

## Quantum Theory of the Equilibrium Order Parameters for Disordered Solid Solutions\*

D. O. CHRISTY AND G. L. HALL  
*Kansas State University, Manhattan, Kansas*  
 (Received 25 April 1963)

Equations for the equilibrium order parameters of substitutional binary alloys are derived from both a classical (bond energy) and a quantum approach. The classical case is presented so as to exhibit that Cowley's equilibrium equations are not valid, principally as a consequence of an incorrect calculation of the internal energy. The work of Flinn is utilized to show that the equilibrium equations have the same form in the classical and the quantum cases. Moreover, the quantum approach is made practical by a simplification of certain integrals which Flinn was unable to evaluate. In both cases, a transition temperature for each atomic distance is found. With these developments, it is now possible to predict order parameters quantum mechanically and to test the predictions directly by x-ray measurements or indirectly by resistivity measurements via Asch and Hall's theory of residual resistivity. Numerical calculations required to compare experiment and theory have not been completed, but a presentation of the theory alone seems justified in view of the appearance of these and papers based on Cowley's incorrect equations.

### 1. INTRODUCTION

A SIGNIFICANT error has been found in Cowley's classical theory of the equilibrium order parameters of substitutional binary alloys.<sup>1,2</sup> Correction of this error leads to two important consequences: (1) The equilibrium equations for the order parameters in the classical theory, a bond energy approach, are considerably simplified; and (2) the quantum approach as developed by Flinn<sup>3</sup> is easily put in the same form as the classical theory. Accordingly, it is now possible to predict order parameters quantum mechanically and to test the predictions directly by x-ray measurements or indirectly by resistivity measurements via Asch and Hall's theory of residual resistivity.<sup>4</sup> The equilibrium equations in the quantum case involve certain integrals, one for each atomic distance, which Flinn introduced but was unable to evaluate except for those associated with first neighbors.<sup>3</sup> The authors have reduced the Flinn integrals to a simple form easily evaluated numerically. Thus, the equilibrium equations for the order parameters from the quantum approach involve only simply evaluated quantities.

The principal error in Cowley's work for the classical case is in the calculation of the internal energy of the disordered alloy. A corrected calculation is presented in Sec. 2 immediately after a discussion of the Cowley order parameters in terms of which the internal energy and configurational entropy are to be expressed. Whereas the calculation of the energy is exact to within the limits of the classical bond energy model, the calculation of the entropy is inexact. It is, nevertheless, possible that the equilibrium order parameters found by minimizing the Helmholtz free energy are exact. This point

is discussed in Sec. 2. Section 3 contains an extension to the quantum case, with the evaluation of the associated Flinn integrals relegated to an Appendix. The paper closes with a summary in Sec. 4. Numerical calculations required to complete the comparison between experiment and theory are in progress and will be reported at a later date. The publication of the theory alone at this time seems justified in view of the appearance of these<sup>5</sup> and papers<sup>1,2,6</sup> based on Cowley's incorrect equations.

### 2. CLASSICAL EQUILIBRIUM EQUATIONS FOR THE ORDER PARAMETERS

#### 2.1 The Cowley Order Parameters

Consider a Bravais  $\tau$  lattice of infinite extent on which  $A$  atoms and  $B$  atoms are placed substitutionally. Let a set of basis vectors be given by  $\{\tau_1, \tau_2, \tau_3\}$  with a unit cell volume  $\Omega$  given by  $|\tau_1 \cdot (\tau_2 \times \tau_3)|$ . Also consider a very large scale superlattice defined by

$$\mathbf{n} = n_1 N_1 \tau_1 + n_2 N_2 \tau_2 + n_3 N_3 \tau_3, \quad (2.1)$$

where  $N_i$  and  $n_i$  are integers. These  $\mathbf{n}$  vectors define periodic replicas of the volume  $N\Omega$ , where  $N = N_1 N_2 N_3$ . In each replica there are  $Nm_A$   $A$  atoms and  $Nm_B$   $B$  atoms with  $m_B$  equal to  $(1 - m_A)$ .

A specific arrangement of the atoms on the  $\tau$  lattice may be conveniently defined by Flinn's  $C_\tau$  function<sup>3,4,7</sup>:

$$C_\tau = m_B, \quad \text{if } A \text{ atom at } \tau, \quad \sum_{\tau}^N C_\tau = 0, \quad (2.2)$$

$$= -m_A, \quad \text{if } B \text{ atom at } \tau$$

$$m_A + C_\tau = 1, \quad \text{if } A \text{ atom at } \tau$$

$$= 0, \quad \text{if } B \text{ atom at } \tau, \quad (2.3a)$$

$$m_B - C_\tau = 0, \quad \text{if } A \text{ atom at } \tau$$

$$= 1, \quad \text{if } B \text{ atom at } \tau. \quad (2.3b)$$

\* This work was supported by the National Science Foundation and Phillips Petroleum Company. Part of this work is a portion of a dissertation presented by D. O. Christy in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics at Kansas State University.

