

Quantum Theory of the Residual Electrical Resistivity of Disordered Alloys*

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 (Received 27 February 1963)

Nordheim's theory for purely random alloys and Hall's extension for nonrandom alloys in terms of Cowley parameters are further developed and applied to substitutional binary systems. The theory is valid for any degree of order, excepting perfect superlattices. Purely random alloys and nonrandom alloys are shown to possess certain analogies with *normal* and *umklapp processes*, respectively. By accounting for those Fermi volume changes with concentration arising when the two atoms are different in size and valence, it is possible to explain the experimental non-parabolic curves of resistivity versus concentration. Applications are made to the cases of the Cu-Au and the Cu-Ni systems rapidly quenched from a high temperature. Results of a limited study of the data for the slowly annealed Cu-Au system are presented, but more experimental measurements of the Cowley parameters are required to test the theory. A few new relations obeyed by the Cowley parameters are given. The work reported here meets certain independent checks carried out by Christy in unpublished calculations on ordering energy.

1. INTRODUCTION

VERY little work has been reported on the quantum theory of the residual resistivity of nondilute disordered alloys. Here the theory of Nordheim¹ for purely random alloys and Hall's² extension for nonrandom alloys are further developed and applied to substitutional binary alloys. In order to explain the nonparabolic curves of resistivity versus concentration for nearly random (rapidly quenched) alloys, it is essential that changes in the volume enclosed by the Fermi surface be taken into account. Fermi volume changes with concentration considered in this paper are of two types: (1) that resulting indirectly from the change in the lattice parameter as the stoichiometric proportion of two ions of appreciably different size is varied, and (2) that arising directly from the change, with concentration, in the effective number of conduction electrons when the two ions possess different valences. Most of the applications reported here are for the nearly random case, which turns out to be somewhat analogous to *normal processes* in thermal resistivity. The theory of nonrandom (slowly annealed) alloys, which is shown to be analogous to *umklapp processes*, is applied to the Cu-Au system. The latter application is somewhat limited at the present by lack of knowledge of the Cowley order parameters³; to proceed further in testing the theory more experimental measurements of the Cowley parameters and knowledge of the geometrical interrelationships between the various Cowley parameters are required.

In 1931, Nordheim¹ used perturbation methods to develop a theory for purely random substitutional alloys which predicts a parabolic dependence of the resistivity on the concentration of one component of a binary alloy. This prediction does not agree with experiment, and various qualitative explanations^{4,5} have been suggested

to explain the discrepancy. Nordheim's theoretical model is one in which each atom is represented by a potential which vanishes at the cell boundary; the total potential representing the disorder is treated as a perturbation. The associated matrix elements, which have many contributing terms, are then calculated approximately by discarding many terms without rigorous justification. Moreover, considerations (1) and (2) above are completely ignored.

In 1959, Hall² considered a more general model in which each atom is permitted to possess a potential "tail" extending over many cells and he introduced the Cowley order parameters into the formalism in a manner similar to that used in Flinn's treatment⁶ of ordering energy. Hall reported that the contributions to the matrix elements discarded by Nordheim turn out to be identically zero for a purely random alloy but constitute the order dependent contributions in the nonrandom case. Hall also found a parabolic resistivity curve for the purely random case, because he, like Nordheim, failed to consider items (1) and (2) above. Furthermore, both Nordheim and Hall failed to notice that in the nonrandom case the k , k' matrix element depends, in general, upon the direction of k with respect to the crystal as well as upon the angle between k and k' . The first of these dependences gives rise to a problem similar to that encountered in *umklapp processes*.⁷ This point will be discussed in detail in Sec. 2.

Criticisms similar to those outlined above can be directed toward the work of Dyhne, Matysina, and Smirnov⁸, who developed a formalism without testing it in detail with an application.

The three main tasks undertaken in this paper are: (A) to develop a method for handling the features, similar to those in *umklapp processes*, which are encountered in the nonrandom case; (B) to demonstrate in the applications the necessity, and success, of ac-

* Work supported by the National Science Foundation.

¹ L. Nordheim, *Ann. Physik* **9**, 607 (1931).

² G. L. Hall, *Phys. Rev.* **116**, 604 (1959).

³ J. M. Cowley, *Phys. Rev.* **77**, 669 (1950).

⁴ H. Jones, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 19, p. 269.

⁵ N. V. Grum-Grzhimailo, *Fiz. Metal. i Metalloved.* **5**, 23 (1957).

⁶ P. A. Flinn, *Phys. Rev.* **104**, 350 (1956).

⁷ H. Jones, *Ref. 4*, p. 245.

⁸ A. M. Dykhne, Z. A. Matysina, and A. A. Smirnov, *Fiz. Metal. i Metalloved.* **5**, (2), 220 (1957).

counting for the changes of the Fermi volume arising from changes in the lattice parameter and the changes in the effective number of conduction electrons; and (C) to point out what experimental information is needed, and to indicate where further knowledge of the interrelations between the various Cowley parameters would be helpful.

Section 2 on theory treats the potentials to be used, introduces the Cowley parameters, and presents a calculation of the relaxation time; Sec. 3 applies this theory to the nearly random case; Sec. 4 reports limited applications to the nonrandom case, particularly for the Cu-Au system; finally, Sec. 5 summarizes the results and discusses the need for further experimental and theoretical work.

2. THEORY

1. Theoretical Model and Cowley Parameters

Consider a binary disordered lattice of A and B atoms placed on a Bravais τ lattice. Let the rigid potential associated with an A atom be $U_A(\mathbf{r})$ and that associated with a B atom be $U_B(\mathbf{r})$, where both potentials do not necessarily vanish outside the unit cell. The total potential $U(\mathbf{r})$ is given by

$$U(\mathbf{r}) = \sum_{A \text{ atoms}}^{\infty} U_A(\mathbf{r}-\boldsymbol{\tau}) + \sum_{B \text{ atoms}}^{\infty} U_B(\mathbf{r}-\boldsymbol{\tau}). \quad (2.1)$$

This total potential can be decomposed into a more workable form by introducing a function C_τ defined at the lattice points as follows:

$$C_\tau = m_B, \quad \text{if an } A \text{ atom is at } \boldsymbol{\tau} \\ = -m_A, \quad \text{if a } B \text{ atom is at } \boldsymbol{\tau},$$

where m_i is the concentration of the i th component. Further, let an average potential be defined by

$$U_1(\mathbf{r}) \equiv \sum_{\tau}^{\infty} [m_A U_A(\mathbf{r}-\boldsymbol{\tau}) + m_B U_B(\mathbf{r}-\boldsymbol{\tau})], \quad (2.2)$$

which is periodic and produces no resistivity; let a "difference potential" be defined by

$$U_2(\mathbf{r}) \equiv \sum_{\tau}^{\infty} C_\tau \Delta U(\mathbf{r}-\boldsymbol{\tau}), \quad \Delta U(\mathbf{r}) \equiv U_A(\mathbf{r}) - U_B(\mathbf{r}), \quad (2.3)$$

which describes the disorder. The various potentials are simply related by

$$U(\mathbf{r}) = U_1(\mathbf{r}) + U_2(\mathbf{r}). \quad (2.4)$$

The theoretical model 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 a volume $N\Omega$ described by the three vectors $N_1\boldsymbol{\tau}_1$, $N_2\boldsymbol{\tau}_2$, and $N_3\boldsymbol{\tau}_3$, where N equals $N_1N_2N_3$ and Ω equals $|\boldsymbol{\tau}_1 \cdot (\boldsymbol{\tau}_2 \times \boldsymbol{\tau}_3)|$. In applying periodic boundary conditions, it is convenient to introduce the infinite set of vectors \mathbf{n} defined by

$$\mathbf{n} \equiv n_1 N_1 \boldsymbol{\tau}_1 + n_2 N_2 \boldsymbol{\tau}_2 + n_3 N_3 \boldsymbol{\tau}_3, \\ n_i = 0, \pm 1, \pm 2, \dots$$

