\sum_i \lambda_{ij}^{st}=\sum_j \lambda_{ij}^{st}=z/3, \quad (\text{all } st \text{ pairs}), \tag{3}$$

since each site has $z/3=2$ nearest neighbors from each of the neighboring sublattices. The direction of the line of centers of a pair connected by a nonvanishing λ_{ij}^{st} may be obtained by reference to the s-t element of Table I. For example, the line of centers of a pair connected by λ_{ij}^{24} lies in the $(0\bar{1}1)$ or $(-y, z)$ direction.

The configurational potential energy for any pair of sites i, j in the crystal may be written in the form

$$\rho_i^s(\nu)\lambda_{ij}^{st}\rho_j^t(\nu')V(\nu,\nu';\mu,\mu'),$$

where $\rho_i^s(\nu)$ and $\rho_j^t(\nu')$ specify the orientations of the octahedra at i and j, and where λ_{ij}^{st} discards those terms for pairs which are not actually nearest neighbors. $V(\nu,\nu';\mu,\mu')$ is the pair interaction potential resulting from the contact of a pair of octahedra distorted in the ν and ν' directions, respectively, and having their line of centers along the (μ,μ') direction (the μ and μ' being taken from the s-t element of Table I). Now, it was shown in Sec. II that there are only four different possible values for $V(\nu,\nu';\mu,\mu')$ depending on the relative orientation of the pair under consideration. Table II lists the pair potentials appropriate to the different combinations of indexes $(\nu,\nu';\mu,\mu')$ generated by the various configurations of pairs in this system. The results are easily verified by examination of Fig. 1. For each neighboring pair i, j in the crystal, there will be nine terms of the form shown above since there are three allowed orientations for each member of the pair.

TABLE II. Pair potentials resulting from different relative configurations of neighboring octahedra.

Configuration	$V(\nu,\nu';\mu,\mu')$
$\nu=\nu'\neq\mu,\mu'$	V_{11}
$\nu=\nu'=\mu$ or μ'	V_{12}
$\nu=\mu\neq\nu'\neq\mu'$	V_{21}
$\nu=\mu'\neq\nu'\neq\mu$	V_{21}
$\nu=\mu\neq\nu'=\mu'$	V_{22}
$\nu=\mu'\neq\nu'=\mu$	V_{22}

Only one of the nine will be nonvanishing, however; by their definition, the occupation variables will discard those terms not actually describing the true situation.

The Hamiltonian function can now be constructed by summing the interaction terms for all pairs in the system, taking proper account of the entires in Tables I and II. The procedure is straightforward but tedious, and shall not be displayed here. A simplified form of the Hamiltonian can be obtained, however, by making use of the relationships satisfied by the occupation variables and nearest neighbor selector factors, Eqs. (1) to (3). Upon collecting terms, the result is

$$\begin{aligned} H&=\tfrac{1}{3}Nz(2V_{21}+V_{12})+(V_{11}+V_{12}-2V_{21})p \\ &\qquad +(V_{22}-V_{12})q, \\ p&=\sum_{s<t}^{4}\sum_{i,j}^{N/2}\rho_i{}^s(\nu)\lambda_{ij}{}^{st}\rho_j{}^t(\nu), \\ q&=\sum_{s<t}^{4}\sum_{i,j}^{N/2}\lambda_{ij}{}^{st}[\rho_i{}^s(\mu)\rho_j{}^t(\mu')+\rho_i{}^s(\mu')\rho_j{}^t(\mu)], \end{aligned} \tag{4}$$

where the μ and μ' are the (μ,μ') of the *s*-*t* element of Table I, and where $\nu\neq\mu$ or μ'. The first term is a constant while p and q are amenable to a simple interpretation. In each term, $\rho_i{}^s(\nu)\lambda_{ij}{}^{st}\rho_j{}^t(\nu)$ of p, $\nu=\nu'\neq\mu$ or μ'. Referring to Table II, it is found that this combination of indexes results from that relative orientation leading to the potential V_{11}. Thus, p is the total number of nearest neighbor pair contacts of the kind contributing V_{11} to the configurational energy. In each term of q, $\nu=\mu$, $\nu'=\mu'$ or $\nu=\mu'$, $\nu'=\mu$. Table II shows that these combinations result from that relative orientation leading to the potential V_{22}. Therefore, q is the total number of nearest neighbor pair contacts of the type contributing V_{22} to the energy.

The Hamiltonian function can be used to deduce the structure of the distorted phase which may result from an ordering of the octahedra at low temperatures. At the absolute zero a stable, ordered crystalline phase is characterized by having a minimum configurational energy and a vanishing configurational entropy (disorder). That completely ordered arrangement of the distorted octahedra which leads to a minimum in H will then represent the low-temperature stable phase. Since $V_{22}-V_{12}>0$ and $V_{11}+V_{12}-2V_{21}<0$, H will be minimized when p and q are simultaneously maximized and minimized, respectively. The only completely ordered arrangement accomplishing this places the long axes of all the octahedra along the same crystallographic direction. In this case p attains its absolute maximum, $Nz/3$ while q is at its absolute minimum, zero. The configurational energy of this phase is $Nz(2V_{12}+V_{11})/3$, one-third of the neighbor contacts contributing V_{11}, two-thirds contributing V_{12}. With all the octahedra distorted in the same direction, the low-temperature structure must be tetragonal and with $c/a>1$ in as much as the individual octahedra are prolately tetragonal. A number of spinels containing $3d^4$ and $3d^9$ cations in the octahedral sites have been found to have the tetragonally distorted structure at low temperatures. Several examples with their room-temperature c/a ratios are Mn_3O_4 (1.16),[14] γ-Mn_2O_3 (1.16),[15] $ZnMn_2O_4$ (1.14),[14] $MgMn_2O_4$ (1.15),[16] $CoMn_2O_4$ (1.15),[16] and $CuFe_2O_4$ (1.06).[17]

IV. THERMODYNAMIC PROPERTIES

The Hamiltonian function in terms of the general occupation variables, Eq. (4), may now be used to form a basis for any one of a number of techniques that have been developed to treat the statistical mechanics of cooperative phenomena. The most convenient technique for this problem is the method of moments developed by Kirkwood.[18] By using this procedure it will be possible to ascertain the approximations made in evaluating the partition function, and to form a framework within which higher approximations may be constructed in a consistent fashion. The first part of the calculation involves the evaluation of an approximate partition function for a fixed but arbitrary set of orientations, $\mathbf{N}=\{N_1{}^x, N_1{}^y, \cdots, N_4{}^y, N_4{}^z\}$, of the octahedra on the sublattices. The equilibrium values of the set $\mathbf{N}$ are then obtained by minimizing the configurational free energy with respect to $\mathbf{N}$. The subsequent determination of the temperature dependence of the thermodynamic functions concludes this section.