<sup>1</sup> J. M. Cowley, Phys. Rev. **120**, 1648 (1960).

<sup>2</sup> J. M. Cowley, Phys. Rev. **77**, 669 (1950).

<sup>3</sup> P. A. Flinn, Phys. Rev. **104**, 350 (1956).

<sup>4</sup> A. E. Asch and G. L. Hall, Phys. Rev. **132**, 1047 (1963).

<sup>5</sup> C. B. Walker, Ph.D. dissertation, Massachusetts Institute of Technology, 1951 (unpublished).

<sup>6</sup> B. M. Korevaar, Physica **25**, 1021 (1959).

<sup>7</sup> G. L. Hall, Phys. Rev. **116**, 604 (1959).

Periodic boundary conditions on the replicas imply that

$$C_{\tau+n} = C_{\tau}. \quad (2.4)$$

The Cowley order parameters are defined by

$$\alpha_{\tau} = \sum_{\tau'}^N C_{\tau'} C_{\tau+\tau'} / N m_A m_B. \quad (2.5)$$

A few important properties of these parameters are

$$\begin{aligned} 1 \geq \alpha_{\tau} \geq 1 - 1/m_B, \quad 0 \leq m_A \leq \frac{1}{2} \\ \geq 1 - 1/m_A, \quad 0 \leq m_B \leq \frac{1}{2}, \end{aligned} \quad (2.6)$$

$$\alpha_0 = 1, \quad \sum_{\tau} \alpha_{\tau} = 0, \quad \alpha_{\tau} = \alpha_{-\tau}, \quad \alpha_{\tau+n} = \alpha_{\tau}. \quad (2.7)$$

The last two relations may be combined to give

$$\alpha_{n-\tau} = \alpha_{\tau}. \quad (2.8)$$

Repeated use of relation (2.8) with the set of  $\{n_i\}$  in  $\mathbf{n}$  successively taken as  $\{0,0,1\}$ ,  $\{0,1,0\}$ ,  $\{1,0,0\}$ , and  $\{1,1,1\}$  exhibits that the  $\alpha_{\tau}$  are strongly *geometrically* related for small  $N$ . However, the internal energy and entropy will be expressed in terms of a more nearly independent group of parameters. These are given by averages of the  $\alpha_{\tau}$  taken over shells of constant  $|\tau|$ , namely,

$$\bar{\alpha}_{\tau} = b_{\tau}^{-1} \sum_{\tau \text{ shell}} \alpha_{\tau}, \quad (2.9)$$

where  $b_{\tau}$  is the coordination number for the distance  $\tau$ .

The average parameters  $\bar{\alpha}_{\tau}$  are less strongly correlated (geometrically) than the  $\alpha_{\tau}$ . (Of course, in one dimension  $\bar{\alpha}_{\tau}$ ,  $\alpha_{\tau}$ , and  $\alpha_{-\tau}$ , are all equal.) The relation (2.8) does not impose any dependences between those  $\bar{\alpha}_{\tau}$  for magnitudes of  $\tau$  much smaller than any  $(\frac{1}{2})N i \tau_i$ . Moreover, the sum rule in Eq. (2.7) is of little importance for very large  $N$ . On the basis of these facts, it seems fairly reasonable to assume that in the limit of large  $N$ , the  $\bar{\alpha}_{\tau}$  for finite  $\tau$  are all geometrically independent. This assumption will be used in the entropy calculation but not in the energy calculation.

## 2.2 The Internal Energy

This quite short subsection contains a very simple and straightforward derivation of the classical internal energy, with the resulting expression in disagreement with Cowley's.<sup>1</sup> The simplicity of the derivation is a direct consequence of the use of Flinn's<sup>3</sup>  $C_{\tau}$  function. The properties of the Flinn function, particularly those given by Eqs. (2.3a) and (2.3b), permit one immediately to write the defining expression (2.10) for the internal energy of an arbitrary, but completely defined, configuration of disorder. A little manipulation of the individual terms in (2.10) leads to (2.11) and (2.14), which show that all configurations having the same set of  $\bar{\alpha}_{\tau}$

possess the same energy and that this energy is *linear* in the  $\bar{\alpha}_{\tau}$ . This statement of linearity is in sharp disagreement with Cowley, and this fact will be discussed at the end of the subsection.