It then follows that

$$C_{\tau+\mathbf{n}} = C_\tau,$$

and U_1 leads to Bloch functions

$$\psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r}) \exp i\mathbf{k} \cdot \mathbf{r}, \\ \exp i\mathbf{k} \cdot \mathbf{n} = 1, \quad u_{\mathbf{k}}(\mathbf{r}+\boldsymbol{\tau}) = u_{\mathbf{k}}(\mathbf{r}), \quad (2.5)$$

where $\boldsymbol{\tau}$ is any Bravais lattice vector. It is imagined that these exact Bloch functions are known. In the second step of the construction, the model is completed with the addition of the potential U_2 , which is assumed to cause only a small perturbation on the Bloch functions. This potential is the source of the residual resistivity. By insisting that $C_{\tau+\mathbf{n}}$ equals C_τ , it is insured that periodic boundary conditions are also applied to the perturbed crystal.

It is then possible to show (see Appendix A) for potentials extending outside the unit cell and for general Bloch functions that the matrix element of U_2 defined by

$$M(\mathbf{k}, \mathbf{k}') \equiv \frac{1}{N\Omega} \int_{N\Omega} \psi_{\mathbf{k}'}^*(\mathbf{r}) U_2(\mathbf{r}) \psi_{\mathbf{k}}(\mathbf{r}) d^3r, \quad (2.6)$$

vanishes if \mathbf{k} equals \mathbf{k}' (first-order perturbation results) and is otherwise given by

$$M(\mathbf{k}, \mathbf{k}') = \frac{1}{N\Omega} \sum_{\tau}^N C_\tau \int_{-\infty}^{+\infty} \psi_{\mathbf{k}'}^*(\mathbf{r}) \Delta U(\mathbf{r}-\boldsymbol{\tau}) \psi_{\mathbf{k}}(\mathbf{r}) d^3r.$$

In the same manner it is also shown that

$$|M(\mathbf{k}, \mathbf{k}')|^2 = \sum_{\tau}^N \alpha_{\tau} J(\mathbf{k}, \mathbf{k}', \boldsymbol{\tau}), \quad (2.7)$$

$$\alpha_{\tau} = \sum_{\tau'}^N C_{\tau'} C_{\tau+\tau'} / N m_A m_B, \quad (2.8)$$

$J(\mathbf{k}, \mathbf{k}', \boldsymbol{\tau})$

$$= N m_A m_B \left| \frac{1}{N\Omega} \int_{-\infty}^{+\infty} \psi_{\mathbf{k}'}^*(\mathbf{r}) \psi_{\mathbf{k}}(\mathbf{r}) \Delta U(\mathbf{r}-\boldsymbol{\tau}) d^3r \right|^2. \quad (2.9)$$

The N Cowley order parameters as defined by Eq. (2.8) are not all independent, but so far no one has reported all the interrelationships. The following properties are easily established⁹:

$$\alpha_{\tau} = \alpha_{-\tau}, \quad \alpha_0 = 1, \quad \sum_{\tau}^N \alpha_{\tau} = 0, \quad \alpha_{\tau+\mathbf{n}} = \alpha_{\tau}, \quad (2.10a)$$

$$1 \geq \alpha_{\tau} \geq \begin{cases} 1 - \frac{1}{m_B}, & 0 \leq m_A \leq \frac{1}{2} \\ 1 - \frac{1}{m_A}, & 0 \leq m_B \leq \frac{1}{2} \end{cases}, \quad (2.10b)$$

$$\alpha_{\tau \neq 0} = -1/(N-1), \text{ random case.} \quad (2.10c)$$

⁹ G. L. Hall and D. O. Christy (to be published).

It should be noted that α_r is a discrete autocorrelation function which describes the arrangement of atoms and is independent of the functional form of the potentials. The quantity J , also expressible as an autocorrelation function, depends only on the potentials and not the arrangement of atoms.

Equation (2.7) is equivalent to Jones¹⁴ Eq. (25.5) in his discussion of the Nordheim¹ theory. In the limit as N approaches infinity all α_r for purely random solutions vanish except α_0 . This proves² that the second sum in Jones' Eq. (25.5) is identically zero for random solutions even if rigid atomic potentials extending over more than one cell and Bloch functions are used. In nonrandom solutions, first- and higher-order neighbors contribute to the matrix elements in (2.7).

It is of importance to note that care has to be exercised in the use of (2.7) for perfectly ordered crystals. Although the α_r can describe perfectly ordered as well as disordered crystals, the finite sum in (2.7) is identically zero for many \mathbf{k}, \mathbf{k}' pairs if α_r represents a perfect superlattice. In the sequel it will be pointed out where it is assumed that no perfect superlattice exists.

When Bloch functions are considered, (2.9) may be rewritten in an alternate form which is more convenient for calculations made later in this paper; this alternate form is

$$J(\mathbf{k}, \mathbf{k}', \boldsymbol{\tau}) = \exp[i(\mathbf{k} - \mathbf{k}') \cdot \boldsymbol{\tau}] H(\mathbf{k}, \mathbf{k}'), \quad (2.11)$$

where

$$H(\mathbf{k}, \mathbf{k}') \equiv N m_A m_B \left| \frac{1}{N\Omega} \int_{N\Omega} u_{\mathbf{k}'}^*(\mathbf{r}) u_{\mathbf{k}}(\mathbf{r}) \times \exp[i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}] \Delta U(\mathbf{r}) d^3r \right|^2. \quad (2.12)$$

2. Calculation of the Relaxation Time

The general theory of a relaxation time $T(\mathbf{k})$ for electrons excited by thermal or structural distortions of a periodic lattice is well known. In a review article, Jones¹⁰ derives the expression

$$\frac{1}{T(\mathbf{k})} = \frac{N\Omega}{8\pi^3} \int_{N\Omega} P(\mathbf{k}, \mathbf{k}') \left[1 - \frac{\chi(\mathbf{k}')}{\chi(\mathbf{k})} \right] d^3k', \quad (2.13)$$

relating the relaxation time T to the probability per unit time P of an electron being excited from the Bloch state \mathbf{k} to the state \mathbf{k}' , where χ is a function related to the general distribution function of the Boltzmann equation. For a large class of phenomena, it is assumed that the scattering is elastic and that the energy E of the electron depends only on the magnitude of the wave vector,

$$E = \frac{\hbar^2}{2\mu} |\mathbf{k}|^2,$$

where μ is the effective electronic mass. Further approximations, which are usually necessary, depend upon the

¹⁰ H. Jones, Ref. 4, p. 237.

nature of the phenomenon under study. Interest here is centered on the residual resistivity of disordered alloys, a structural effect, but it is instructive to draw an analogy between this and thermal resistivity. The main justification for this analogy is for the nonrandom case where $P(\mathbf{k}, \mathbf{k}')$ will be approximated by an averaging process similar to that used for *umklapp processes*.