The partition function, Z_N for a fixed set of orientations, $\mathbf{N}$ is obtained by summing the Boltzmann factor, $\exp(-\beta H)$ over all the distinguishable configurations of the system that can be generated from the set $\mathbf{N}$. Following the method of moments, this is expressed as

$$\begin{aligned} Z_N&=P_NQ_N\exp[-\beta Nz(2V_{21}+V_{12})/3], \\ P_N&=[(N/2)!]^4/\prod_\nu\prod_s N_s{}^\nu!\,, \\ Q_N&=P_N{}^{-1}\textstyle\sum'\exp[-\beta W(p,q)], \\ W(p,q)&=(V_{11}+V_{12}-2V_{21})p+(V_{22}-V_{12})q, \end{aligned} \tag{5}$$

where $\beta=1/kT$, k being the Boltzmann constant and T the thermodynamic temperature. The symbol $\sum'$ means a summation over the two allowed values of all $6N$ occupation variables:

$$\textstyle\sum'\rightarrow\sum_{\rho_1{}^1(x)=0}^{1}\ \sum_{\rho_1{}^1(y)=0}^{1}\cdots(6N\text{ sums})\cdots\sum_{\rho_{N/2}{}^4(z)=0}^{1}, \tag{6}$$

subject to the restrictions expressed in Eqs. (1) and (2). P_N is the number of distinguishable configurations for

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[14] B. Mason, Am. Mineralogist **32**, 426 (1947).

[15] E. J. Verwey and J. H. deBoer, Rec. trav. chem. **55**, 531 (1936).

[16] P. F. Bongers, thesis, University of Leiden, 1957 (unpublished).

[17] E. F. Bertaut, J. phys. radium **12**, 252 (1951).

[18] J. G. Kirkwood, J. Chem. Phys. **6**, 70 (1938).

the set **N**, and hence is the number of nonvanishing terms generated by $\sum'$. P_N serves as a normalizing factor for the configuration sum Q_N; when βW vanishes, Q_N reduces to unity.

The configuration sum may be expanded in a power series in $-\beta$ in terms of the moments M_n:

$$Q_N=\sum_{n=0}^{\infty}\frac{(-\beta)^n}{n!}M_n,\qquad M_n=P_N^{-1}\sum{}' W^n=\langle W^n\rangle. \tag{7}$$

By their definition above, the moments are just the *a priori* (that is, unweighted) averages of the simple powers of W, averaged over all the permitted distinguishable configurations of the system. A more useful expansion utilizes the semi-invariants of Thiele, λ_m:

$$Q_N=\exp\left[\sum_{m=1}^{\infty}\frac{(-\beta)^m}{m!}\lambda_m\right]. \tag{8}$$

The semi-invariants may be computed from the moments by equating the two expressions for Q_N and separating terms of the same order in $-\beta$. The details of this procedure have been published elsewhere.[18,19] The first few λ_m are given by

$$\begin{aligned}\lambda_1&=M_1,\\ \lambda_2&=M_2-M_1^2,\\ \lambda_3&=M_3-3M_2M_1+2M_1^3.\end{aligned} \tag{9}$$

A consistent sequence of approximations to Q_N may be obtained by retaining one, two, $\cdots$, n semi-invariants in Eq. (8). We shall make use of the first approximation in which all terms beyond λ_1 are neglected:

$$Q_N=\exp(-\beta\lambda_1)=\exp(-\beta M_1). \tag{10}$$

The nature of this approximation is demonstrated by examination of the form of the invariants, Eq. (9), or by comparing Eqs. (7) and (10). In either case, it is seen that retaining only λ_1 is equivalent to assuming that $M_n=M_1{}^n$, all higher moments are powers of the first. This is true if the orientations on neighboring sites are uncorrelated, for then the averages over different sites are independent, leading to a set of moments having no dispersion. Thus, the approximation adopted is based on the premise that there is little short range ordering between neighboring octahedra; the system may be completely described by a long range order, that is by the set **N**. The present treatment is therefore analogous to the well-known "molecular field" theory of magnetism and to the "random mixing" approximation in the theory of mixtures.

The evaluation of the first moment is made straightforward by expression in terms of the occupation variables:

$$\begin{aligned}M_1&=(V_{11}+V_{12}-2V_{21})\langle p\rangle+(V_{22}-V_{12})\langle q\rangle,\\ \langle p\rangle&=\sum_{s<t}^{4}\sum_{i}^{N/2}\langle\rho_i{}^s(\nu)\rangle\langle\sum_{j}^{N/2}\lambda_{ij}{}^{st}\rho_j{}^t(\nu)\rangle,\\ \langle q\rangle&=\sum_{s<t}^{4}\sum_{i}^{N/2}\{\langle\rho_i{}^s(\mu)\rangle\langle\sum_{j}^{N/2}\lambda_{ij}{}^{st}\rho_j{}^t(\mu')\rangle\\ &\qquad+\langle\rho_i{}^s(\mu')\rangle\langle\sum_{j}^{N/2}\lambda_{ij}{}^{st}\rho_j{}^t(\mu)\rangle\},\end{aligned} \tag{11}$$

where the summations over s, t, and i have been removed from the brackets since averages of sums are sums of averages. In addition, since *a priori* distributions on different sublattices are independent, the averages can be decomposed in products in as much as the ρ^s and ρ^t refer to sites on different lattices. Because the *a priori* average value of $\rho_i{}^s(\omega)$, $(\omega=x, y, z)$, is the same for all sites i,

$$\begin{aligned}\langle\rho_i{}^s(\omega)\rangle&=\frac{2}{N}\sum_i\langle\rho_i{}^s(\omega)\rangle=\frac{2}{N}\langle\sum_i\rho_i{}^s(\omega)\rangle\\ &=\frac{2}{N}\langle N_s{}^\omega\rangle=\frac{2}{N}N_s{}^\omega,\end{aligned} \tag{12}$$

where Eq. (2) was used in passing from the first to the second line above. In a similar way,

$$\begin{aligned}\langle\sum_j\lambda_{ij}{}^{st}\rho_j{}^t(\omega)\rangle&=\frac{2}{N}\langle\sum_i\sum_j\lambda_{ij}{}^{st}\rho_j{}^t(\omega)\rangle\\ &=\frac{2}{N}\left\langle\frac{z}{3}N_t{}^\omega\right\rangle=\frac{2z}{3N}N_t{}^\omega,\end{aligned} \tag{13}$$

where in this case it was necessary to use Eq. (3) in addition to Eq. (2). Collecting terms, the value of the first moment is

$$\begin{aligned}M_1=\frac{2z}{3N}\sum_{s<t}^{4}[&(V_{11}+V_{12}-2V_{21})N_s{}^\nu N_t{}^\nu\\ &+(V_{22}-V_{12})(N_s{}^\mu N_t{}^{\mu'}+N_s{}^{\mu'}N_t{}^\mu)],\end{aligned} \tag{14}$$

where again $\nu\neq\mu$ or μ', the μ and μ' being taken from the s-t element of Table I. The configurational partition function for the set **N** is then obtained (in the first approximation) by combining Eqs. (5), (10), and (14).

