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Cation Distributions in Ferrospinels. Theoretical*

HERBERT B. CALLEN, *Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania*

AND

S. E. HARRISON AND C. J. KRIESSMAN, *Remington Rand Univac, Division of Sperry Rand Corporation, Philadelphia, Pennsylvania*

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The statistical thermodynamics underlying the distribution of cations over the tetrahedral and octahedral sites in ferrospinels is developed. The temperature dependence of the distribution law is analyzed by invoking the Debye approximation for the vibrational spectrum. The resultant equations permit the internal energy terms of interest to be deduced from measurements of magnetic moment and specific heats of various quenched samples.

1. INTRODUCTION

THE distribution of cations within a ferrospinel lattice is related to the functional dependence of the thermodynamic internal energy on ionic configuration. Study of this internal energy function, theoretically and experimentally, is significant for the following reasons.

First, the parameters which are computed in the fundamental theories of magnetic oxides are exchange interaction energies, covalent bonding energies, and other such contributions to the internal energy function. In order to confront such theories with experimental data, one must develop the theory of the relationship between the energy function and the observed macroscopic properties.

Second, empirical evaluation of the internal energy for a variety of different cations in the spinel structure would permit us to replace certain qualitative rules of ferrite synthesis by quantitative data. Chiefly useful among such qualitative rules are the lists of relative preferences of various cations for octahedral or tetrahedral sites, as given by Verwey and Heilman,[1] Gorter,[2] and Greenwald, Pickart, and Grannis.[3]

Third, the practical problem of understanding the role of heat treatment and quench temperature in the preparation of ferrites with desired magnetic characteristics depends upon the thermodynamics of the ionic distribution.

A highly simplified treatment of the thermodynamics of cation distributions in spinels has been given by Néel[4] and by Smart.[5] These authors treat only the permutational contribution to the entropy explicitly, representing all other contributions to the free energy in a single term of unspecified temperature dependence. The resulting equation can be used for the interpretation of experimental data only by the arbitrary assignment of some specific temperature dependence to this term. Nevertheless the Néel-Smart work has been of great heuristic value in guiding preliminary investigations, and it has been used in correlation of experimental data by Pauthenet and Bochirol,[6] by Sakamoto, Asahi, and Miyahara,[7] and by Callen, Harrison, and Kriessman.[8] In order to permit interpretation of the more detailed recent experimental investigations, we attempt, in this paper, to develop a fully explicit thermodynamic analysis of the distribution of cations in ferrospinels.

In the second portion of this paper we introduce the Debye model for the lattice vibrations and the Madelung model for the ionic binding in order to evaluate particular terms in the general thermodynamic formula. Other terms remain, as yet, unevaluated. A complete treatment in terms of adequate models presumably awaits the insight to be gained from a series of experimental investigations such as that described in the following paper.

2. FORMAL THERMODYNAMIC SOLUTION

We consider the case of a mixed ferrite, of composition $X_xY_y\mathrm{Fe}_2\mathrm{O}_4$, where

$$x+y=1, \tag{1}$$

and where X and Y denote appropriate divalent cations. Let ξ be the fraction of X ions on tetrahedral sites and let η be the fraction of Y ions on tetrahedral sites. Then, denoting tetrahedrally situated ions by enclosure in parentheses, and octahedrally situated ions by enclosure in square brackets, a distribution may be characterized by the formula

$$(X_{\xi x}Y_{\eta y}\,\mathrm{Fe}_{1-\xi x-\eta y})[X_{(1-\xi)x}Y_{(1-\eta)y}\,\mathrm{Fe}_{1+\xi x+\eta y}]\mathrm{O}_4.$$

We assume throughout that the distribution of the ions within the tetrahedral sites is completely random, and similarly within the octahedral sites. We thereby ex-

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clude systems exhibiting such phenomena as the low temperature ordering in magnetite[9] or the octahedral site ordering in $Li_{\frac{1}{2}}Fe_{\frac{5}{2}}O_4$.[10]

We assume that the ferrite is prepared by a suddeh quench from some "soak temperature" T, at whicn temperature it is presumed to be in equilibrium. The ionic distribution corresponding to equilibrium at temperature T is "frozen" in by the quench, and it is this distribution which we wish to compute.