Consider a specific arrangement of the atoms uniquely designated by the set  $\{C_{\tau}\}$ . The internal energy  $U(\{C_{\tau}\})$  of the  $N$  atoms of one replica is found by summing the interactions of each of these  $N$  atoms with all other atoms of all replicas. Use of relations (2.3) yields

$$\begin{aligned} U(\{C_{\tau}\}) = \frac{1}{2} \sum_{\tau} \sum_{\tau'}^N \{ (m_A + C_{\tau})(m_A + C_{\tau'}) E_{AA}(\tau - \tau') \\ + (m_A + C_{\tau})(m_B - C_{\tau'}) E_{AB}(\tau - \tau') \\ + (m_B - C_{\tau})(m_A + C_{\tau'}) E_{AB}(\tau - \tau') \\ + (m_B - C_{\tau})(m_B - C_{\tau'}) E_{BB}(\tau - \tau') \} \\ + \frac{1}{2} \sum_{\tau} \sum_{\tau' > N}^N \{ \dots \}, \end{aligned} \quad (2.10)$$

where the "surface terms" expressed by the last double sum can be neglected in the limit of large  $N$ , and where  $E_{ij}(\mathbf{r})$  is the bond energy of the  $ij$  type and depends only on the magnitude of  $\mathbf{r}$ . By neglecting the "surface term" in Eq. (2.10), by using the sum rule of Eq. (2.2), and by using the defining relations (2.5) and (2.9), it is readily shown that  $U$  reduces to

$$U(\{C_{\tau}\}) = U_0 + N m_A m_B \sum_{\tau} b_{\tau} \bar{\alpha}_{\tau} E_{\tau}, \quad (2.11)$$

where  $U_0$  and  $E_{\tau}$  are defined by

$$\begin{aligned} U_0 = \frac{1}{2} N \sum_{\tau} [m_A^2 E_{AA}(\tau) \\ + 2m_A m_B E_{AB}(\tau) + m_B^2 E_{BB}(\tau)], \end{aligned} \quad (2.12)$$

$$E_{\tau} = \frac{1}{2} \{ E_{AA}(\tau) + E_{BB}(\tau) - 2E_{AB}(\tau) \}. \quad (2.13)$$

In Eq. (7) of his paper,<sup>1</sup> Cowley has an expression essentially identical to that presented in the above equation (2.11), but Cowley misinterprets the quantity. The defining expression in (2.10) and the properties of the Flinn function as expressed in (2.3a) and (2.3b) permit a definite interpretation of  $U(\{C_{\tau}\})$  as the internal energy of all  $N$  atoms for a particular configuration  $\{C_{\tau}\}$ .

It is clear from (2.11) that the  $U(\{C_{\tau}\})$  for all sets  $\{C_{\tau}\}$  leading to the same set  $\{\bar{\alpha}_{\tau}\}$  are equal. The next problem is to calculate the configurational entropy associated with a given set, say the  $i$ th, of  $\{\bar{\alpha}_{\tau}\}$ . For the sequel, it is convenient to rewrite (2.11) as

$$U_i = U_0 + N m_A m_B \sum_{\tau} b_{\tau} \bar{\alpha}_{\tau} E_{\tau}, \quad (2.14)$$

where each  $\bar{\alpha}_{\tau}$  is contained in the set  $\{\bar{\alpha}_{\tau}\}_i$ .

The preceding derivation of the internal energy involves no probabilities and is easily checked step by step. That Cowley<sup>1</sup> is in error is evident, but the question remains of exactly where does he go astray. The authors have had difficulty in trying to pin down exactly what Cowley has done, but a few definite statements can be made.

Both Cowley and the present authors use the method of most probable values, although one might gather from the first part of Sec. 4 of Cowley's paper<sup>1</sup> that he intends to use the Darwin-Fowler method of mean values. The final results for the classical energy in the present paper, given by Eqs. (2.11) and (2.14), are equivalent to Cowley's Eq. (7), which he misinterprets. Cowley goes on from his Eq. (7), without derivation, to his Eq. (8). The present authors are able to reconstruct Cowley's incorrect Eq. (8) by introducing nonvalid assumptions concerning certain conditional probabilities; presumably, Cowley's error is of this general nature. The Flinn function avoids the pitfalls of calculation of probabilities.