The determination of the equilibrium values of the set **N** is considerably simplified once it is recognized that the twelve members of the set are not all independent. In fact, this large number resulted only because of the division of the system into sublattices, a concept introduced solely for the purpose of simplifying the calculation of the Hamiltonian and partition function. Four dependent members can be eliminated immediately by the relations

$$\textstyle\sum_\nu N_s{}^\nu=N/2,\quad(s=1, 2, 3, 4), \tag{15}$$

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[19] R. W. Zwanzig, J. Chem. Phys. 22, 1420 (1954).

since the total number of octahedra on any sublattice is fixed. Seven more members can be eliminated by symmetry considerations. If the z direction is defined to be the unique direction of the completely ordered tetragonal phase, then at the absolute zero, all N_s^z will equal $N/2$, their maximum value. Since the Hamiltonian is invariant to the labeling of the sublattices,[20] the deviations with temperature of the N_s^z from $N/2$ are independent of lattice index s, and hence must be identical for all temperatures, so that

$$N_1^z=N_2^z=N_3^z=N_4^z. \tag{16}$$

Furthermore, in the perfectly ordered configuration, the individual octahedra, the bulk phase, *and* the nearest neighbor environment about any given octahedron all have tetragonal symmetry with coincident unique axes (z direction). The deviations from perfect order must therefore occur by the orientation of the octahedra into the x and y directions equally, so that on each sublattice, and for all temperatures,

$$N_s^x=N_s^y, \quad (s=1, 2, 3, 4). \tag{17}$$

The eleven relationships between the members of the set $\mathbf{N}$, Eqs. (15) through (17), now permit the specification of all the configurations of the system in terms of a single long-range order parameter σ which may be defined as follows:

$$\begin{aligned} &N_s^x=N_s^y=N(1-\sigma)/6, \\ &N_s^z=N(1+2\sigma)/6, \quad (s=1, 2, 3, 4). \end{aligned} \tag{18}$$

σ ranges in value from unity in the perfectly ordered tetragonal structure to zero in the randomly oriented statistically cubic phase. Substitution of Eq. (18) in Eqs. (5), (10), and (14) yields the partition function in terms of σ:

$$\begin{aligned} Z_N&=P_N \exp\{-\beta[E(0)-2NzV\sigma^2/9]\}, \\ V&=V_{22}-V_{11}+2V_{21}-2V_{12}>0, \\ E(0)&=Nz(V_{11}+2V_{12}+4V_{21}+2V_{22})/9, \end{aligned} \tag{19}$$

where $E(0)$ is the configurational energy of the randomly oriented phase, $\sigma=0$. The molar configurational free energy, $F(\sigma)=-kT \ln Z_N$, is given by the following:

$$\begin{aligned} \frac{F(\sigma)-F(0)}{2NkT/3}&=(1+2\sigma)\ln(1+2\sigma) \\ &\quad +2(1-\sigma)\ln(1-\sigma)-\sigma^2/J, \end{aligned} \tag{20}$$

$$F(0)=E(0)-2NkT\ln 3,$$

where Stirling's approximation was used to compute P_N in terms of σ, while $F(0)$ is the free energy of the cubic phase, and $J=3kT/zV$ is a reduced temperature.

The equilibrium values of the long range order for all temperatures are determined by minimizing F with respect to σ at constant J. Setting $(\partial F/\partial\sigma)_J$ to zero provides the following transcendental equation between σ and J:

$$\ln(1+2\sigma)-\ln(1-\sigma)=\sigma/J. \tag{21}$$

The multivalued solution of this equation for positive J was obtained by numerical methods on an IBM-650 electronic computer. The results are displayed graphically in Fig. 3. The solid branches are those values of σ which give an absolute minimum to the free energy, and therefore represent the thermodynamically stable phases. The location of the transformation temperature is accomplished by the determination of the conditions under which a phase of finite order σ can be in equilibrium with the cubic phase. The usual requirement for the coexistence of two phases is the equality of their molar free energies. Thus, setting $F(\sigma)-F(0)$ to zero in Eq. (20) and solving simultaneously with Eq. (21) should give the transformation temperature. The analytical solution of this system of equations reveals that at a single temperature, $J_t=(4\ln 2)^{-1}$, a tetragonal phase with $\sigma=\frac{1}{2}$ is in equilibrium with the cubic phase. Reference to Fig. 3 shows that above J_t the cubic phase alone is stable, while below J_t only tetragonal phases having $\sigma>\frac{1}{2}$ are stable. It is therefore demonstrated that the transformation from tetragonal to cubic symmetry in transition metal spinels is a *first order* phase transformation.

Other thermodynamic quantities of interest may be derived from the free energy by the use of the familiar formulas of thermodynamics. The results for the molar configurational internal energy, entropy and heat capacity, respectively, are

$$\begin{aligned} E(\sigma)&=E(0)-2NzV\sigma^2/9, \\ s(\sigma)&=\tfrac{2}{3}Nk[3\ln 3-(1+2\sigma)\ln(1+2\sigma) \\ &\qquad -2(1-\sigma)\ln(1-\sigma)], \\ C(\sigma)&=\frac{4Nk\sigma^2/3J^2}{[3/(1-\sigma)(1+2\sigma)]-1/J}. \end{aligned} \tag{22}$$

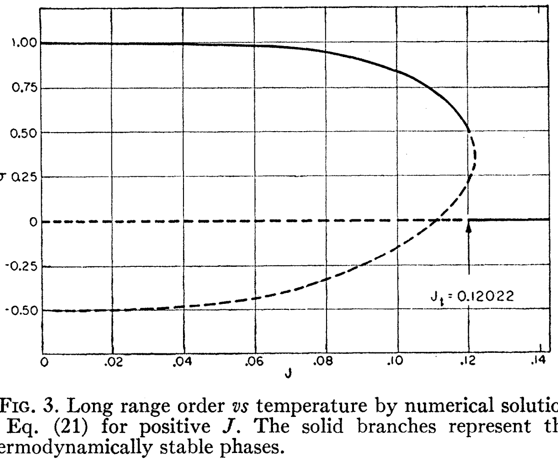

FIG. 3. Long range order *vs* temperature by numerical solution of Eq. (21) for positive J. The solid branches represent the thermodynamically stable phases.

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[20] Note that the configurational energy of the system, Eq. (4), depends only on the values of p and q. These in turn are just the number of certain kinds of interactions, and are independent of the notion of sublattices or the labeling of directions.

The explicit temperature dependence of these quantities may be calculated by the substitution of the solutions of Eq. (21), $\sigma(J)$ into Eq. (22). The theoretical curve for the heat capacity $C(J)$ is shown in Fig. 4 where the typical lambda shape characteristic of cooperative phenomena is in evidence. The discontinuities in the thermodynamic quantities at the transformation temperature are computed from Eq. (22) by accounting for the jump in σ from $\frac{1}{2}$ to zero. The values for the latent heat, entropy change, and heat capacity discontinuity are $\Delta E = NzV/18$, $\Delta S = 0.918$ cal/°mole, and $\Delta C = 22.4$ cal/°mole, respectively.