The spinel structure is a structure with a crystallographic parameter and is determined by specifying the lattice constant, a, and the "oxygen parameter," u. In place of u it is sometimes the practice to introduce a parameter δ, defined as $u-0.375$, and this is the choice which we shall make. The significance of the parameter δ may be appreciated by noting that the distance from a tetrahedral site to the four surrounding oxygen ions is $(\sqrt{3}/8)a(1+8\delta)$, and the distance from an octahedral site to the six surrounding oxygen ions is $\frac{1}{4}a(1-8\delta+48\delta^2)^{\frac{1}{2}}$.

At the soak temperature T the system comes to equilibrium by simultaneous adjustment of four parameters; the lattice parameter a, the oxygen parameter δ, and the two parameters ξ and η which specify the ionic distribution. The four parameters are closely coupled, and all four must be considered in the analysis of the ionic distribution problem.

To set up the thermodynamics of the problem, we note that the thermodynamic extensive parameter corresponding to the lattice constant is the volume. We have, in fact,

$$V=\tfrac{1}{8}NN_Aa^3, \tag{2}$$

where N is the mole number, N_A is Avogadro's number, and the number 8 enters because there are 8 "molecules" per unit cell.

Introducing the molar volume

$$v=V/N=\tfrac{1}{8}N_Aa^3, \tag{3}$$

the molar internal energy

$$u=U/N, \tag{4}$$

and the molar entropy

$$s=S/N, \tag{5}$$

we can now write the thermodynamic fundamental relation in the form

$$u=u(s,v,\delta,\xi,\eta). \tag{6}$$

Whereas s and v are conventional thermodynamic parameters, with associated intensive parameters defined by

$$T\equiv\partial u/\partial s, \tag{7}$$

and

$$-P\equiv\partial u/\partial v, \tag{8}$$

the remaining three parameters δ, ξ, and η are so-called "quasi-thermodynamic parameters." That is, the corresponding, formally defined, intensive parameters cannot take any values other than zero in equilibrium:

$$-P_\delta\equiv\partial u/\partial\delta=0, \tag{9}$$

$$-P_\xi\equiv\partial u/\partial\xi=0, \tag{10}$$

$$-P_\eta\equiv\partial u/\partial\eta=0. \tag{11}$$

As we are interested in the equilibrium values of ξ and η, established in an open system, we follow the standard recipe of introducing a "free energy" or "thermodynamic potential," which is the Legendre transform of u with respect to the remaining parameters. We thus define a function u^* as

$$u^*=u-s\frac{\partial u}{\partial s}-v\frac{\partial u}{\partial v}-\delta\frac{\partial u}{\partial \delta} \tag{12}$$

$$=u-Ts+Pv+P_\delta\delta. \tag{13}$$

The potential u^* is a proper function of the variables T, P, P_δ $(=0)$, ξ, and η; that is, of T, P, ξ, and η. If we put $P_\delta=0$ in Eq. (13), the definition of u^* becomes similar to that of the common Gibbs function, and u^* may therefore be thought of as the Gibbs function minimized with respect to δ.

The formal solution of the problem is now that u^* is minimum with respect to ξ and η, at constant T, P, and $P_\delta(=0)$.

$$\partial u^*/\partial\xi=0, \tag{14}$$

$$\partial u^*/\partial\eta=0. \tag{15}$$

3. FORM OF THE FUNCTION u^*

To proceed further than the formal solutions (14) and (15), it is necessary to ascertain at least some information about the explicit form of the potential u^*. We return to the fundamental relation in the form

$$s=s(u,v,\delta,\xi,\eta), \tag{16}$$

for which our intuition is most direct. Any information which may be obtained concerning the form of this equation can be translated into information relative to u^* by inverting Eq. (16) to the form (6), and then carrying out the triple Legendre transformation indicated in Eq. (12).

There are two contributions to the entropy of the ferrite, which we denote by s_0 and s_1:

$$s=s_0+s_1. \tag{17}$$

The entropy s_1 is a function of ξ and η only, and arises from the fact that many different permutations of the ions correspond to a given pair of values of ξ and η. The entropy s_0 is analogous to the entropy of any solid of definite configuration: it arises essentially from the possibility of distributing the energy over the vibra-

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tional modes in many different ways. Thus s_0 is the "normal" entropy, and s_1 is the "permutational" entropy, which embodies the unique features of our problem.