Finally, the authors claim that their expression (2.14) for the classical internal energy is exact (to within the limitations of the classical model), whereas they readily admit that both Cowley's and their expressions for the entropy are approximate.

### 2.3 The Configurational Entropy

The configurational entropy corresponding to all sets of  $C_\tau$  configurations contained in  $\{\bar{\alpha}_\tau\}_i$  is given by

$$S_i = k \ln g_i, \quad (2.15)$$

where  $g_i$  is the number of distinct complexions of a replica leading to the given set  $\{\bar{\alpha}_\tau\}_i$  for fixed  $N$  and  $m_A$ . It is only required that  $S_i$  be known to within an additive (or  $g_i$  to within a multiplicative) constant independent of the  $\bar{\alpha}_\tau$  in order that the equilibrium equations for the  $\bar{\alpha}_\tau$  be exact. On this basis, the  $(N-1)$  complexions arising from a translation of the set  $\{C_\tau\}$  on the  $\tau$  lattice are ignored, since this number does not vary with  $\bar{\alpha}_\tau$ . Similarly, complexions arising from certain crystallographic space group operations may be ignored. It is assumed that the  $\bar{\alpha}_\tau$  are independent in the limit of large  $N$  and that pairs of atoms may be treated as entities separate from other pairs. This last assumption is certainly incorrect, but studies of a few one-dimensional cases lead the authors to conjecture that the  $g_i$  derived on the basis of this assumption are exact, for large  $N$ , to within the multiplicative constant mentioned earlier. This conjecture remains to be examined, but two facts should be kept in mind: (1) All reported derivations of  $g_i$  for the three-dimensional case are admittedly incorrect, and (2) the major simplification of the equilibrium equations here reported over those of Cowley arise from a correction to his derivation of the internal energy. A derivation of  $g_i$  based on the preceding considerations follows,

Let  $N_{ij\tau}$  be the number of pairs of the  $ij$  type separated by a distance  $\tau$ . It is readily shown that these quantities are given by

$$\begin{aligned} N_{AA\tau} &= \frac{1}{2} N b_\tau m_A (m_A + m_B \bar{\alpha}_\tau), \\ N_{AB\tau} &= N b_\tau m_A m_B (1 - \bar{\alpha}_\tau), \\ N_{BB\tau} &= \frac{1}{2} N b_\tau m_B (m_B + m_A \bar{\alpha}_\tau), \end{aligned} \quad (2.16)$$

where the total number of pairs at a distance  $\tau$  is given by  $\frac{1}{2} N b_\tau$ . The interchange of the atoms of an  $AB$  pair generates distinguishable crystals. When this fact is taken into account and when the pairs are treated as separate entities, the total number of distinguishable crystals is given by the product of an unknown number  $M_\tau$  independent of  $\bar{\alpha}_\tau$  and the quantity

$$2^{N_{AB\tau}} / (N_{AA\tau}! N_{AB\tau}! N_{BB\tau}!). \quad (2.17)$$

The associated number of complexions  $g_i$  is then given by

$$g_i = \prod_\tau M_\tau 2^{N_{AB\tau}} / (N_{AA\tau}! N_{AB\tau}! N_{BB\tau}!). \quad (2.18)$$

The configurational entropy is given by

$$S_i = -k \sum_\tau \ln [N_{AA\tau}! N_{AB\tau}! N_{BB\tau}! 2^{-N_{AB\tau}}], \quad (2.19)$$

to within an additive constant independent of the  $\bar{\alpha}_\tau$ . The relations in (2.16) are substituted into (2.19) and the Stirling approximation is applied. These results are, in turn, substituted into the Helmholtz free energy,

$$F_i = U_i - TS_i \quad (2.20)$$

and  $F_i$  is minimized with respect to the  $\bar{\alpha}_\tau$ , assumed independent. The final equilibrium equations are

$$\bar{\alpha}_\tau / (1 - \bar{\alpha}_\tau)^2 = m_A m_B \{ \exp[-2E(\tau)/kT] - 1 \}, \quad (2.21)$$

from which it is found that

$$\bar{\alpha}_\tau = 1 + \frac{1 - \{1 + 4m_A m_B [\exp(-2E(\tau)/kT) - 1]\}^{1/2}}{2m_A m_B \{ \exp[-2E(\tau)/kT] - 1 \}}. \quad (2.22)$$

In the special case of  $m_A = \frac{1}{2}$ , Eq. (2.22) reduces to the simpler form

$$\bar{\alpha}_\tau = \tanh[-E(\tau)/2kT]; \quad m_A = \frac{1}{2}. \quad (2.23)$$