The temperature dependence of the lattice parameters cannot be derived from the present model of the spinel in a rigorous way, but an adequate approximation can be deduced from the following considerations. We shall assume that the c and a parameters of the average tetragonal unit cell are proportional to the mean lengths of the octahedral axes aligned along and perpendicular to the unique axis (z direction). Let P_ν be the probability of finding an octahedron with long axis oriented in the ν direction, and let α and $\gamma\alpha$ be the lengths of the short and long octahedral axes. The mean length in the z direction is $\alpha(\gamma P_z + P_x + P_y)$, while in a perpendicular direction, say x, the mean length is $\alpha(\gamma P_x + P_y + P_z)$. If we neglect the normal thermal expansion of the lattice or assume that it is isotropic, the constants of proportionality for c and for a are equal, and it becomes possible to express the c/a ratio as

$$c/a = (\gamma P_z + P_x + P_y)/(\gamma P_x + P_y + P_z). \tag{23}$$

The probability P_ν is just the fraction of octahedra oriented in the ν direction, equal to $\sum_s N_s^\nu/2N$. The relationship between the c/a ratio and the long-range order is therefore

$$\frac{c}{a} = \frac{3+(\gamma-1)(1+2\sigma)}{3+(\gamma-1)(1-\sigma)} \approx 1+(\gamma-1)\sigma, \tag{24}$$

where $(\gamma-1)$ is the deviation of the octahedral axial ratio from unity. Equation (24) shows that the curve of c/a *vs* T will closely resemble the solid branches in Fig. 3, showing a finite discontinuity, $\Delta(c/a) = (\gamma-1)/2$ at the transformation temperature.

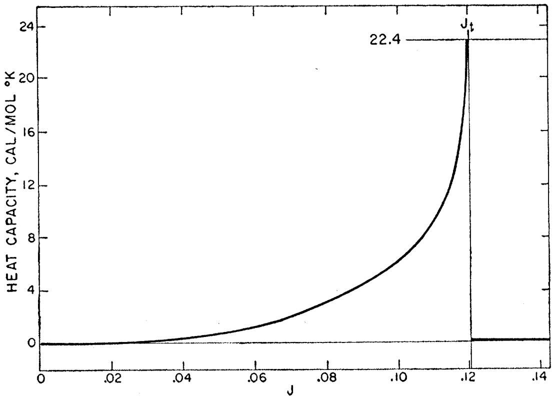

FIG. 4. Theoretical heat capacity *vs* temperature by substitution of solutions of Eq. (21) into Eq. (22).

If the normal thermal expansion of the lattice is neglected, it is also possible to derive the influence of disordering on the unit cell volume. Using the same procedure as above, the volume of the unit cell (equal to ca^2) is found to be proportional to the following function of the long range order parameter:

$$\alpha^3[\gamma + \tfrac{1}{3}(\gamma-1)^2(1-\sigma^2) + (1/27)(\gamma-1)^3 \times (1-3\sigma^2+2\sigma^3)]. \tag{25}$$

The fractional volume change on passing from the tetragonal to cubic phase at the transformation temperature can be computed from (25) and is given by $\Delta v/v = (\gamma-1)^2/12\gamma$. For a typical case, $\gamma = 1.16$, and the fractional volume expansion predicted by the model is 0.0018.

Having completed the thermodynamic analysis of the model, we shall now compare these results with those obtained by Finch, Sinha, and Sinha.[6] As stated previously, these authors based their calculation on the consideration of the number of octahedra oriented in "right" and "wrong" directions. What they failed to account for, however, is the fact that there are twice as many wrong directions (x and y) available as there are right directions (z). One must then conclude that at the highest temperatures this model would have half the octahedra oriented in the z direction with the remaining half oriented in x and y [see Eq. (3) of reference 6, $\beta \rightarrow 0$]. It is clear, however, that the high-temperature phase must have equal populations in all three directions in order that the structure be cubic.

The seriousness of this error is demonstrated most clearly upon examination of the relationship between long-range order and temperature obtained by Finch *et al.*:

$$S = \tanh(\beta W_0 S),$$

where in their notation, S is the long-range order, and W_0 is an (undefined) interaction energy [see Eq. (8) of reference 6]. This form of equation is well-known in theories of cooperative phenomena, and it has been demonstrated[21] that its solution always leads to second-order phase changes. Thus, Finch's treatment would predict the continuous variation of lattice parameters and the absence of a latent heat and entropy change. The accumulated experimental evidence appears to support our prediction of a first-order change, as we shall show in the final section.

V. COMPOSITION DEPENDENCE

In this section we briefly consider the results obtained from the theoretical model appropriate to spinels having the formula $AB_{2-2x}C_{2x}O_4$, where a fraction x of

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[21] H. N. V. Temperley, *Changes of State* (Interscience Publishers, Inc., New York, 1956), p. 26.

the octahedrally coordinated B ions are replaced by the cation C. Unlike the B ions, C does not produce Jahn-Teller distortions in the octahedral sites. Distributed randomly among the octahedral sites, the C ions merely serve to dilute the nearest neighbor interaction structure of the B ions. The efficiency of the cooperative transformation is thereby reduced; the transformation temperature is lowered, and the maximum deviation of the c/a ratio from one is diminished.

The Hamiltonian of this model is derived by the same technique as used in Sec. III. The dilution of the distorted octahedra by the regular octahedra of the C now requires the introduction of an additional set of occupation variables, $\rho_i^s(0)$ which are defined to have the value one when site i of sublattice s is occupied by an undistorted C octahedron, and the value zero otherwise. The occupation variables still satisfy Eq. (1), except that ν is now summed over x, y, z, *and* 0. In addition to Eq. (2), the following sums also obtain:

$$\begin{gathered}\textstyle\sum_i \rho_i^s(0)=xN/2, \quad (s=1,2,3,4),\\ \sum_s \sum_{\nu\neq 0} N_s^\nu=(1-x)2N.\end{gathered} \tag{26}$$

The presence of the undistorted C octahedra also introduces three new pair interaction potentials. Since the C octahedra do not possess a unique axis, the pair interaction potentials resulting from the nearest neighbor contact of a B and C octahedron will depend only on the relative orientation of the long axis of the B with respect to the line of centers joining the B and C. Thus, the potential V_{02} will result when $\nu=\mu$ or μ', while V_{01} obtains when $\nu\neq\mu$ or μ', where again ν is the direction of the unique axis of the B, and (μ,μ') is the direction of the line of centers joining the pair in question. The configurations leading to V_{02} and V_{01} closely resemble those producing V_{12} and V_{11}, respectively, Fig. 1. Moreover, because of the lack of unique axes, the contact between two nearest neighbor C octahedra will always be V_{00}, independent of the (μ,μ') of the pair. With these new quantities, the configurational Hamiltonian of the model can be derived as before, the result being given by

$$\begin{aligned}H=\tfrac{1}{3}Nz[&2V_{21}+V_{12}+x(4V_{02}+2V_{01}-4V_{12}-2V_{21})\\ &+x^2(3V_{00}-2V_{01}-4V_{02}+3V_{12})]\\ &+(V_{11}+V_{22}-2V_{21})p+(V_{22}-V_{12})q,\end{aligned} \tag{27}$$

where p and q retain their former significance, Eq. (4). The form of H has not changed upon dilution, so that the structure of the low-temperature phase will remain tetragonal with $c/a>1$. The maximum value of p however, is diminished by the factor $(1-x)^2$.