Purely Random Case Similar to Normal Processes

In *normal processes* it is assumed that the solid is isotropic, which leads to three results: (i) $P(\mathbf{k}, \mathbf{k}')$ becomes a function of the magnitudes of \mathbf{k} and \mathbf{k}' and the relative direction between them, and is independent of the current; (ii) $\chi(\mathbf{k})$ becomes a function of the magnitude of \mathbf{k} and the angle between \mathbf{k} and the direction of the current; and (iii) $T(\mathbf{k})$ depends only on the magnitude of \mathbf{k} . The probability $P(\mathbf{k}, \mathbf{k}')$ is then simply related to the modulus squared of the scattering matrix by

$$P(\mathbf{k}, \mathbf{k}') = \frac{2\pi\mu}{\hbar^2 k} |M(\mathbf{k}, \mathbf{k}')|^2 \delta(k' - k). \quad (2.14)$$

For this type of thermal resistivity, $M(\mathbf{k}, \mathbf{k}')$ is the matrix element of an instantaneous configuration of vibration, and it is understood, although the notation does not indicate it, that an average over all possible configurations is to be performed. In normal processes, $M(\mathbf{k}, \mathbf{k}')$ cannot depend upon the relation of \mathbf{k} or \mathbf{k}' to a crystallographic direction.

Although a purely random array of atomic potentials placed on a Bravais lattice does not yield an isotropic total potential, it still follows under certain conditions that the associated matrix elements are similar to those for normal processes. Sufficient conditions for a significant correspondence are that $\Delta U(\mathbf{r})$ and $u_{\mathbf{k}}(\mathbf{r})$ be spherically symmetric. Under these conditions it follows from (2.7) and (2.10) that in the limit of large N one has for the random case

$$|M(\mathbf{k}, \mathbf{k}')|^2 = J(\mathbf{k}, \mathbf{k}', \mathbf{0}), \quad (2.15)$$

where $J(\mathbf{k}, \mathbf{k}', \mathbf{0})$ is a function of the magnitudes of \mathbf{k} and \mathbf{k}' and of the relative angle between them. With these restrictions the relaxation time for the purely random case becomes

$$\frac{1}{T} = \frac{\mu N\Omega}{4\pi^2 \hbar^3 k_0} \int J(\mathbf{k}, \mathbf{k}', \mathbf{0}) \left[1 - \frac{\mathbf{k}' \cdot \hat{\mathbf{z}}}{\mathbf{k} \cdot \hat{\mathbf{z}}} \right] dS', \quad (2.16)$$

where the integration is over all \mathbf{k}' lying on the spherical Fermi surface denoted by k_0 and where $\hat{\mathbf{z}}$ is a unit vector in the direction of the electric field. Equation (2.16) will be evaluated for specific potentials after the analog of (2.16) has been developed for the nonrandom case.

Nonrandom Contributions Similar to Umklapp Processes

In *umklapp processes* the transition probability is dependent on the direction of \mathbf{k} relative to the crystallo-

graphic axes of the crystal; accordingly, the crystal can no longer be assumed to be isotropic. The usual method of handling the associated difficulty⁷ in (2.13) is to average the transition probability over all possible directions of \mathbf{k} . Similarly for a disordered alloy the transition probability is dependent on the relative directions of \mathbf{k} , \mathbf{k}' , and $\boldsymbol{\tau}$. A solution to this problem is obtained in the same manner as used for U processes. Thus, for a disordered alloy, (2.13) may be written

$$\frac{1}{T} = \frac{N\Omega}{8\pi^3} \int_{N\Omega} \langle P(\mathbf{k}, \mathbf{k}') \rangle_{\text{av}} \left[1 - \frac{\mathbf{k}' \cdot \hat{\mathbf{z}}}{\mathbf{k} \cdot \hat{\mathbf{z}}} \right] d^3k', \quad (2.17)$$

where $\langle P(\mathbf{k}, \mathbf{k}') \rangle_{\text{av}}$ is the average of the transition probability over all possible directions of \mathbf{k} . Note that this averaging procedure need not be applied to the random case. Equations (2.7), (2.14), and (2.17) give for the relaxation time

$$\frac{1}{T} = \frac{\mu N\Omega}{4\pi^2 \hbar^3 k_0} [I(0) + \sum'_{\tau} \alpha_{\tau} I(\boldsymbol{\tau})], \quad (2.18)$$

where

$$I(0) = \int J(\mathbf{k}, \mathbf{k}', 0) \left[1 - \frac{\mathbf{k}' \cdot \hat{\mathbf{z}}}{\mathbf{k} \cdot \hat{\mathbf{z}}} \right] dS', \quad (2.19)$$

$$I(\boldsymbol{\tau}) = \int \langle J(\mathbf{k}, \mathbf{k}', \boldsymbol{\tau}) \rangle_{\text{av}} \left[1 - \frac{\mathbf{k}' \cdot \hat{\mathbf{z}}}{\mathbf{k} \cdot \hat{\mathbf{z}}} \right] dS', \quad (2.20)$$

and where Eq. (2.16) has been used for the random case, that is, for $\boldsymbol{\tau} = 0$. The only restrictions on (2.18) are that both ΔU and $u_{\mathbf{k}}$ must be spherically symmetric.

Relaxation Time for the Yukawa Potential

In order to proceed further with Eq. (2.18), it is necessary to specify the potentials U_A and U_B and, hence, ΔU . In most of the applications reported here the Yukawa potentials

$$U_i(\mathbf{r}) = Z_i e^2 (4\pi\epsilon_0 r)^{-1} \exp(-q_i r), \quad i = A, B,$$

will be used with q_A equal to q_B . With this simplification ΔU becomes

$$\Delta U(\mathbf{r}) = \Delta Z e^2 (4\pi\epsilon_0 r)^{-1} \exp(-qr), \quad (2.21)$$

where

$$\Delta Z \equiv |Z_A - Z_B|, \quad q = q_A = q_B.$$

It is evident that for some alloy systems q_A cannot be taken equal to q_B . A few calculations will be reported for¹¹

$$U_i(\mathbf{r}) = Z_i e^2 (4\pi\epsilon_0 r)^{-1} (\cos \phi_i r) \exp(-p_i r),$$

but the detailed calculations in the sequel are for the Yukawa potentials with both screening constants set

equal to q . Substitution of (2.21) into (2.12) yields

$$H(\mathbf{k}, \mathbf{k}') = \frac{m_A m_B Q^2}{N\Omega^2} \left| \int_{N\Omega} u_{\mathbf{k}'}^*(\mathbf{r}) u_{\mathbf{k}}(\mathbf{r}) r^{-1} \times \exp(-qr) \exp(i\Delta\mathbf{k} \cdot \mathbf{r}) d^3r \right|^2, \quad (2.22)$$

where

$$Q \equiv \Delta Z e^2 / 4\pi\epsilon_0, \quad \Delta\mathbf{k} \equiv \mathbf{k} - \mathbf{k}'. \quad (2.23)$$

The exact forms of $u_{\mathbf{k}'}^*(\mathbf{r})$ and $u_{\mathbf{k}}(\mathbf{r})$ are not known, so it is assumed that the product of these two quantities can be taken outside the integral and approximated as follows

$$|u_{\mathbf{k}'}^*(\mathbf{r}) u_{\mathbf{k}}(\mathbf{r})|^2 \approx C, \quad \text{a const.}$$