Analysis of Eq. (2.22) shows that  $\bar{\alpha}_\tau$  is a monotonically decreasing or increasing function of temperature for negative or positive  $E(\tau)$ , respectively, with zero first derivative at the origin and at infinity. The temperature at which  $\bar{\alpha}_\tau$  assumes a value one-half of that at zero temperature can be called the transition temperature  $T_c(\tau)$  associated with the atomic distance  $\tau$ . From

(2.22), it is found that  $T_c(\tau)$  is proportional to the magnitude of  $E(\tau)$  as follows:

$$T_c(\tau) = 2|E(\tau)| / \left[ k \ln \left( \frac{m_A m_B + 2}{m_A m_B} \right) \right], \quad E(\tau) < 0, \quad (2.24)$$

and

$$T_c(\tau) = 2|E(\tau)| / \left[ k \ln \left( \frac{m_A m_B (\xi + 2)^2}{m_A m_B (\xi + 2)^2 - 2\xi} \right) \right], \quad E > 0, \quad (2.25)$$

where  $\xi$  is the smaller of the two quantities  $m_A/m_B$  or  $m_B/m_A$ .

If  $E(\tau)$  decreases in magnitude with  $\tau$ , the onset of disorder occurs first at long range when the temperature is increased from a very low to a high temperature. It is also clear that whereas there is a range of transition temperatures for the  $\bar{\alpha}_\tau$ , there is still the possibility that any given functional (resistivity or specific heat) of the  $\bar{\alpha}_\tau$  may have a single, well-defined, transition temperature. These results will be further discussed in Sec. 4.

### 3. QUANTUM EQUILIBRIUM EQUATIONS FOR THE ORDER PARAMETERS

In this section the preceding calculations of configurational entropy will be used in conjunction with Flinn's quantum mechanical calculation of the internal energy.<sup>3</sup> Hall has already pointed out that certain of Flinn's approximations cancel making the theory more accurate than previously supposed.<sup>7</sup> However, there are two numerical errors which, when corrected, vitiate his reported agreement between experiment and theory. The authors have found, as reported by Asch and Hall,<sup>4</sup> that agreement can be regained for the Cu-Au system by the introduction of a certain parameter  $C$  representing an improvement on Flinn's approximation of Bloch functions with free electron functions. For this particular system, the agreement between experiment and theory is regained with the limitation of only first neighbor contributions to which Flinn restricted himself. Inclusion of higher neighbor contributions may be required for other systems, and this in turn will require evaluation of certain difficult integrals. These will be treated in an Appendix. The outline of Flinn's theory with these minor extensions now follows, the reader is referred to Flinn,<sup>3</sup> Hall,<sup>7</sup> and Asch and Hall<sup>4</sup> for details.

Consider, as in Sec. 2.1 a Bravais  $\tau$  lattice of infinite extent on which  $A$  atoms and  $B$  atoms are placed substitutionally. Let the rigid potentials associated with an  $A$  atom and a  $B$  atom be  $U_A(\mathbf{r})$  and  $U_B(\mathbf{r})$ , respectively, where both potentials do not necessarily vanish outside the unit cell. The total potential  $U(\mathbf{r})$  is given by the sum of an "average" potential  $U_1(\mathbf{r})$  and a

"disordered" potential  $U_2(\mathbf{r})$  defined by

$$U_1(\mathbf{r}) = \sum_{\tau} [m_A U_A(\mathbf{r} - \tau) + m_B U_B(\mathbf{r} - \tau)], \quad (3.1)$$

$$U_2(\mathbf{r}) = \sum_{\tau} C_{\tau} \Delta U(\mathbf{r} - \tau), \quad \Delta U(\mathbf{r}) = U_A(\mathbf{r}) - U_B(\mathbf{r}). \quad (3.2)$$

The theoretical model of the disordered alloy is constructed in two steps: In the first step, a crystal of infinite extent is imagined to exist with the periodic potential  $U_1$ . Periodic boundary conditions are applied to the volume  $N\Omega$ , which leads to Bloch functions,

$$\psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{r}), \quad (3.3)$$

$$\psi_{\mathbf{k}}(\mathbf{r} + \mathbf{n}) = \psi_{\mathbf{k}}(\mathbf{r}), \quad u_{\mathbf{k}}(\mathbf{r} + \tau) = u_{\mathbf{k}}(\mathbf{r}). \quad (3.4)$$