Using the same arguments as in Sec. IV, the description of the system can again be reduced to the specification of the value of a single long-range order parameter σ. Because of the dilution by C, σ must be renormalized, so that it is now defined by

$$\begin{gathered}N_s^x=N_s^y=N(1-x)(1-\sigma)/6,\\ N_s^z=N(1-x)(1+2\sigma)/6, \quad (s=1,2,3,4).\end{gathered} \tag{28}$$

Application of the moment method to first approximation for a fixed value of σ gives the free energy of the diluted system as

$$\begin{aligned}\frac{F(\sigma)-F(0)}{2NkT/3}=(1-x)[&(1+2\sigma)\ln(1+2\sigma)\\ &+2(1-\sigma)\ln(1-\sigma)]-(1-x)^2\sigma^2/J,\end{aligned} \tag{29}$$

where J retains its former significance, and where the free energy $F(0)$ now contains the additional free energy of mixing of x moles AC_2O_4 with $(1-x)$ moles of *cubic* AB_2O_4. Differentiation with respect to σ at constant J provides the analog of Eq. (21):

$$\ln(1+2\sigma)-\ln(1-\sigma)=(1-x)\sigma/J. \tag{30}$$

Thus for any value of x, the dependence of σ on J is the same as depicted in Fig. 3, except that the abscissa must be properly scaled by the factor $(1-x)$. The first-order nature of the phase change is unaltered by the dilution of the interactions, the parameter σ still changing discontinuously from $\frac{1}{2}$ to zero at the transformation temperature J_t. Solving for J_t, it is found that $J_t(x)=(1-x)(4\ln 2)^{-1}=(1-x)J_t(0)$, showing that the reduction of the transformation temperature is proportional to the dilution. The internal energy, entropy and heat capacity may be obtained from the free energy by the straightforward differentiation with respect to T. The derived result for the heat capacity, analogous to Eq. (22), is

$$C(\sigma,x)=\frac{4Nk(1-x)^3\sigma^2/3J^2}{[3/(1-\sigma)(1+2\sigma)]-(1-x)/J}. \tag{31}$$

For any value of x, the heat capacity curve will have the same shape as in Fig. 4, except that the ordinate and the abscissa must be properly scaled by the factor $(1-x)$. The latent heat, entropy change, and heat capacity discontinuity at J_t are likewise all reduced from their corresponding "undiluted" values by the factor $(1-x)$.

The conspicuous appearance of the scaling factor $(1-x)$ demonstrates the possibility of a corresponding states principle between the thermodynamic functions of spinels of different composition x. We define a new reduced temperature by $\tilde{J}=J/(1-x)$ and a set of reduced molar thermodynamic functions by $\tilde{G}=G/(1-x)$, where $G=F$, E, S and C. By applying these definitions to the results of this section it is seen that all the thermodynamic equations assume the same form as those obtained in Sec. IV; the composition dependence no longer appears explicitly having been completely absorbed in $\tilde{J}$ and the $\tilde{G}$. The corresponding states principle must be used with caution, however. An examination of the manner in which it develops during the derivation reveals that it is a particular consequence of the approximations used in the evaluation of the partition function. If higher moments than the first were included, terms of higher order in $(1-x)$ would have appeared destroying the simplicity of the equations and preventing the use of scaling factors. The corresponding states principle should, therefore, be considered accurate only for small values of x.

The combined composition and temperature dependence of the c/a ratio has also been computed within the same approximation used in Sec. IV. An additional simplification was introduced by assuming that the axial lengths of the undistorted C octahedra are equal to α, the length of the short axes of the tetragonal B octahedra. This assumption eliminates the introduction of an additional parameter into the equations. Moreover, since we are primarily interested in the ratio of c to a, the errors introduced by this assumption will largely cancel out. Within this framework, the result for c/a is

$$\frac{c}{a}=\frac{3+(1-x)(\gamma-1)(1+2\sigma)}{3+(1-x)(\gamma-1)(1-\sigma)}\approx 1+(1-x)(\gamma-1)\sigma. \qquad (32)$$

The temperature dependence of c/a for different compositions is displayed in Fig. 5 where $[(c/a-1)/(\gamma-1)]$ is plotted as a function of J for several values of x. The composition dependence of c/a at different constant temperatures is shown in Fig. 6. Here $[(c/a-1)/(\gamma-1)]$ is plotted as a function of x for different ratios of the ambient temperature, T to the transformation temperature, $T_t(0)$ of pure AB_2O_4. The most prominent and noteworthy feature of the latter set of curves is the abrupt change in c/a at a certain critical composition characteristic of the ambient temperature. These results show that as the composition is changed, the onset of tetragonality will not be gradual with the appearance of arbitrarily small values of $(c/a)-1$, but rather that the first tetragonal phases to form will immediately possess large deviations of c/a from one. This behavior is, of course, a direct consequence of the first order nature of these transformations.

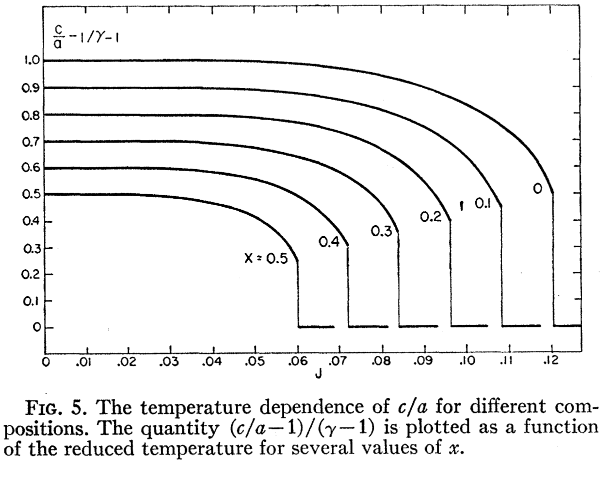

FIG. 5. The temperature dependence of c/a for different compositions. The quantity $(c/a-1)/(\gamma-1)$ is plotted as a function of the reduced temperature for several values of x.

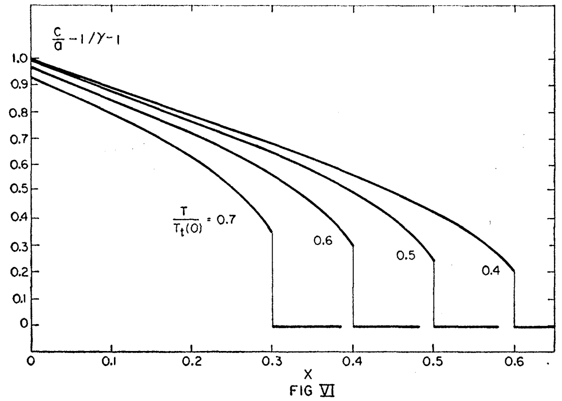

FIG. 6. The composition dependence of c/a for different temperatures. The quantity $(c/a-1)/(\gamma-1)$ is plotted as a function of the composition for several values of $T/T_t(0)$.

VI. COMPARISON WITH EXPERIMENT AND DISCUSSION

A list of compounds which exhibit the tetragonally distorted spinel structure (with $c/a>1$) at room temperature was presented at the end of Sec. III. We shall now consider some of these compounds individually, comparing the properties and predictions of the theoretical model with the available experimental evidence.