The permutational entropy may be computed simply and directly. The system contains NN_A tetrahedral sites, of which ξxNN_A are occupied by X ions, ηyNN_A by Y ions, and $(1-\xi x-\eta y)NN_A$ by Fe ions. The number of permutations of these ions is]

$$\frac{(NN_A)!}{(\xi xNN_A)!(\eta yNN_A)![(1-\xi x-\eta y)NN_A]!}. \tag{18}$$

Similarly, the system contains $2NN_A$ octahedral sites, of which $(1-\xi)xNN_A$ are occupied by X ions, $(1-\eta)\times yNN_A$ by Y ions, and $(1+\xi x+\eta y)NN_A$ by Fe ions. The number of permutations of these ions is

$$\frac{(2NN_A)!}{[(1-\xi)xNN_A]![(1-\eta)yNN_A]![(1+\xi x+\eta y)NN_A]!}. \tag{19}$$

The number of ionic permutations of the whole system is the product of these numbers, and the permutational entropy consequently is

$$\begin{aligned} s_1= & (k/N)\ln(NN_A)!-(k/N) \\ & \times\ln\{(\xi xNN_A)!(\eta yNN_A)![(1-\xi x-\eta y)NN_A]!\} \\ & +(k/N)\ln(2NN_A)!-(k/N)\ln\{[(1-\xi)xNN_A]! \\ & \times[(1-\eta)yNN_A]![(1+\xi x+\eta y)NN_A]!\}. \end{aligned} \tag{20}$$

Invoking the Stirling approximation this becomes

$$\begin{aligned} s_1= & -R\ln[\xi^{\xi x}(1-\xi)^{(1-\xi)x}\eta^{\eta y}(1-\eta)^{(1-\eta)y} \\ & \times(1-\xi x-\eta y)^{(1-\xi x-\eta y)}(1+\xi x+\eta y)^{(1+\xi x+\eta y)}x^x y^y]. \end{aligned} \tag{21}$$

The "normal" entropy s_0 depends upon the spectrum of the vibrational energy eigenvalues and upon the amount of energy u_0 available for distribution among those modes. We shall assume that the spectrum is characterized by one or more parameters analogous to the Debye temperature, and we denote these parameters collectively by the symbol Θ. Then we have some definite functional relation of the form

$$s_0=s_0(u_0,\Theta), \tag{22}$$

and

$$\Theta=\Theta(v,\delta,\xi,\eta). \tag{23}$$

Now the energy u_0 is only the vibrational energy and is but one of a number of contributions to the total internal energy u. Other contributions are the Madelung energy u_M, the covalent bonding energy u_c, the Born repulsive energy u_B, and the magnetic exchange energy u_E. In those particular cases in which the quench temperatures of interest are far above the magnetic Curie temperature, the contribution of the magnetic exchange energy u_E vanishes, but u_E must be included in the general case. We thus write

$$u=u_0+u_M+u_c+u_B+u_E\equiv u_0+u_1, \tag{24}$$

and Eq. (22) becomes

$$s_0=s_0(u-u_1,\Theta). \tag{25}$$

Finally, our fundamental thermodynamic relation is

$$s=s_1+s_0(u-u_1,\Theta), \tag{26}$$

where s_1 is given explicitly by Eq. (21).

According to the procedure previously outlined, we must invert this equation so as to solve for u in terms of s, and we must then perform our Legendre transformation. Inverting Eq. (26) gives

$$u=u_1+u_0(s-s_1,\Theta), \tag{27}$$

and

$$u=u_1+u_0(s-s_1,\Theta)-Ts+Pv+P_\delta\delta. \tag{28}$$

Inserting Eq. (28) into Eq. (14) and carrying out the indicated differentiation at constant T, P, P_δ, and η:

$$\begin{aligned} \frac{\partial u^*}{\partial\xi}= & \left.\frac{\partial u_1}{\partial\xi}+T\frac{\partial(s-s_1)}{\partial\xi}+\frac{\partial u_0}{\partial\Theta}\right)_{s_0}\frac{\partial\Theta}{\partial\xi} \\ & -T\frac{\partial s}{\partial\xi}+P\frac{\partial v}{\partial\xi}+P_\delta\frac{\partial\delta}{\partial\xi}=0, \end{aligned} \tag{29}$$

or

$$T\frac{\partial s_1}{\partial\xi}=\left.\frac{\partial u_1}{\partial\xi}+\frac{\partial u_0}{\partial\Theta}\right)_{s_0}\frac{\partial\Theta}{\partial\xi}+P\frac{\partial v}{\partial\xi}+P_\delta\frac{\partial\delta}{\partial\xi}. \tag{30}$$