It is further imagined that these Bloch functions are known and that they lead to an internal energy  $U_0^Q$  per replica. In the second step, the model is completed with the addition of the potential  $U_2$  [for one definite configuration represented by  $\{C_{\tau}\}$ ] and the requirement that  $C_{\tau+n} = C_{\tau}$ . Perturbation theory to second order in the energy is then applied. The first-order results vanish and the second-order results are derivable from (see Asch and Hall<sup>4</sup> for definition and derivation)

$$|M(\mathbf{k}, \mathbf{k}')|^2 = \sum_{\tau} \alpha_{\tau} J(\mathbf{k}, \mathbf{k}', \tau), \quad (3.5)$$

where  $J$  does not depend on the direction of  $\tau$ . For large  $N$ , this expression reduces to

$$|M(\mathbf{k}, \mathbf{k}')|^2 = \sum_{\tau} b_{\tau} \bar{\alpha}_{\tau} J(\mathbf{k}, \mathbf{k}', \tau). \quad (3.6)$$

The analog of the sum in (2.14) is derivable from (3.6) by the techniques introduced by Flinn.<sup>3</sup> However, a few extensions and corrections to Flinn's work must be enumerated: (1) Flinn used potentials that vanished outside the unit cell  $\Omega$  and used free electron functions for the unperturbed functions, but Hall<sup>7</sup> has shown that some of his approximations cancel thereby permitting a trivial extension to potentials with "tails" outside the unit cell. (2) Asch and Hall<sup>4</sup> have shown that the first-order results vanish even for Bloch functions. (3) In calculating the second-order results, it is necessary to know or to approximate the unperturbed Bloch functions; Asch and Hall<sup>4</sup> found it very useful to make the replacement

$$|u_{\mathbf{k}'}^*(\mathbf{r}) u_{\mathbf{k}}(\mathbf{r})|^2 = C, \quad (3.7)$$

a real positive number, where  $C$  is left as an adjustable constant. Setting  $C=1$  corresponds to Flinn's assumption of free electron wave functions. (4) The right-hand side (rhs) of Flinn's equations (24) should be multiplied by 8 to compensate for an incorrect integration; the rhs of his Eq. (19) should be multiplied by 2 to take account

of the two electrons with opposite spins in each state. These two facts imply that his final Eq. (44) should be multiplied on the rhs by a factor 16, or 16C if we include (3) above.<sup>3</sup>

When all the preceding considerations are incorporated into Flinn's work, his Eq. (44) becomes in the notation of (2.14)

$$U^Q - U_0^Q = -\frac{32mCNm_A m_B (\Delta Z)^2}{\hbar^2 (4\pi)^3} \sum_{\tau} b_{\tau} \bar{\alpha}_{\tau} f_{\tau}, \quad (3.8)$$

where

$$f_{\tau} = \frac{1}{2K\tau} \int_0^{\infty} \frac{yg(y)(\sin 2K\tau y)}{[(q/2K)^2 + y^2]^2} dy, \quad (3.9)$$

where  $K$  is the magnitude of the propagation vector at the Fermi surface, where the two atomic potentials are given in Hartree units by

$$V_i(\mathbf{r}) = Z_i r^{-1} \exp(-qr), \quad i = A \text{ or } B, \quad (3.10)$$

and  $\Delta Z$  is defined as  $|Z_A - Z_B|$ . The definition of  $g(y)$  is given in the Appendix where the integral in (3.9) is evaluated. These results are easily extended to a variety of other potentials, for example ones for which  $q_A \neq q_B$  as in (3.10). The quantum results are placed in the same form as (2.14) by defining a generalization of  $E_{\tau}$  from (2.13) to

$$E_{\tau}^Q = -\frac{32mC(\Delta Z)^2}{\hbar^2 (4\pi)^3} f_{\tau}. \quad (3.11)$$

The analog of (2.14) is

$$U_i^Q - U_0^Q = Nm_A m_B \sum_{\tau} b_{\tau} \bar{\alpha}_{\tau} E_{\tau}^Q, \quad (3.12)$$

and the analog of (2.22) is

$$\bar{\alpha}_{\tau} = 1 + \frac{1 - \{1 + 4m_A m_B [\exp(-2E_{\tau}^Q/kT) - 1]\}^{1/2}}{2m_A m_B [\exp(-2E_{\tau}^Q/kT) - 1]}. \quad (3.13)$$

#### 4. DISCUSSION

The equilibrium equations for the order parameters of Cowley have been derived both for a classical bond energy model and for a quantum model. In the two cases the equilibrium equations are of the same form, which is considerably simpler than the incorrect equations of Cowley. Cowley's main error is in the calculation of the internal energy. There are also some differences between Cowley's expression of the configurational entropy and the expression derived in this paper, but these differences have a minor effect on the equilibrium equations. Neither Cowley nor the authors have established their entropy expressions to be exact, but the authors have attempted to clarify the nature of the approximations involved.