$CuFe_2O_4$

Properly prepared, $CuFe_2O_4$ is an inverse spinel so that half of the octahedral sites are occupied by the distorting $Cu^{2+}(3d^9)$ ions. The remaining cation sites contain the nondistorting $Fe^{3+}(3d^5)$ ions. As observed by several investigators, $c/a=1.06$ at room temperature.[6,17,22] The transformation temperature has been found to fall in the range, 360°C to 390°C.[22–24] The temperature dependence of the c/a ratio has been determined by Ohnishi, Teranishi, and Miyahara.[23] The experimental points are shown in Fig. 7(a) along with the theoretically computed curve. Equations (30) and (32) were used to compute the curve, the two adjustable parameters therein being given the following values: $T_t=633°K$ and $(1-x)(\gamma-1)=0.057$. The agreement between theory and experiment is exceptionally good; it is unfortunate, however, that not enough points were taken near T_t so that a definite experimental verification of the first order nature of the phase change could not be established. Also included in Fig. 7(a) is the c/a *vs* T data[23] for the compound $CuFe_{1.8}Cr_{0.2}O_4$. In this ma-

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[22] S. Miyahara and H. Ohnishi, J. Phys. Soc. (Japan) **12**, 1296 (1956).

[23] Ohnishi, Teranishi, and Miyahara, J. Phys. Soc. (Japan) **14**, 106 (1959).

[24] T. Inone and S. Iida, J. Phys. Soc. (Japan) **13**, 656 (1958).

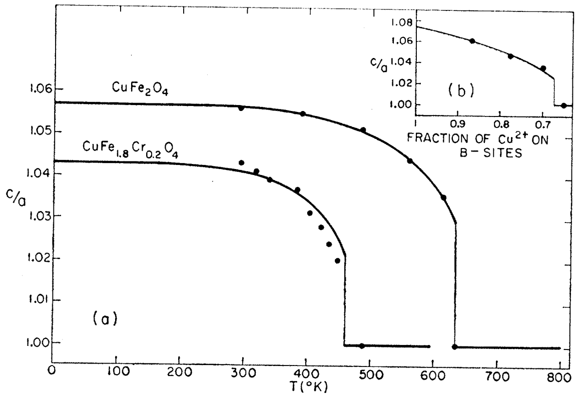

FIG. 7. (a) Temperature dependence of c/a for $CuFe_2O_4$ and $CuFe_{1.8}Cr_{0.2}O_4$ (data of reference 23). (b) The c/a ratio for $CuFe_2O_4$ as a function of the fraction of Cu actually in B sites (data of reference 6). See text for discussion of the theoretical curves.

terial a significant fraction of the Cu is present in the tetrahedral sites[23]; the transformation temperature and the limiting c/a ratio are therefore both reduced. The theoretical curve was computed using the valuse, $T_t=458$°K and $(1-x)(\gamma-1)=0.043$. The agreement between theory and experiment is not as good for this case, the reason being that the displacement of the Cu^{2+} onto the A sites does not just dilute the interaction between the distorted octahedra of the B lattice. Ions with the configuration $3d^9$ oblately distort the oxygen tetrahedra about the A sites, thereby introducing new distortions and interactions which are not accounted for in the present model.

The c/a ratio of $CuFe_2O_4$ has been measured as a function of the fraction of Cu^{2+} ions actually in B sites by Finch, Sinha, and Sinha.[6] The experimental results are shown in Fig. 7(b) along with the theoretical curve computed from Eqs. (30) and (32) with the parameters, $\gamma-1=0.157$ and $J(T_r)=0.0406$, where $J(T_r)$ is the value of J at the room temperature, T_r. The agreement is remarkably good despite the neglected effects of the Cu^{2+} on the A sites.

The heat capacity of $CuFe_2O_4$ has been measured over a wide temperature range by Inone and Iida.[24] The typical λ-anomaly is plainly in evidence, the shape of the experimental curve being quite similar to that given by Eq. (22) or (31), Fig. 4. The observed heat capacity discontinuity at 390°C is about 14 cal/mole°K in good agreement with the theoretical value of 11.2 cal/mole°K computed from Eq. (31) with $x=\frac{1}{2}$.

Mn_3O_4

The c/a ratio of Mn_3O_4 is 1.16 at room temperature.[14] Because of this large distortion from cubic symmetry, Mn_3O_4 has been assumed[1,5] to be a normal spinel with Mn^{2+} occupying the A sites and $Mn^{3+}(3d^4)$ filling all the available B sites. This assignment of configuration is compatible with other properties of the material, and is consistent with similar assignments required to explain the properties of $ZnMn_2O_4$ and γ-Mn_2O_3.[1] The temperature dependence of the lattice parameters of Mn_3O_4 has been determined recently by VanHooke and Keith.[25] The c/a ratio remains relatively constant at 1.16 from room temperature to about 1000°C, after which it declines rapidly with the eventual formation of a cubic phase. Not enough measurements were made near the transformation temperature to permit the determination of the order of the transformation, but quite significantly there is a short temperature range in which the coexistence of cubic and tetragonal phases is in evidence. Positive proof of the first order nature of the transformation is provided by the thermodynamic measurements of Southard and Moore.[26] A very sharp transformation is observed at 1445°K exhibiting a latent heat of 4500 cal/mole and an entropy change of 3.11 cal/°mole. An analysis of the enthalpy data taken from room temperature to far above the transformation temperature reveals that there is a heat capacity discontinuity at 1445°K amounting to roughly 12 cal/°mole.

Although the experimental results are found to be in substantial agreement with the predictions derived from the model, several significant quantitative differences exist. The degree of disorder introduced into the tetragonal phase is far less at T_t than predicted from the model; the structure is still considerably ordered before the transformation occurs. The values found for the entropy change and heat capacity discontinuity, being larger and smaller, respectively, than predicted in Sec. IV also indicates that the greater fraction of disordering occurs *at* T_t rather than before. Equation (22) would predict an entropy change of 4.36 cal/°mole if *all* the disordering occurred at T_t.

There are several reasons why the model developed here disorders with temperature at a rate faster than that observed in Mn_3O_4. It has been assumed throughout that the energy of the system could be decomposed into a sum of pair-interaction potentials alone. The presence of three-body potentials which favor the ordered arrangement would tend to "stiffen" the system and aid in resisting the thermal disordering of the octahedra below the transformation temperature. The thermodynamic properties of the model were further derived within the approximation that the short-range order played a minor role. The inclusion of higher moments than the first in Eq. (10) to take account of the influence of short-range order would most probably have the effect of shifting the σ *vs* T curve, Fig. 3, to higher values of σ near T_t, thus improving the agreement with experiment. This analysis of the discrepancies found for Mn_3O_4 is also consistent with the very good agreement obtained for $CuFe_2O_4$. In the latter compound, only half of the B sites are occupied by the

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[25] H. J. VanHooke and M. L. Keith, Am. Mineralogist **43**, 69 (1958).

[26] J. C. Southard and G. E. Moore, J. Am. Chem. Soc. **64**, 1769 (1942).

distorting Cu^{2+} ions reducing the number of Cu-Cu nearest neighbor pairs by $\frac{1}{4}$. Thus, the contribution of possible three-body forces and/or short-range order is minimized, and a model containing pair interactions and long-range order alone should prove to be an adequate approximation.