The fact that P_δ is zero by Eq. (9), and the explicit value for s_1 given in Eq. (21), now permit us to write this equation in the form

$$\begin{aligned} & \frac{\xi(1+\xi x+\eta y)}{(1-\xi)(1-\xi x-\eta y)} \\ & \qquad =\exp\left\{\frac{-1}{xRT}\left[\left.\frac{\partial u_1}{\partial\xi}+\frac{\partial u_0}{\partial\Theta}\right)_{s_0}\frac{\partial\Theta}{\partial\xi}+P\frac{\partial v}{\partial\xi}\right]\right\}, \end{aligned} \tag{31}$$

and similarly

$$\begin{aligned} & \frac{\eta(1+\xi x+\eta y)}{(1-\eta)(1-\xi x-\eta y)} \\ & \qquad =\exp\left\{\frac{-1}{yRT}\left[\left.\frac{\partial u_1}{\partial\eta}+\frac{\partial u_0}{\partial\Theta}\right)_{s_0}\frac{\partial\Theta}{\partial\eta}+P\frac{\partial v}{\partial\eta}\right]\right\}. \end{aligned} \tag{32}$$

In these equations the partial differentiations are to be carried out at constant T, P, P_δ, and either ξ or η. The right-hand members of Eqs. (31) and (32) are to be considered as functions of T, P, ξ, and η. Elimination of the variables s, v, and δ in favor of T, P, and P_δ $(=0)$ is to be done by solution of the following three equations [obtained by substituting (27) into (7), (8) and

(9)]:

$$T \equiv \left.\frac{\partial u}{\partial s}\right]_{v,\delta,\xi,\eta} = \left.\frac{\partial u_0}{\partial s}\right]_{v,\delta,\xi,\eta}, \tag{33}$$

$$-P \equiv \left.\frac{\partial u}{\partial v}\right]_{s,\delta,\xi,\eta} = \left.\frac{\partial u_1}{\partial v}\right]_{\delta,\xi,\eta} + \left.\frac{\partial u_0}{\partial \Theta}\right]_{s_0} \left.\frac{\partial \Theta}{\partial v}\right]_{\delta,\xi,\eta}, \tag{34}$$

$$-P_\delta \equiv \left.\frac{\partial u}{\partial \delta}\right]_{s,v,\xi,\eta} = 0 = \left.\frac{\partial u_1}{\partial \delta}\right]_{v,\xi,\eta} + \left.\frac{\partial u_0}{\partial \Theta}\right]_{s_0} \left.\frac{\partial \Theta}{\partial \delta}\right]_{v,\xi,\eta}. \tag{35}$$

Our solutions (31) and (32) can be written in another form of interest. Consider the quantity $\partial u_1/\partial\xi)_{T,P,P_\delta,\eta}$ which appears in Eq. (31). We may expand this derivative as follows, noting that u_1 is a function only of v, δ, ξ, and η:

$$\left.\frac{\partial u_1}{\partial \xi}\right]_{T,P,P_\delta,\eta} = \left.\frac{\partial u_1}{\partial v}\right]_{\delta,\xi,\eta} \left.\frac{\partial v}{\partial \xi}\right]_{T,P,P_\delta,\eta} + \left.\frac{\partial u_1}{\partial \delta}\right]_{v,\xi,\eta} \left.\frac{\partial \delta}{\partial \xi}\right]_{T,P,P_\delta,\eta} + \left.\frac{\partial u_1}{\partial \xi}\right]_{v,\delta,\eta}. \tag{36}$$