For the quantum case, the authors rely heavily on Flinn's calculation of the internal energy. A few minor extensions are included; and, more importantly, certain

difficult integrals are reduced to a simple form easily evaluated numerically.

The Cowley parameter  $\bar{\alpha}_{\tau}$  associated with the distance  $\tau$  has a transition temperature proportional to the absolute value of the characteristic energies associated with that distance. Thus, there is a range of transition temperatures for the order parameters, but there still may exist a definite transition temperature for given functions (resistivity or specific heat) of the  $\bar{\alpha}_{\tau}$ . As the temperature of the alloy is increased from very low temperatures, where the greatest degree of order exists, disorder will occur at each given distance independently with the transition temperatures proportional to the associated characteristic energies. Since the characteristic energies for large distances are expected to fall off rapidly with distance, the onset of disorder will, in general, first take place at large distances as the temperature is increased.

The theory developed here is not necessarily valid for concentrations at which superlattices may exist.

Numerical calculations are under way to compare experiment and theory in two ways: (1) a direct comparison of theoretically predicted order parameters with those measured by x-ray techniques and (2) a comparison of experimental and theoretical residual electrical resistivity.<sup>4</sup>

#### APPENDIX A: A METHOD OF EVALUATING THE ENERGY INTEGRALS

It is possible to reduce the integrals appearing in (3.9),

$$f_{\tau} = \frac{1}{2K\tau} \int_0^{\infty} \frac{yg(y)(\sin 2K\tau y)}{[(q/2K)^2 + y^2]^2} dy, \quad (A1)$$

$$g(y) = 2\pi \left[ 1 - \frac{1}{2}(y - y^{-1}) \ln \left| \frac{y+1}{y-1} \right| \right], \quad (A2)$$

to the simple form,

$$f_{\tau} = \frac{\pi^2}{B} \int_0^1 \frac{(1-x^2)(\cos Bx)}{(A^2+x^2)^2} dx + \pi^2 \exp(-AB) \left\{ \frac{1}{2A} \frac{2 + [A^{-1} - A + B(1+A^2)][\pi - 2 \arctan A]}{4BA^2} \right\}, \quad (A3)$$

$$B = 2K\tau, \quad A = q/2K.$$

An outline of this reduction follows.

When (A2) is substituted into (A1), the first term of  $g(y)$  leads to an integral simply evaluated by standard procedures of contour integration. To complete the problem it is necessary to evaluate an integral of the form

$$I = \int_{-\infty}^{\infty} \frac{(1-x^2)(\sin Bx)}{[A^2+x^2]^2} \ln \left| \frac{x+1}{x-1} \right| dx, \quad (A4)$$

where the integrand is not an analytic function. A little analysis immediately shows that (I4) can be rewritten

$$I = \int_{\Gamma} \frac{(1-z^2)(\sin Bz)}{(A^2+z^2)^2} \ln\left(\frac{z+1}{z-1}\right) dz, \quad (\text{A5})$$

where the contour  $\Gamma$  runs along the real axis from  $-\infty$  to  $\infty$  except in the region of a cut lying on the real axis from  $-1$  to  $1$ . The contour  $\Gamma$  may be taken either just

above or just below the cut. The next step is to write the  $(\sin Bz)$  in terms of exponentials and to write  $I$  as the sum of two integrals, where the contours for both integrals must be taken on the same side of the cut. By the use of Jordan's lemma and deformations of the contours of integration, the integral in (A5) is reduced to the evaluation of two residues and an integral around the cut. The latter integral is the source of the integral appearing in the final form (A3), and the residues are readily evaluated. This completes the outline.

## Thermal Conductivity of Some Alkali Halides Containing $F$ Centers\*

CHARLES T. WALKER†

Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York

(Received 19 July 1963)

Thermal conductivity measurements are used to study phonon scattering by  $F$  centers in NaF, KCl, KBr, and KI.  $F$  centers were produced by additive coloration and by  $x$  and  $\gamma$  irradiation. The total effect on the thermal conductivity is seen to be different for the two methods of preparation. The additively colored data display two features: a low-temperature depression due to phonon scattering by colloids and quench-induced defects, and a high-temperature effect due to phonon scattering by  $F$  centers. The irradiated samples also display two features, a high-temperature effect due to  $F$  centers and a different low-temperature depression of unknown origin. The high-temperature data in irradiated samples can be explained if one assumes that  $F$  centers are formed in regions of high concentration during irradiation. Several mechanisms are discussed for the low-temperature depression in irradiated crystals, including interstitials and the effect of dislocations on  $F$ -center formation. The  $F$  center is shown to produce quasilocalized impurity modes with frequencies of the order of  $10^{13}$  sec $^{-1}$ , and is seen to scatter phonons elastically primarily through its strain field.