This constant and other parameters appearing in the potential will be chosen so that the theoretical resistivity curves for the random case are fitted to the experimental data. Integration of (2.22) now yields

$$H(\mathbf{k}, \mathbf{k}') = \frac{2^4 \pi^2 Q^2 C m_A m_B}{N\Omega^2 (q^2 + \Delta k^2)^2}. \quad (2.24)$$

If α_{τ} does not represent a superlattice, then (2.24) can be used for all $\Delta\mathbf{k}$. It is shown in Appendix II that (2.24), (2.11), and (2.16) yield for the purely random case.

$$\frac{1}{T} = \frac{\mu e^4 (\Delta Z)^2 C m_A m_B}{8\pi\epsilon_0^2 \hbar^3 k_0^3 \Omega} \left\{ \ln \left| 1 + \frac{4k_0^2}{q^2} \right| - \frac{4k_0^2}{q^2 + 4k_0^2} \right\}, \quad (2.25)$$

In the same Appendix it is shown for the case of general order (other than superlattices) that (2.18) gives

$$\frac{1}{T} = \frac{\mu e^4 (\Delta Z)^2 C m_A m_B}{8\pi\epsilon_0^2 \hbar^3 k_0^3 \Omega} \left\{ G(k_0, q) + \sum'_{\tau} b(\tau) \bar{\alpha}_{\tau} F(k_0, q, \tau) \right\}, \quad (2.26)$$

where τ is the magnitude of $\boldsymbol{\tau}$, $\bar{\alpha}_{\tau}$ is the average of all α_{τ} over a shell, $G(k_0, q)$ is the bracketed portion of (2.25), $b(\tau)$ is the coordination number of the τ th shell, and $F(k_0, q, \tau)$ is given by

$$F(k_0, q, \tau) = \frac{2A}{(A^2 - 1)^{3/2}} \left\{ \frac{\sin^2 B}{B^2} + \left[\frac{3A}{A^2 - 1} - \frac{1}{A} \right] \left[\frac{\sin B - B \cos B}{B^2} \right]^2 - \left[\frac{3}{A^2 - 1} \right] \left[\frac{\sin B}{B} + \frac{2}{B^3} (B \cos B - \sin B) \right]^2 \right\}, \quad (2.27)$$

$$A \equiv 1 + (q^2 / 2k_0^2), \quad B \equiv k_0 \tau. \quad (2.28)$$

It should be noted that only the averages of α_{τ} over a shell, the $\bar{\alpha}_{\tau}$, are required. More complicated potentials may require more information about the α_{τ} .

The resistivity ρ is related to the relaxation time by

$$\rho = \mu / e^2 \eta T, \quad (2.29)$$

where η is the number of conduction electrons per unit

¹¹ E. C. McIrvine, J. Phys. Soc. Japan 15, 928 (1960).

volume. For a face-centered cubic (fcc) lattice, one has the relation

$$\eta = 4n/a_0^3, \quad (2.30)$$

where n is the electron to atom ratio and a_0 is the fcc cube edge. It is also noted that for this lattice

$$12\pi^2 n = k_0^3 \Omega. \quad (2.31)$$

Substitution of (2.30), (2.31), and (2.26) into (2.29) gives for the residual resistivity of a fcc binary alloy

$$\rho = DCa_0^3 (\Delta Z)^2 n^{-2} m_A m_B \times \{G(k_0, q) + \sum_{\tau'} b(\tau) \bar{\alpha}_{\tau} F(k_0, q, \tau)\}, \quad (2.32)$$

where

$$D \equiv \mu^2 e^2 / 384 \pi^3 \epsilon_0^2 \hbar^3.$$

When the ions in the alloy are appreciably different in size, the change of the lattice parameter a_0 as a function of concentration is taken into account through the relation

$$a_0 = a_A m_A + a_B m_B, \quad (2.33)$$

where a_i is the lattice parameter of the i th component.

When the ions have different valences, the change in the effective number of conduction electrons as a function of concentration is taken into account through the relation

$$n = V_A m_A + V_B m_B, \quad (2.34)$$

where V_i is the valence of the i th component.

It should be noted that, in the random case, parabolic shaped curves are predicted by (2.32) if both a_0 and n (and, therefore, k_0) are independent of the concentration. In general, a_0 and n depend on the concentration and vary according to Eqs. (2.33) and (2.34), respectively. Consequently, the above theory does not predict perfectly parabolic curves even in the random case. The theory does, however, predict zero resistivity for concentrations of zero and unity.

3. GENERAL PROBLEMS OF APPLICATIONS AND THE NEARLY RANDOM CASE

The final equation (2.32) for the residual resistivity is expressed in terms of the Cowley order parameters, which must be supplied theoretically or experimentally before the theory can be compared with experiment. A quantum theory of the order parameters has been developed by Christy and Hall¹² for a theoretical model identical to that of this paper. With these two theories it is now possible to calculate a theoretical resistivity which can be compared directly with experiment. This program is in progress but the associated numerical calculations have not been completed. In the meantime, certain rough checks on the theory of this paper are being supplied in this section and Sec. 4.

It would be desirable to have measurements of both the residual resistivity and several order parameters on the same specimen for a range of concentrations. Such

¹² D. O. Christy and G. L. Hall (to be published).

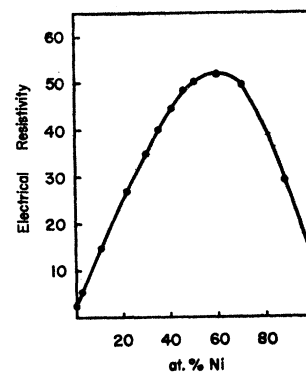


FIG. 1. Residual electrical resistivity (expressed in $\mu\Omega$ cm) as a function of concentration for copper-nickel alloys. The circles (\bullet) indicate experimental measurements (B. R. Coles, Ref. 16). The solid curve is simply a visual aid.

data has not been reported. A great deal of work has been reported on measurements of residual resistivity (usually at concentrations for which perfect superlattices can exist at sufficiently low temperatures), but the Cowley parameters have not been reported for the same specimens. Confronted with this situation, the authors have used the order parameters reported by Cowley¹³ as a function of quench temperature for single crystals of Cu_3Au to calculate a resistivity and compared this with the measurements of Damask¹⁴ on small (0.017-in.-diam) wires. It was found that the three significant figure accuracy to which Cowley's measurements were made produced only one significant figure in the calculated (change of) resistivity to be compared with that of Damask. The possibility of the propagation of round-off error raises doubts as to the significance of these calculations. Nevertheless, these questionable calculated values (for $q \doteq 2.5$) fall on a curve of roughly the same magnitude and slope as that of Damask.

With the preceding limitations in mind, the authors concentrate in this section on checking the power of the theory to explain nonparabolic curves of resistivity versus concentration for the nearly random case. The rough checks are to be considered only as illustrations of how the theory can be applied.