Expanding the derivative $\partial\Theta/\partial\xi]_{T,P,P_\delta,\eta}$ in Eq. (31) in precisely the same fashion, and employing Eqs. (33)–(35), finally permits us to write Eq. (31) in the alternative form

$$\frac{\xi(1+\xi x+\eta y)}{(1-\xi)(1-\xi x-\eta y)} = \exp\left\{\frac{-1}{xRT}\left(\left.\frac{\partial u_1}{\partial \xi}\right]_{v,\delta,\eta} + \left.\frac{\partial u_0}{\partial \Theta}\right]_{s_0} \left.\frac{\partial \Theta}{\partial \xi}\right]_{v,\delta,\eta}\right)\right\}, \tag{37}$$

and similarly for Eq. (32):

$$\frac{\eta(1+\xi x+\eta y)}{(1-\eta)(1-\xi x-\eta y)} = \exp\left\{\frac{-1}{yRT}\left(\left.\frac{\partial u_1}{\partial \eta}\right]_{v,\delta,\xi} + \left.\frac{\partial u_0}{\partial \Theta}\right]_{s_0} \left.\frac{\partial \Theta}{\partial \eta}\right]_{v,\delta,\xi}\right)\right\}. \tag{38}$$

Although the partial derivatives in the right-hand members are now carried out at constant v and δ instead of T, P, and P_δ, the resultant quantities are still to be considered as functions of T, P, ξ, and η. As before, the variables s, v, and δ are to be eliminated by solution of Eqs. (33)–(35).

The forms of the distribution laws (31)–(32) and (37)–(38) differ in the variables to be held constant during differentiation and in the appearance in the former equations of an additional term $P\partial v/\partial\xi$. A frequent approximation adopted in solid-state theories is to put the pressure equal to zero; few solid properties are particularly sensitive to the magnitude of the pressure in the low-pressure range. We therefore see that to this degree of approximation the solutions (31)–(32) and (37)–(38) become identical in form, and it is immaterial which set of variables is held constant in the indicated differentiations.

We note in passing that the derivative $(\partial u_0/\partial\Theta)_{s_0}$, which appears in the solutions, may be interpreted as the work absorbed in an adiabatic quasistatic process which alters the vibrational spectrum by a unit change in Θ.

We have now carried the solution as far as possible without the introduction of specific models. In the second part of this paper we introduce certain simple models in order to evaluate the quantities appearing in the right-hand members of our general distribution laws.

4. DEBYE SPECTRUM

Equations (37) and (38) are quite general and, being thermodynamic in nature, are independent of any model. In order to apply the solutions to particular cases one must either evaluate the partial derivatives in the right-hand members from some independent experiments, or one must compute them from specific models. We therefore turn our attention to a simple model.

An immediate simplification of Eqs. (37) and (38) follows if we assume that the entropy is, in particular, a function only of the ratio u_0/Θ, rather than a function of both u_0 and Θ separately as in Eq. (22).

$$s_0 = f(u_0/\Theta). \tag{39}$$

If the vibrational spectrum of the crystal is approximated by a Debye spectrum, Eq. (39) is true. This may be shown by taking the conventional Debye equation for u_0 as a function of T, computing s_0 as a function of T by integration of $ds_0 = du_0/T$, and elimination of T between the two equations. Although the algebra cannot easily be carried out explicitly, it is a simple matter at least to show that Eq. (39) is valid. The only feature of the Debye model which we shall actually employ is Eq. (39), so that our result may reasonably be expected to be valid independently of the more detailed and precise aspects of the Debye theory.

Differentiating Eq. (39) with respect to Θ at constant s_0 gives

$$\left.\frac{\partial u_0}{\partial \Theta}\right]_{s_0} = \frac{u_0}{\Theta}. \tag{40}$$

At the high temperatures of interest to us T is generally greater than Θ/k, and u_0 may be approximated sufficiently accurately by its equipartition value

$$u_0 \simeq 21RT. \tag{41}$$

Thus, in Eqs. (37) and (38) the derivative may be replaced, to a reasonable approximation, by

$$\frac{1}{RT}\left.\frac{\partial u_0}{\partial \Theta}\right]_{s_0} = \frac{21}{\Theta}. \tag{42}$$