### I. INTRODUCTION

AS was first demonstrated by Berman<sup>1</sup> low-temperature thermal conductivity measurements provide a sensitive method for investigating the scattering of phonons by lattice defects. In the decade since Berman's original work the technique has been applied to study many defect systems, running the gamut from simple isotopic impurities,<sup>2-4</sup> substitutional chemical impurities,<sup>5-8</sup> molecular impurities,<sup>9</sup> dislocations,<sup>10</sup> colloids<sup>11</sup>

up to such esoteric studies as phonon-spin interactions<sup>12</sup> and acoustic phonon-optic phonon interactions.<sup>13</sup> During this time there has been continued interest in the scattering of phonons by point defects, where "point" has the usual meaning of an object whose size is of atomic dimensions. The early interest in point defects arose from the fact that the initial theories<sup>14,15</sup> predicted an especially simple scattering law for point defects, namely a Rayleigh-type law. The more recent interest arises from the experimental<sup>16</sup> and theoretical<sup>17-19</sup> evidence for a resonant phonon scattering by quasilocalized impurity modes in addition to the elastic Rayleigh scattering.

The  $F$  center, an electron occupying a negative ion vacancy, satisfies all the criteria for a point defect since its mass is certainly different from the mass of

\* Supported in part by the Advanced Research Projects Agency and the U. S. Atomic Energy Commission.

† Present address: Department of Physics, Northwestern University, Evanston, Illinois.

<sup>1</sup> R. Berman, Proc. Roy. Soc. (London) **A208**, 90 (1951); Suppl. Phil. Mag. **2**, 103 (1953).

<sup>2</sup> T. H. Geballe and G. W. Hull, Phys. Rev. **110**, 773 (1958).

<sup>3</sup> R. Berman, P. T. Nettley, F. W. Sheard, A. N. Spencer, R. W. H. Stevenson, and J. M. Ziman, Proc. Roy. Soc. (London) **A253**, 403 (1959).

<sup>4</sup> E. J. Walker and H. A. Fairbank, Phys. Rev. **118**, 913 (1960).

<sup>5</sup> G. A. Slack, Phys. Rev. **105**, 832 (1957).

<sup>6</sup> W. S. Williams, Phys. Rev. **119**, 1021 (1960).

<sup>7</sup> B. Abeles, D. S. Beers, G. D. Cody, J. P. Dismukes, Phys. Rev. **125**, 44 (1962).

<sup>8</sup> M. V. Klein, Phys. Rev. **123**, 1977 (1961).

<sup>9</sup> R. O. Pohl, Phys. Rev. Letters **8**, 481 (1962).

<sup>10</sup> R. L. Sproull, M. Moss, H. Weinstock, J. Appl. Phys. **30**, 334 (1959).

<sup>11</sup> J. M. Worlock, Ph.D. thesis, Cornell University, 1962 (unpublished).

<sup>12</sup> I. P. Morton and H. M. Rosenberg, Phys. Rev. Letters **8**, 200 (1962); R. Berman, J. C. F. Brock, and D. J. Huntley, Phys. Letters **3**, 310 (1963).

<sup>13</sup> A. J. Sievers, III, Bull. Am. Phys. Soc. **8**, 208 (1963).

<sup>14</sup> P. G. Klemens, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 7, p. 1.

<sup>15</sup> P. Carruthers, Rev. Mod. Phys. **33**, 92 (1961).

<sup>16</sup> C. T. Walker and R. O. Pohl, Phys. Rev. **131**, 1428 (1963).

<sup>17</sup> M. Wagner, Phys. Rev. **131**, 1443 (1963).

<sup>18</sup> J. A. Krumhansl, Bull. Am. Phys. Soc. **8**, 207 (1963).

<sup>19</sup> M. V. Klein, Bull. Am. Phys. Soc. **8**, 207 (1963). S. Takeno, Progr. Theoret. Phys. (Kyoto) **29**, 191 (1963); **29**, 328 (1963).