Figure 1 is typical of the experimental data found in the literature^{15,16} for resistivity curves for an alloy rapidly quenched from a temperature near the melting point. After the quenching procedure, the measurement of resistivity is frequently performed near room temperature where thermal resistivity is not negligible. In Fig. 1 it is seen that the resistivity is appreciable at concentrations of zero and unity. Furthermore, the thermal resistivity is not in general independent of the concentration,⁵ so some method of reducing the data is required. The assumption made here is that the thermal resistance varies linearly with concentration so that the residual resistivity reduces to zero at concentrations of zero and unity. The parameters of the potential and

¹³ J. M. Cowley, J. Appl. Phys. **21**, 24 (1950).

¹⁴ A. C. Damask, J. Phys. Chem. Solids **1**, 23 (1956).

¹⁵ V. Johansson and J. O. Linde, Ann. Physik **25**, 1 (1936).

¹⁶ B. R. Coles, Proc. Phys. Soc. (London) **B65**, 221 (1952).

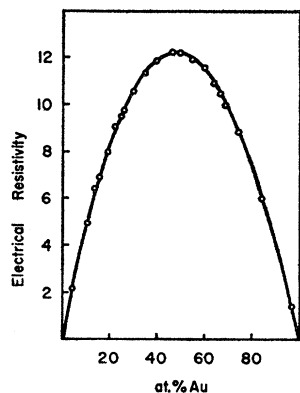


Fig. 2. Residual electrical resistivity (expressed in $\mu\Omega$ cm) for copper gold alloys. The circles (O) indicate reduced experimental values taken from measurements (Johansson and Linde, Ref. 15) made at 20°C for samples quenched from 650°C. The solid line gives the theoretical results. The values for the adjustable parameters used in the theory are $V_{Au}=1.075$, $V_{Cu}=0.925$, $q=2$ (in Hartree units), and $C=2.71 \times 10^{-3}$.

and the constant C are chosen to fit the theory to experiment by assuming that the rapidly quenched alloys are purely random. Figures 2 and 3 demonstrate the agreement between experiment and theory for the Cu-Au and the Cu-Ni systems, respectively. These two particular systems illustrate the necessity of accounting for types 1 and 2 (Sec. 1) changes of the Fermi volume as a function of concentration. Equations (2.33) and (2.34) are used for both systems. Although the assumptions of pure randomness and linear thermal resistivity may not be valid, it is nevertheless demonstrated that the theory is capable of explaining nonparabolic curves.

The adjustable constant C and the parameters of the potential thus determined for the purely random case were used to investigate the nonrandom (slowly annealed) case. Although it was quite easy to pick out the fits reported in Figs. 2 and 3 as the best for the range of potentials investigated, it must be admitted that good fits were obtained for values of q ranging from 1.0 to 10.0 in Hartree units with large associated variations in C . It was also possible to obtain good fits using a potential of the form

$$r^{-1}(\cos pr) \exp(-pr).$$

In view of the apparent arbitrariness in the choice of the potential parameters, it was desirable to have an independent test of the selections represented by Figs. 2 and 3. For the case depicted in Fig. 2, an inde-

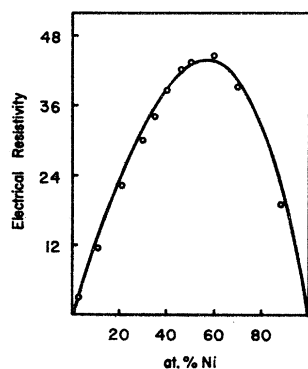


Fig. 3. Residual electrical resistivity (expressed in $\mu\Omega$ cm) for copper nickel alloys. The circles (O) indicate reduced experimental values (Coles, Ref. 14) taken from measurements at 100°C. The solid line gives the theoretical results. The values for the adjustable parameters used in theory are $V_{Ni}=0.54$, $V_{Cu}=1.00$, $q=2$ (in Hartree units), and $C=18.4$.

pendent test has been supplied by unpublished calculations of Christy¹⁷ on ordering energy. Christy has found several errors in Flinn's⁶ theory of ordering energy which worsen Flinn's reported agreement between experiment and theory by a factor of sixteen. When Christy uses the parameters of Fig. 2, good agreement between experiment and theory is regained for the Cu-Au system. Christy's work also confirms some of the work reported in the next section.

4. NONRANDOM CASE. LIMITED APPLICATION TO Cu-Au SYSTEM

Because of a lack of experimental measurements of the Cowley order parameters and theoretical knowledge of the interrelationships between them, exact comparison of the above theory to experimental data, such as curve B in Fig. 4, is not possible at the present time.

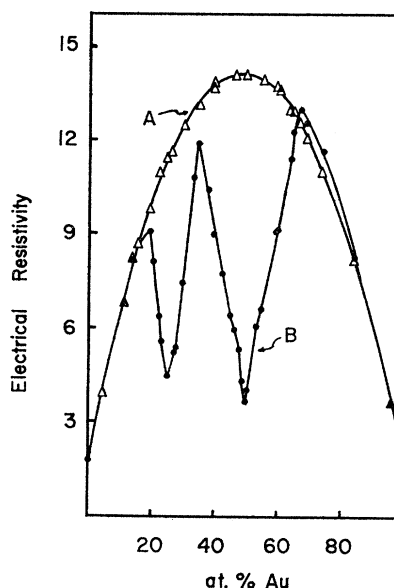


Fig. 4. Resistivity (expressed in $\mu\Omega$ cm) as a function of concentration for copper gold alloys; curve A, quenched from 650°C; curve B, annealed at 200°C (i.e., cooled from 400 to 200°C in 380 h, at 200°C 150 h). (Johansson and Linde, Ref. 15.)

But if the quickly quenched case (curve A in Fig. 4) is assumed to represent a purely random alloy and if the annealed case (curve B in Fig. 4) is assumed to represent a nonrandom alloy, then it is possible, by the following technique, to predict an "average" order parameter $\bar{\alpha}_1$ for first neighbors. The technique is as follows: (1) The experimental data is reduced as indicated in Sec. 3. (2) All $\bar{\alpha}_r$ for second- and higher order neighbors are assumed equal to zero. (3) The theoretical resistivity [Eq. (2.32)], now a function of $\bar{\alpha}_1$, is fitted to curve B wherever possible without $\bar{\alpha}_1$ exceeding its bounds (Sec. 2). In the remaining regions of curve B, $\bar{\alpha}_1$ is taken equal

¹⁷ D. O. Christy (unpublished).

to the appropriate bound and curve B is approximated as seen in Fig. 5. Figure 6 gives $\bar{\alpha}_1$ so calculated.

The portions of curve B not fitted by this first approximation possess a degree of order extending beyond first neighbors, but even these rough results suggest that, with a few more $\bar{\alpha}_r$, experiment and theory might agree except at concentrations very close to those for which perfect superlattices exist.

This method of predicting an $\bar{\alpha}_1$ is very rough, because it ignores any interrelationships existing between the $\bar{\alpha}_r$ and because the bounds on α_r , which are also bounds on $\bar{\alpha}_r$, yield little information about $\bar{\alpha}_r$. An illustration of the latter point is given by the ordered CuAu structure for which it is easy to show that $\bar{\alpha}_1$ equals $-\frac{1}{3}$ whereas the α_r for the various first neighbors are either +1 or -1.

The predicted $\bar{\alpha}_1$ of Fig. 6 has been examined by Christy to see if the first-neighbor contribution, using $\bar{\alpha}_1$, tends to increase the cohesive energy beyond that of a purely random alloy. This question is answered in the affirmative for all concentration less than 66% Au in Cu.

Clearly, more experimental measurements of order parameters and further knowledge of the interrelationships between the α_r are needed.