This approximation has significant consequences with respect to the form of the distribution law, and with respect to its temperature dependence. We first consider the form of the solution. From (37)–(38) and (42) we have

$$\frac{\xi(1+\xi x+\eta y)}{(1-\xi)(1-\xi x-\eta y)}=\exp\left\{\frac{-1}{xRT}\left[\frac{\partial u_1}{\partial \xi}+21RT\frac{\partial \ln\Theta}{\partial \xi}\right]\right\}, \tag{43}$$

$$\frac{\eta(1+\xi x+\eta y)}{(1-\eta)(1-\xi x-\eta y)}=\exp\left\{\frac{-1}{yRT}\left[\frac{\partial u_1}{\partial \eta}+21RT\frac{\partial \ln\Theta}{\partial \eta}\right]\right\}, \tag{44}$$

and, by (34)–(35), the variables v and δ are to be eliminated in favor of T and P by solution of the two equations

$$-P=\left.\frac{\partial u_1}{\partial v}\right]_{\delta,\xi,\eta}+21RT\left.\frac{\partial \ln\Theta}{\partial v}\right]_{\delta,\xi,\eta}, \tag{45}$$

$$0=\left.\frac{\partial u_1}{\partial \delta}\right]_{v,\xi,\eta}+21RT\left.\frac{\partial \ln\Theta}{\partial \delta}\right]_{v,\xi,\eta}. \tag{46}$$

Inspection of the above set of equations indicates that a considerable simplification has been achieved in that only two auxiliary equations [(45) and (46)] rather than three are necessary. This simplification arose as follows. The right-hand members of Eqs. (37)–(38) were functions initially of s, v, and δ, for which variables the alternate set, T, P, and P_δ $(=0)$ were to be replaced via the three auxiliary Eqs. (33)–(35). However, the variable s could appear only through the derivative $\partial u_0/\partial\Theta]_{s0}$. Our approximation (42) based on the Debye spectrum, was such that $\partial u_0/\partial\Theta]_{s0}$ did not, in fact, involve s. The right-hand members of (37)–(38) thereby became functions of v and δ only, rather than of s, v, and δ. To eliminate the two variables v and δ requires only the two auxiliary equations (45) and (46).

5. TEMPERATURE DEPENDENCE OF THE DISTRIBUTION

As mentioned previously, the Debye approximation simplifies both the form of the distribution law, as in Eqs. (43)–(46), and the temperature dependence. We now consider the latter problem. For simplicity we shall invoke the additional approximation that the pressure vanishes. In this case the partial derivatives in Eqs. (43)–(44) may be interpreted as being at constant T rather than at constant v and δ, as noted at the end of Sec. 3.

We consider the temperature dependence of the square brackets in Eq. (43); that is, of the quantity

$$f\equiv\left.\frac{\partial u_1}{\partial \xi}\right]_{T,\eta}+21RT\left.\frac{\partial \ln\Theta}{\partial \xi}\right]_{T,\eta}. \tag{47}$$

Differentiating with respect to T

$$\left.\frac{\partial f}{\partial T}\right]_{\xi,\eta}=\left.\frac{\partial}{\partial T}\right]_{\xi,\eta}\left.\frac{\partial u_1}{\partial \xi}\right]_{T,\eta}+21R\left.\frac{\partial \ln\Theta}{\partial \xi}\right]_{T,\eta}+21RT\left.\frac{\partial}{\partial T}\right]_{\xi,\eta}\left.\frac{\partial \ln\Theta}{\partial \xi}\right]_{T,\eta}. \tag{48}$$

Interchanging the order of differentiation, we may write this equation as

$$\begin{aligned}\left.\frac{\partial f}{\partial T}\right]_{\xi,\eta}=&\left.\frac{\partial}{\partial \xi}\right]_{T,\eta}\left\{\left.\frac{\partial u_1}{\partial v}\right]_{\delta,\xi,\eta}\left.\frac{\partial v}{\partial T}\right]_{\xi,\eta}+\left.\frac{\partial u_1}{\partial \delta}\right]_{v,\xi,\eta}\left.\frac{\partial \delta}{\partial T}\right]_{\xi,\eta}\right\}\\&+21R\left.\frac{\partial \ln\Theta}{\partial \xi}\right]_{T,\eta}+21RT\left.\frac{\partial}{\partial \xi}\right]_{T,\eta}\\&\times\left\{\left.\frac{\partial \ln\Theta}{\partial v}\right]_{\delta,\xi,\eta}\left.\frac{\partial v}{\partial T}\right]_{\xi,\eta}+\left.\frac{\partial \ln\Theta}{\partial \delta}\right]_{v,\xi,\eta}\left.\frac{\partial \delta}{\partial T}\right]_{\xi,\eta}\right\}.\end{aligned} \tag{49}$$