$(Mn_3O_4)_{1-x}(Fe_3O_4)_x$

The crystallographic properties of the mixed system $(Mn_3O_4)_{1-x}(Fe_3O_4)_x$ have been studied extensively, but serious difficulties have prevented their full interpretation. The two pure compounds are known to be incompletely miscible[25] so that there is always some doubt as to the exact composition of phase whose tetragonal cell edges are being measured. Even if the exact composition of the tetragonal phase were known, there is still considerable doubt as to the cationic and electronic distributions among the *A* and *B* sites. For simplicity, we shall assume that for all values of the over-all composition x, a fraction $(1-x)$ of the *B* sites are actually occupied by Mn^{3+} ions. The lattice parameters of this system have been measured as a function of composition and temperature by McMurdie, Sullivan, and Mauer.[27] The experimental results on the room temperature c/a ratios for different values of x are plotted in Fig. 8(a) (a number of points obtained by Finch *et al.*[6] are also included). The curve is computed from Eqs. (32) and (30) using the following values for the parameters: $\gamma-1=0.161$ and $J(T_r)=0.0751$.

The c/a ratios for different compositions diminish with temperature in much the same way as pure Mn_3O_4. The discrepancy between theory and experiment lessens as x increases, however, further substantiating our notions concerning the behavior of Mn_3O_4 as discussed in previous paragraphs. The composition dependence of the transformation temperature has also been determined by McMurdie *et al.*[27] For small values of x the depression of the transformation temperature is proportional to dilution as predicted in Sec. V. For larger values of x the transformation temperature drops much more rapidly with increasing dilution, so that by $x=0.4$ the transformations occur below room temperature. Thus the corresponding states principle is indeed obeyed, provided the degree of dilution is not too great.

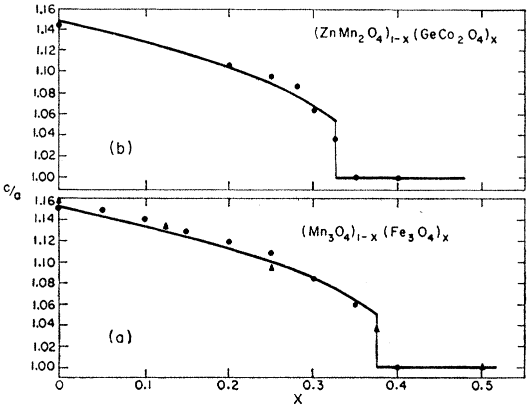

FIG. 8. (a) The c/a ratios at room temperature in the system $(Mn_3O_4)_{1-x}(Fe_3O_4)_x$ (● are data of reference 27, ▲ are data of reference 6). (b) The c/a ratios at room temperature in the system $(ZnMn_2O_4)_{1-x}(GeCo_2O_4)_x$ (data of reference 28). See text for discussion of the theoretical curves.

The crystallographic properties of several other systems containing Mn_3O_4 plus a cubic ferrite have been examined. In particular, Finch *et al.*[6] have determined the composition dependence of the lattice parameters of mixtures of Mn_3O_4 with $NiFe_2O_4$, $MnFe_2O_4$, and $CoFe_2O_4$. The c/a ratio of each of these systems behaves very much like that of $(Mn_3O_4)_{1-x}(Fe_3O_4)_x$, Fig. 8(a), except that the break from tetragonal to cubic phases occurs at a different value of x for each example. The fitting of theoretical curves therefore requires different values of the parameters $\gamma-1$ and $J(T_r)$ for each case. Since these parameters depend on the properties of pure Mn_3O_4 alone, the necessity of changing their values from one system to the next suggests that our knowledge of the actual occupation of the *B* sites by Mn^{3+} is indeed imprecise in these compositions.

$(ZnMn_2O_4)_{1-x}(GeM^{2+}{}_2O_4)_x$

The problems encountered in the specification of the cation and valence distributions in spinels containing both manganese and iron have been fully recognized by Wickham and Croft. In a recent study[28] of spinels containing trivalent manganese, these authors have explicitly avoided compositions containing iron, and have further chosen systems which appear to present little ambiguity in the composition and cation distribution. The lattice parameters of the system $(ZnMn_2O_4)_{1-x}(GeMn_2O_4)_x$ were determined at room temperature; not enough points were taken to make a good comparison with experiment, however. The composition at which the tetragonal phase ceases to be stable at room temperature is found to lie between $x=0.35$ and $x=0.40$.

The c/a ratios in the system $(ZnMn_2O_4)_{1-x}(GeCo_2O_4)_x$ were measured at room temperature,[28] the results being presented in Fig. 8(b). The theoretical curve was computed from Eqs. (32) and (30) using the following values for the parameters: $\gamma-1=0.158$ and $J(T_r)=0.0811$. The break from tetragonal to cubic is seen to occur between $x=0.325$ and $x=0.35$, at a value significantly less than that observed for the previous example. It is our belief that this difference may be due to the presence of the $Co^{2+}(3d^7)$ ions on the *B* sites. The Co^{2+} ion has its own small but not insignificant

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[27] McMurdie, Sullivan, and Mauer, J. Research Natl. Bur. Standards **45**, 35 (1950).

[28] D. G. Wickham and W. J. Croft, J. Phys. Chem. Solids **7**, 351 (1958).

Jahn-Teller distortion[5] and could very well act to oppose the cooperative action of the Mn^{3+}. On the other hand, the large difference in break points could merely be the result of chemically inhomogeneous experimental materials; the somewhat larger scatter of the experimental points in these cases suggests that this may be true (this will, of course, be a problem in most systems studied).

The following approximate values of the transformation temperatures in the system $(ZnMn_2O_4)_{1-x}$-$(GeCo_2O_4)_x$ were also obtained by Wickham and Croft: $T_t=1290$, 790 and 710°K for $x=0$, 0.30 and 0.32, respectively. Using the value of 1290 for $T_t(0)$, the corresponding states principle predicts 903 and 877°K for $x=0.30$ and 0.32, respectively. Both of these values are too high indicating the invalidity of corresponding states at these values of x (the Co^{2+} ions may also be contributing to this discrepancy).

On the basis of their own work and the observations of others on the manganates, Wickham and Croft[28] have been led to conclude that a fraction of about 0.60 to 0.65 of the B sites must be occupied by distorting cations in order for the crystal to be tetragonal at room temperature. We should like to point out that this "critical" fraction observed in many spinels containing Mn^{3+} is strictly a property of the ratio V/kT_r appropriate to the interactions between Mn^{3+} octahedra, and does not depend critically on any specific geometric property of the spinel B lattice (at the absolute zero there will be, of course, a critical fraction which depends solely on geometrical considerations). The different values of critical fraction actually observed are then a reflection of the influence of other B site cations in aiding or hindering the cooperative action of the Mn^{3+}. Two particularly drastic examples of such a behavior are provided by the compounds $ZnCrMnO_4$ and $CrMn_2O_4$. Although only a half of the B sites contain Mn^{3+}, the c/a ratios have been found[16] to be 1.04 and 1.05, respectively, at room temperature. To date, only Cr^{3+} has exhibited such a dramatic effect on the critical fraction in the manganates, however.

The compound $CuFe_2O_4$ further illustrates the dependence of the critical fraction on V/kT_r. Fitting the data on Cu^{2+} systems, Fig. 7(b), required a larger value of V (smaller $J(T_r)$ value) than that needed in the Mn^{3+} systems, Fig. 8. The interactions are thus more effective among the Cu^{2+}, and a smaller critical fraction at T_r is to be expected. The data of Fig. 7(b) does indeed show the reduction of the critical fraction to approximately 0.35. Ohnishi *et al.*[23] have also estimated the critical fraction for Cu^{2+} on the B sites to have a value near 0.37.