5. SUMMARY

A quantum theory of the residual electrical resistivity of binary disordered alloys is developed in terms of Cowley order parameters and for atomic potentials extending outside the unit cell. The theory is valid for any degree of order, excepting perfect superlattices. The purely random case possesses certain analogies with *normal processes* in thermal resistivity, and the nonrandom case with *umklapp processes*. Fermi volume changes with concentration are taken into account; indeed, this is the factor that gives the theory the flexibility to explain nonparabolic curves of resistivity versus concentration in the random case.

Most of the details of the calculations are presented for the particular case in which the two atomic potentials are of the Yukawa type. The parameters of the potentials and a certain adjustable constant are fixed by fitting the theory to the experimental data for quickly quenched alloys. In this case the alloys are assumed to be purely random, but the fitting procedure can be carried out just as well if the Cowley parameters are supplied (experimentally) as measures of the deviations from purely randomness. With the potentials determined, the data for slowly annealed (nonrandom) alloys is investigated. The lack of experimentally measured order parameters and the lack of theoretical knowledge of all interrelationships between the Cowley parameters at the present time limit this investigation, and hence prevent a very exacting test of the theory. Nevertheless, it is possible to produce a crude predicted value for the average of the Cowley parameters for the first neighbors. Both the choice of potential and the predicted order

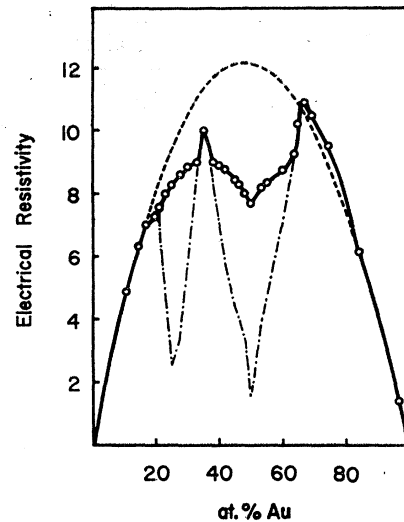


FIG. 5. Resistivity (expressed in $\mu\Omega$ cm) of copper-gold alloys; the dashed curve indicates the reduced experimental results for the purely random case; the dot-dashed curve indicates the reduced experimental results for the nonrandom case; and the solid curve indicates the theoretical results using only the first neighbor order parameter $\bar{\alpha}_1$. The circles (O) are the points at which calculations were made. The values used for the adjustable parameters are the same as those used for Fig. 2.

parameter meet checks supplied by independent unpublished calculations by Christy on ordering energy.

It would be very helpful at this stage to have more and better experimental data. Measurements of the Cowley parameters are needed for stoichiometric ratios for which perfect superlattices do not exist. Resistivity measurements at temperatures sufficiently low to eliminate thermal contributions are also essential.

With the unpublished theoretical developments of Christy and Hall¹² mentioned at the beginning of Sec. 3, it is now possible to predict order parameters for the theoretical model of this paper. This will permit the calculation of the residual resistivity which can be directly compared with experiment. Associated numerical work is in progress. In this connection it should be noted that some care has been taken in Appendix A and Sec. 2 to indicate limits of the defining summations for the Cowley parameters. The Cowley parameters introduced here are not identical to Mattuck's¹⁸ version.

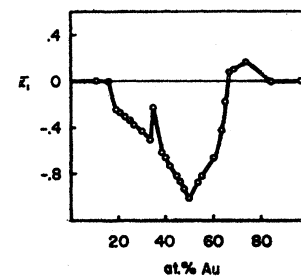


FIG. 6. Behavior of the theoretical $\bar{\alpha}_1$ as a function of concentration for copper-gold alloys. The circles (O) indicate the points at which calculations were made.

¹⁸ R. D. Mattuck, Phys. Rev. 127, 738 (1962).

The present theory is not valid for perfect superlattices and is not a very practical formulation for situations where only a few Cowley parameters differ from those for a perfect superlattice. In the latter case, it seems more reasonable to start with the Bloch functions for the perfect superlattice (rather than for U_1) and to treat the deviation from the superlattice as a perturbation. Such a formulation has been essentially completed. New order parameters enter but they are as susceptible to experimental measurement as are those of Cowley. It is perhaps from this approach that data such as that of Damask¹⁴ should be analyzed.

ACKNOWLEDGMENTS

The authors would like to express appreciation to D. O. Christy for supplying preprints of unpublished work.

APPENDIX A

A few properties of the matrix elements of U_2 defined in Sec. 2 by

$$M(\mathbf{k}, \mathbf{k}') \equiv \frac{1}{N\Omega} \int_{N\Omega} \psi_{\mathbf{k}'}^*(\mathbf{r}) U_2(\mathbf{r}) \psi_{\mathbf{k}}(\mathbf{r}) d^3r, \quad (\text{A1})$$

are presented in this section.

1. First-Order Perturbation Results

When \mathbf{k} equals \mathbf{k}' , Eq. (A1) reduces to

$$\begin{aligned} \int_{N\Omega} |u_{\mathbf{k}}(\mathbf{r})|^2 U_2(\mathbf{r}) d^3r \\ = \sum_{\tau} \int_{\tau \text{ cell}} |u_{\mathbf{k}}(\mathbf{r})|^2 U_2(\mathbf{r}) d^3r \\ = \int_{\Omega} |u_{\mathbf{k}}(\mathbf{r})|^2 \sum_{\tau} U_2(\mathbf{r} + \boldsymbol{\tau}) d^3r = 0, \quad (\text{A2}) \end{aligned}$$

because the sum is identically zero. This is shown as follows:

$$\begin{aligned} \sum_{\tau} U_2(\mathbf{r} + \boldsymbol{\tau}) &= \sum_{\tau} \sum_{\tau'} C_{\tau'} \Delta U(\mathbf{r} + \boldsymbol{\tau} - \boldsymbol{\tau}') \\ &= \sum_{\tau'} \Delta U(\mathbf{r} + \boldsymbol{\tau}') \sum_{\tau} C_{\tau - \tau'} = 0, \quad (\text{A3}) \end{aligned}$$

where use has been made of the relations,

$$\sum_{\tau} C_{\tau} = \sum_{\tau} C_{\tau - \tau'} = 0. \quad (\text{A4})$$

Thus the first-order perturbation results, which are of interest in ordering energy calculations, vanish,

2. The Cross-Correlation Function

Equation (A3) is useful in examining the cross correlation of U_1 and U_2 . It follows immediately that

$$\int_{N\Omega} U_1(\mathbf{x}) U_2(\mathbf{x} + \mathbf{r}) d^3x = \int_{\Omega} U_1(\mathbf{x}) \sum_{\tau}^N U_2(\mathbf{x} + \mathbf{r} + \boldsymbol{\tau}) d^3x,$$

which vanishes by virtue of (A3). If U_1 and U_2 are multiplied by a factor periodic with a period of the unit cell [say the factor $u_{\mathbf{k}}^*(\mathbf{r}) u_{\mathbf{k}}(\mathbf{r})$] the new cross correlation also vanishes.