We now introduce Eqs. (45) and (46), with $P=0$. These equations lead to the cancellation of the first and third terms above, leaving simply

$$\left.\frac{\partial f}{\partial T}\right]_{\xi,\eta}=21R\left.\frac{\partial \ln\Theta}{\partial \xi}\right]_{T,\eta}. \tag{50}$$

The second derivative of f is

$$\left.\frac{\partial^2 f}{\partial T^2}\right]_{\xi,\eta}=21R\left.\frac{\partial}{\partial T}\right]_{\xi,\eta}\left.\frac{\partial \ln\Theta}{\partial \xi}\right]_{T,\eta}, \tag{51}$$

and again inverting the order of differentiation,

$$\left.\frac{\partial^2 f}{\partial T^2}\right]_{\xi,\eta}=21R\left.\frac{\partial}{\partial \xi}\right]_{T,\eta}\left.\frac{\partial \ln\Theta}{\partial T}\right]_{\xi,\eta}. \tag{52}$$

Now the very essence of the Debye theory depends upon the insensitivity of the dependence of Θ on T. Although in principle Θ may depend upon T, the usual treatment of specific heat and many other properties is based upon the assumption that Θ is independent of T. The success of such theories encourages us to believe at least that the quantity (52) is very small. In order to exhibit the temperature dependence of f directly we utilize the evident identity

$$f(T)=f(T_0)+\int_{T_0}^{T}f'(T')dT', \tag{53}$$

which, with Eqs. (47) and (50) can be put in the form

$$f(T)=\left.\frac{\partial u_1}{\partial \xi}\right]_{T_0,\eta}+21RT\left.\frac{\partial \ln\Theta}{\partial \xi}\right]_{T_0,\eta}$$
$$+21R\int_{T_0}^{T}\left\{\left.\frac{\partial \ln\Theta}{\partial \xi}\right]_{T',\eta}-\left.\frac{\partial \ln\Theta}{\partial \xi}\right]_{T_0,\eta}\right\}dT', \qquad (54)$$

or

$$f(T)=\left.\frac{\partial u_1}{\partial \xi}\right]_{T_0,\eta}+21RT\left.\frac{\partial \ln\Theta}{\partial \xi}\right]_{T_0,\eta}+\left.\frac{\partial \epsilon}{\partial \xi}\right]_{T,\eta}, \qquad (55)$$

where

$$\epsilon(T,\xi,\eta;T_0)\equiv 21R\int_{T_0}^{T}[\ln\Theta(T')-\ln\Theta(T_0)]dT'. \qquad (56)$$

The quantity ϵ is very small in accordance with our discussion of the temperature insensitivity of Θ. By choosing the reference temperature T_0 close to the temperatures of interest, $\epsilon(T,\xi,\eta;T_0)$ may be made even smaller. We believe, however, that even with the very convenient choice of $T_0=0$, the quantity ϵ will be negligibly small.

We may now rewrite Eqs. (43) and (44) as

$$\frac{\xi(1+\xi x+\eta y)}{(1-\xi)(1-\xi x-\eta y)}=\exp\left\{\frac{-1}{xRT}\left(\left.\frac{\partial u_1}{\partial \xi}\right]_{T_0,\eta}\right.\right.$$
$$\left.\left.+21RT\left.\frac{\partial \ln\Theta}{\partial \xi}\right]_{T_0,\eta}+\left.\frac{\partial \epsilon}{\partial \xi}\right]_{T,\eta}\right)\right\}, \qquad (57)$$

$$\frac{\eta(1+\xi x+\eta y)}{(1-\eta)(1-\xi x-\eta y)}=\exp\left\{\frac{-1}{yRT}\left(\left.\frac{\partial u_1}{\partial \eta}\right]_{T_0,\xi}\right.\right.$$
$$\left.+21RT\left.\frac{\partial \ln\Theta}{\partial \eta}\right]_{T_0,\xi}+\left.\frac{\partial \epsilon}{\partial \eta}\right]_{T,\xi}\right\}. \qquad (58)$$