$NiCr_2O_4$

Certain very general considerations plus the similarities actually encountered in deriving the properties of the present model and the model for the perovskites[7] permit the induction of a generalized rule concerning the behavior of a certain class of tetragonal-to-cubic transformations. In those situations (independent of the detailed crystal geometry) where the tetragonal structure results from a parallel alignment of tetragonally distorted basic units (octahedra, tetrahedra, etc.), a single long range order parameter will be found to suffice, and the derived thermodynamic equations will have the same form as those obtained in this investigation. The transformation from such a tetragonal structure to the cubic counterpart will therefore be a phase change of the first order. The long-range order parameter, moreover, should diminish with temperature to about half its initial value before the macroscopic phase transformation takes place.

The compound $NiCr_2O_4$ provides a particularly striking confirmation of the validity of this rule. This compound is a normal spinel[29] with a tetragonal unit cell[30] having $c/a>1$. Since $Ni^{2+}(3d^8)$ is assumed[5] to cause prolate tetragonal Jahn-Teller distortions in the tetrahedral sites, it is clear that the bulk distortion arises from the parallel alignment of the distortions in the tetrahedral sites. The general rule is therefore applicable to $NiCr_2O_4$.

The behavior of the transformation in $NiCr_2O_4$ is especially convenient to study since the phase change occurs very near room temperature. The temperature dependence of the lattice parameters in a polycrystalline sample has been measured by White[31] of this laboratory. At −170°C the c/a ratio is 1.040 and is presumably at or very near its maximum value. At 27°C the c/a ratio is reduced to 1.022, while at 34°C the entire sample has become cubic. Between the latter temperatures both a tetragonal and cubic phase are present, the initially small amount of cubic phase growing with temperature at the expense of the tetragonal material. This behavior is believed to be caused by composition deviations from one crystallite to the next producing a distribution of transformation temperatures. The significant feature of this experiment, however, is the observation that the c/a ratio of the disappearing tetragonal phase remains at or above 1.016 during the entire transformation range. Tetragonal phases with c/a ratios less than this value are just not observed. We believe this to be the first truly definite structural verification of the first order nature of this kind of phase transformation. It is also noteworthy that the deviation of c/a from unity is actually found to diminish to about half its initial value before the phase change takes place.

The volume discontinuity accompanying the first order phase change in $NiCr_2O_4$ can be estimated from the structure data. The calculated unit cell volumes[31] display an expansion of about 2 parts in 10^3 as expected. Similar measurements by Ullman[32] demonstrate a unit-

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[29] F. C. Romeijn, Philips Research Repts. 8, 304 (1953).

[30] F. K. Lotgering, Philips Research Repts. 11, 190 (1956).

[31] J. G. White (private communication, 1958).

[32] S. G. Ullman (private communication, 1958).

cell volume expansion of about one part in 10^3. Both of these determinations are in agreement with a macroscopic measurement of the volume. Using a strain gauge technique, the volume of a pressed pellet of polycrystalline $NiCr_2O_4$ was observed to increase about 0.8 parts in 10^3 on passing through the transformation temperature.[33]

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[33] P. J. Wojtowicz and L. A. Zanoni (unpublished results, 1958).

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Isotope Effect in the Bardeen-Cooper-Schrieffer and Bogoliubov Theories of Superconductivity

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It is shown that the Bardeen-Cooper-Schrieffer and Bogoliubov theories of superconductivity predict an isotope effect which is the same for all superconductors, so long as the Coulomb interaction is neglected. This is demonstrated by writing the system of integral equations in a mass-invariant form, and it does not involve finding actual solutions. The theories predict that H_0, T_c, and the energy gap at $T=0$ are proportional to $M^{-\frac{1}{2}}$. The inclusion of the Coulomb interaction destroys the invariance of the equations and introduces deviations from the $-\frac{1}{2}$ in the exponent. The magnitude of the deviation depends on the particular superconductor considered.

I. INTRODUCTION

THE experimentally determined fact that the critical temperature T_c of a superconductor is proportional to $M^{-\frac{1}{2}}$ where M is the atomic mass, the so-called isotope effect, is one of the phenomena that must be explained by any successful theory of superconductivity.[1] This effect now seems to hold without exception for the superconductors tested, Sn, Hg, Tl, and Pb. For the recent theory of Bardeen, Cooper, and Schrieffer,[2] the proof of the isotope effect as given by these authors is based on an approximate solution. First the electron-electron interaction is set equal to zero if either electron in either the initial or final state is outside a certain region R about the Fermi surface. It is then found that T_c is proportional to the width of R in terms of the energy. This width is taken to be $\langle\hbar\omega\rangle_{\text{Av}}$, an average phonon energy, which[3] is proportional to $M^{-\frac{1}{2}}$. Hence the isotope effect follows. The proof is thus directly dependent on the choice for the width of the interaction range R. This particular value for the width is taken since the phonon part of the electron-electron interaction changes from a negative to a positive quantity if the energy change of one of the electrons becomes larger than the phonon energy corresponding to the momentum transferred. However, it does not seem justifiable to discard the interaction where it is repulsive. Besides, for the Bardeen-Pines interaction[3] the phonon part becomes repulsive when the energy *difference* becomes larger than $\hbar\omega$, whereas BCS cuts off the interaction if either electron energy falls outside R.[4]

We give here a proof of the isotope effect for the BCS and Bogoliubov[5] theories which is based on the invariance properties of the Bogoliubov[5]-Valatin[6] integral equations under changing mass and does not involve finding explicit solutions. Neglecting the Coulomb interaction, the isotope effect can be demonstrated by this method even when band structures, anisotropies, and the functional dependence of $\mu(\nu)$ [$2\mu(0)$ is the energy gap] are considered as well as the exchange energy by a Hartree-Fock approximation. It is found that T_c, H_0, and the energy gap at $T=0$ are all proportional to $M^{-\frac{1}{2}}$.

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[1] For a discussion of the experimental results and references to the literature, see B. Serin, *Handbuch der Physik* (Springer-Verlag, Berlin, 1956), Vol. 15, p. 237. The most recent work on Pb is by Hake, Mapother, and Decker, Phys. Rev. **112**, 1522 (1958).

[2] Bardeen, Cooper, and Schrieffer, Phys. Rev. **108**, 1175 (1957); referred to as BCS.

[3] J. Bardeen and D. Pines, Phys. Rev. **99**, 1140 (1955); referred to as BP.

[4] It has been pointed out by J. Bardeen (private communication) that the scale of energies is determined by $\hbar\omega$ since it is the only energy which enters the problem. Thus even if there is a distribution of frequencies, the energy scale is proportional to $M^{-\frac{1}{2}}$. Despite these general arguments, it seems desirable to the author to see the proof carried through explicitly. The author wishes to thank Professor Bardeen for communicating this argument.

[5] N. N. Bogoliubov, Nuovo cimento **7**, 794 (1958); Bogoliubov, Tolmachev, and Shirkov, *A New Method in the Theory of Superconductivity* (Consultants Bureau, Inc., New York, 1959).

[6] J. G. Valatin, Nuovo cimento **7**, 843 (1958).