3. The Matrix Element

The matrix element of U_2 defined by (A1) is easily simplified as follows:

$$\begin{aligned} M(\mathbf{k}, \mathbf{k}') &= (N\Omega)^{-1} \sum_{\tau} C_{\tau} \int_{N\Omega} \Delta U(\mathbf{r} - \boldsymbol{\tau}) \exp(i\Delta\mathbf{k} \cdot \mathbf{r}) d^3r \\ &= (N\Omega)^{-1} \sum_{\mathbf{n}} \sum_{\tau}^N C_{\tau + \mathbf{n}} \int_{N\Omega} \Delta U(\mathbf{r} - \mathbf{n} - \boldsymbol{\tau}) \\ &\quad \times \exp(i\Delta\mathbf{k} \cdot \mathbf{r}) d^3r, \end{aligned}$$

where \mathbf{n} is defined early in Sec. 2. Periodic boundary conditions,

$$C_{\tau + \mathbf{n}} = C_{\tau}, \quad \exp(i\Delta\mathbf{k} \cdot \mathbf{n}) = 1, \quad (\text{A5})$$

are now applied to yield

$$\begin{aligned} M(\mathbf{k}, \mathbf{k}') &= (N\Omega)^{-1} \sum_{\tau} C_{\tau} \sum_{\mathbf{n}} \int_{N\Omega} \Delta U(\mathbf{r} - \mathbf{n} - \boldsymbol{\tau}) \\ &\quad \times \exp[i\Delta\mathbf{k} \cdot (\mathbf{r} - \mathbf{n})] d^3r \\ &= (N\Omega)^{-1} \sum_{\tau} C_{\tau} \int_{-\infty}^{+\infty} \Delta U(\mathbf{r} - \boldsymbol{\tau}) \\ &\quad \times \exp(i\Delta\mathbf{k} \cdot \mathbf{r}) d^3r. \quad (\text{A6}) \end{aligned}$$

4. Derivation of Eq. (2.7)

The modulus squared of the matrix element is given by

$$\begin{aligned} |M(\mathbf{k}, \mathbf{k}')|^2 &= (N\Omega)^{-2} \sum_{\tau'} \sum_{\tau''} C_{\tau'} C_{\tau''} \int_{N\Omega} \int_{N\Omega} \Delta U(\mathbf{z} - \boldsymbol{\tau}') \Delta U(\mathbf{r}' - \boldsymbol{\tau}'') \\ &\quad \times \exp[i\Delta\mathbf{k} \cdot (\mathbf{r}' - \mathbf{z})] d^3r' d^3z \\ &= (N\Omega)^{-2} \sum_{\tau} \sum_{\tau'} C_{\tau} C_{\tau + \tau'} \\ &\quad \times \int_{N\Omega} \int_{N\Omega} \Delta U(\mathbf{z} - \boldsymbol{\tau}') \Delta U(\mathbf{r} - \boldsymbol{\tau}' - \boldsymbol{\tau}) \\ &\quad \times \exp[i\Delta\mathbf{k} \cdot (\mathbf{r}' - \mathbf{z})] d^3r' d^3z \end{aligned}$$

$$\begin{aligned}
 &= (N\Omega)^{-2} \sum_{\tau} \sum_{\tau'}^N C_{\tau} C_{\tau+\tau'} \\
 &\quad \times \sum_n \sum_{n'}^{\infty} \int_{N\Omega-z-n}^{\infty} \exp(i\Delta\mathbf{k}\cdot\mathbf{r}) d^3r \\
 &\quad \times \int_{N\Omega-\tau'-n'}^{\infty} \Delta U(\mathbf{z}) \Delta U(\mathbf{r}+\mathbf{z}-\boldsymbol{\tau}) d^3z \\
 &= \frac{Nm_{AM_B}}{(N\Omega)^2} \sum_{\tau}^N \alpha_{\tau} \\
 &\quad \times \int_{-\infty}^{+\infty} \exp(i\Delta\mathbf{k}\cdot\mathbf{r}) d^3r \int_{-\infty}^{+\infty} \Delta U(\mathbf{z}) \Delta U(\mathbf{r}+\mathbf{z}) d^3z \quad (\text{A7}) \\
 &= \frac{Nm_{AM_B}}{(N\Omega)^2} \sum_{\tau}^N \alpha_{\tau} \left| \int_{-\infty}^{+\infty} \Delta U(\mathbf{r}) \exp(i\Delta\mathbf{k}\cdot\mathbf{r}) d^3r \right|^2, \quad (\text{A8})
 \end{aligned}$$

where the Cowley order parameter α_{τ} is defined by

$$\alpha_{\tau} \equiv \sum_{\tau'}^N C_{\tau'} C_{\tau+\tau'} / Nm_{AM_B}. \quad (\text{A9})$$

Use of the definition given by (2.9) leads to Eq. (2.7).

APPENDIX B

1. Integration of Eq. (2.16) for the Yukawa Potential

Substitution of (2.24) and (2.11) into (2.16) yields

$$\frac{1}{T} = \frac{4\mu Q^2 C m_{AM_B}}{\hbar^3 k_0 \Omega} \int (q^2 + \Delta k^2)^{-2} \left[1 - \frac{\mathbf{k}' \cdot \hat{\mathbf{z}}}{\mathbf{k} \cdot \hat{\mathbf{z}}} \right] dS', \quad (\text{B1})$$

where

$$|\mathbf{k}| = |\mathbf{k}'| = k_0.$$

From Fig. 7, which is a spherical triangle determined by \mathbf{k} , \mathbf{k}' , and $\hat{\mathbf{z}}$, it is seen that

$$\begin{aligned}
 \Delta k^2 &= |\mathbf{k} - \mathbf{k}'|^2 = 2k_0^2(1 - \cos\theta), \\
 \mathbf{k} \cdot \hat{\mathbf{z}} &= k_0 \cos\alpha, \\
 \mathbf{k}' \cdot \hat{\mathbf{z}} &= k_0 \cos\beta, \\
 dS' &= k_0^2 \sin\theta d\theta d\phi.
 \end{aligned}$$

FIG. 7. Spherical triangle on the surface of a unit sphere showing the relative directions between the unit vectors $\hat{\mathbf{k}}$, $\hat{\mathbf{k}'}$, and $\hat{\mathbf{z}}$.

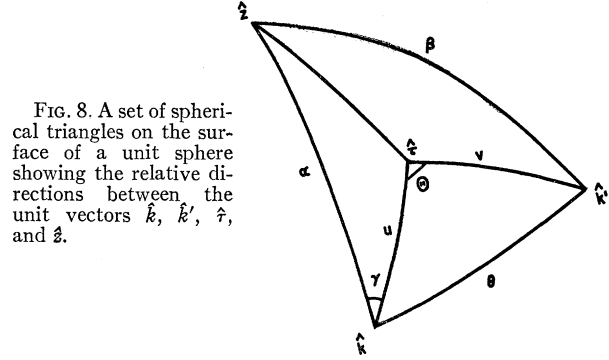
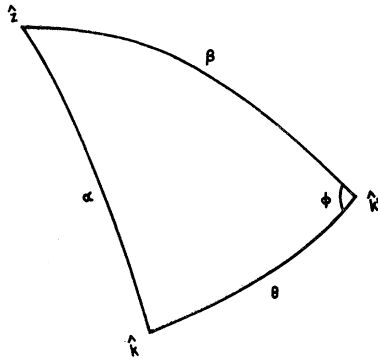


FIG. 8. A set of spherical triangles on the surface of a unit sphere showing the relative directions between the unit vectors $\hat{\mathbf{k}}$, $\hat{\mathbf{k}'}$, $\hat{\boldsymbol{\tau}}$, and $\hat{\mathbf{z}}$.