In order to relate the distribution equations as directly as possible to experimentally observable quantities we note that the lattice contribution to the specific heat, in the vicinity of $T_0 \cong 0$, is of the form

$$c_v^{(0)}=\text{const}(T_0/\Theta)^3, \qquad (59)$$

whence

$$\left.\frac{\partial \ln\Theta}{\partial \eta}\right]_{T_0,\xi}=-\frac{1}{3}\left.\frac{\partial \ln c_v^{(0)}}{\partial \eta}\right]_{T_0,\xi}, \qquad (60)$$

and we thus obtain

$$\frac{\xi(1+\xi x+\eta y)}{(1-\xi)(1-\xi x-\eta y)}=\exp\left\{\frac{-1}{xRT}\left(\left.\frac{\partial u_1}{\partial \xi}\right]_{T_0,\eta}\right.\right.$$
$$\left.\left.-7RT\left.\frac{\partial \ln c_v^{(0)}}{\partial \xi}\right]_{T_0,\eta}+\left.\frac{\partial \epsilon}{\partial \xi}\right]_{T,\eta}\right)\right\}, \qquad (61)$$

$$\frac{\eta(1+\xi x+\eta y)}{(1-\eta)(1-\xi x-\eta y)}=\exp\left\{\frac{-1}{yRT}\left(\left.\frac{\partial u_1}{\partial \eta}\right]_{T_0,\xi}\right.\right.$$
$$\left.\left.-7RT\left.\frac{\partial \ln c_v^{(0)}}{\partial \eta}\right]_{T_0,\xi}+\left.\frac{\partial \epsilon}{\partial \eta}\right]_{T,\xi}\right)\right\}. \qquad (62)$$

These equations are to be coupled with Eqs. (45) and (46) with P put equal to zero, to predict the ionic distribution.

6. MADELUNG ENERGY

The distribution law as expressed in Eqs. (61)–(62) and (45)–(46) is as explicit as it can be made without entering into the detailed atomistic theory of the various contributions to the energy. However, one of these contributions, and very probably the most important of them has been treated by Verwey, de Boer, and van Santen.[11] This contribution is the Madelung energy, or the Coulomb interaction energy of the ionic charges. Verwey, de Boer, and van Santen have computed arithmetically the Madelung energy for a range of values of δ and of the ionic charges. Their numerical results can be fitted by the following analytic expression:

$$U_M=-(N_Ae^2/a)$$
$$\times\{[139.8-10.84(3-\xi x-\eta y)+2.61(3-\xi x-\eta y)^2]$$
$$+[1463.2-461.4(3-\xi x-\eta y)$$
$$-3.6(3-\xi x-\eta y)^2]\delta\}. \qquad (63)$$

The quantity $(3-\xi x-\eta y)$ which enters this expression has the significance of the average charge of a tetrahedrally situated ion, as can be checked easily if we recall that both X and Y are assumed to be doubly charged, and Fe triply charged.

Evaluation of the other energy contributions to u_1 and of the functional dependence of the specific heat $c_v^{(0)}$ require further theoretical or experimental investigations.

CONCLUSION

In Eqs. (61)–(62), (45)–(46) we have derived the distribution law for the cations in a ferrospinel. The temperature dependence of the distribution law has been evaluated by means of the Debye approximation for the vibrational spectrum. The only portion of the temperature dependence which cannot be explicitly evaluated has been isolated, in Eqs. (61)–(62), in a small and presumably negligible quantity. The distribution law thereby is put in a form which permits interpretation of experimental data.

The distribution law contains the nonthermal portion of the thermodynamic internal energy. Although the dominant contribution (the Madelung energy) may be treated theoretically, the remaining terms are, as yet, unanalyzed. The distribution law which we have derived consequently provides a method of experimental study of these contributions to the internal energy.

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[11] Verwey, de Boer, and van Santen, J. Chem. Phys. 16, 1091 (1948); 18, 1032 (1950).