Therefore, (B1) may be written

$$\frac{1}{T} = \frac{\mu Q^2 C m_{AM_B}}{\hbar^3 k_0^3 \Omega} \int_0^{\pi} \sin\theta d\theta \times \int_0^{2\pi} \frac{(1 - \cos\theta - \tan\alpha \sin\theta \cos\phi)}{[1 - \cos\theta + q^2(2k_0^2)^{-1}]^2} d\phi, \quad (\text{B2})$$

where

$$\cos\beta / \cos\alpha = \cos\theta + \tan\alpha \sin\theta \cos\phi.$$

Integration of (B2) yields (2.25).

2. Integration of Eq. (2.20) for the Yukawa Potential

Consider the evaluation of

$$\langle J(\mathbf{k}, \mathbf{k}', \boldsymbol{\tau}) \rangle_{\text{av}} \equiv (4\pi k_0^2)^{-1} \int J(\mathbf{k}, \mathbf{k}', \boldsymbol{\tau}) dS. \quad (\text{B3})$$

Substitution of (2.24) and (2.11) into (B3) yield

$$\langle J(\mathbf{k}, \mathbf{k}', \boldsymbol{\tau}) \rangle_{\text{av}} = [\pi Q^2 C m_{AM_B} \exp(-i\mathbf{k}' \cdot \boldsymbol{\tau}) K] / N\Omega^2 k_0^4, \quad (\text{B4})$$

where

$$\begin{aligned}
 K &\equiv k_0^{-2} \int \exp(i\mathbf{k} \cdot \boldsymbol{\tau}) (A - \hat{\mathbf{k}} \cdot \hat{\mathbf{k}'})^{-2} dS, \\
 A &\equiv 1 + \frac{q^2}{2k_0^2}.
 \end{aligned} \quad (\text{B5})$$

From Fig. 8, which is a set of spherical triangles determined by \mathbf{k} , \mathbf{k}' , $\boldsymbol{\tau}$, and $\hat{\mathbf{z}}$, it is seen that

$$\begin{aligned}
 \mathbf{k} \cdot \boldsymbol{\tau} &= B \cos u, \\
 \mathbf{k}' \cdot \boldsymbol{\tau} &= B \cos v, \\
 \hat{\mathbf{k}} \cdot \hat{\mathbf{k}'} &= \cos\theta = \cos u \cos v + \sin u \sin v \cos\Theta,
 \end{aligned}$$

where B equals $k_0\tau$ and where Θ is the angle between the plane formed by $\boldsymbol{\tau}$ and \mathbf{k} and the plane formed by $\boldsymbol{\tau}$ and \mathbf{k}' . It follows that

$$dS = k_0^2 \sin u du d\Theta.$$

With the change of variable

$$x = \cos v,$$

(B5) may be written in the form

$$K = \int_{-1}^{+1} \exp(iBx) dx \times \int_0^{2\pi} [A - x \cos v - (1-x^2)^{1/2} \sin v \cos \Theta]^2 d\Theta. \quad (B6)$$

The Θ integration can be evaluated by making the change of variable

$$z = \exp i\Theta,$$

and using residue theory, hence it follows that

$$K = \frac{2\pi A}{(A^2-1)^{3/2}} \times \int_{-1}^{+1} [1 + (A^2-1)^{-1}(x^2 - 2Ax \cos v + \cos^2 v)]^{-3/2} \times \left[1 - \frac{\cos v}{A} x\right] \exp(iBx) dx. \quad (B7)$$

For the values of A (i.e., q and k_0) of interest in this paper

$$A^2 - 1 \gg 1,$$

therefore, the terms

$$x^2/(A^2-1) \quad \text{and} \quad \cos^2 v/(A^2-1)$$

are neglected, and the denominator in (B7) is expanded. Neglecting all but the first two terms of this expansion, one can write (B5) as follows:

$$K = 2\pi A(A^2-1)^{-3/2} \left\{ \int_{-1}^{+1} \exp(iBx) dx + (2A^2+1)(A^3-A)^{-1} \cos v \int_{-1}^{+1} x \exp(iBx) dx - 3(A^2-1)^{-1} \cos v \int_{-1}^{+1} x^2 \exp(iBx) dx \right\}. \quad (B8)$$

Integration yields

$$K = 4\pi A(A^2-1)^{-3/2} (L_1 + iL_2 \cos v + L_3 \cos^2 v), \quad (B9)$$

where

$$\begin{aligned} L_1 &= B^{-1} \sin B, \\ L_2 &= (2A^2+1)(A^3-A)B^{-2}(\sin B - B \cos B), \\ L_3 &= -3(A^2-1)^{-1} [B^{-1} \sin B + 2B^{-3}(B \cos B - \sin B)]. \end{aligned}$$

Substitution of (B9) into (B4) gives $\langle J(\mathbf{k}, \mathbf{k}', \boldsymbol{\tau}) \rangle_{av}$.

Equation (2.20) can now be written as

$$I(\boldsymbol{\tau}) = \frac{4\pi^2 Q^2 C m_A m_B A}{N \Omega^2 k_0^4 (A^2-1)^{3/2}} [I_1(\boldsymbol{\tau}) - I_2(\boldsymbol{\tau})], \quad (B10)$$

where

$$I_1(\boldsymbol{\tau}) = \text{Re} \left\{ \int [L_1 + iL_2 \cos v + L_3 \cos^2 v] \times \exp(-iB \cos v) dS' \right\}, \quad (B11)$$

$$I_2(\boldsymbol{\tau}) = \text{Re} \left\{ \int [L_1 + iL_2 \cos v + L_3 \cos^2 v] \left[\frac{\cos \beta}{\cos \alpha} \right] \times \exp(-iB \cos v) dS' \right\}, \quad (B12)$$

$$dS' = k_0^2 \sin v dv d\Theta.$$

The evaluation of (B11) is straightforward; the result is

$$I_1(\boldsymbol{\tau}) = 4\pi k_0^2 \{ L_1^2 + L_2 B^{-2} (\sin B - B \cos B) + L_3 [B^{-1} \sin B + 2B^{-3} (B \cos B - \sin B)] \}. \quad (B13)$$

In order to evaluate (B12), the ratio of the $\cos \beta$ to the $\cos \alpha$ must be expressed in terms of v and Θ . By use of identities from spherical trigonometry it is found that

$$\begin{aligned} \cos \beta / \cos \alpha &= \cos u \cos v + \sin u \sin v \cos \Theta - \tan \alpha \sin \gamma \sin v \sin \Theta \\ &\quad + \tan \alpha \cos \gamma (\sin u \cos v - \sin v \cos \Theta). \end{aligned} \quad (B14)$$

Substitution of (B14) into (B12) and evaluation of the Θ integration yields

$$I_2(\boldsymbol{\tau}) = 2\pi k_0^2 f \text{Re} \left\{ \int_{-1}^{+1} (L_1 x + iL_2 x^2 + L_3 x^3) \times \exp(-iBx) dx \right\}, \quad (B15)$$

where

$$f \equiv \cos u + \tan \alpha \cos \gamma \sin u.$$

Integration of (B15) yields

$$I_2(\boldsymbol{\tau}) = 0. \quad (B16)$$

Substitution of (B16) and (B13) into (B10) gives the value of (2.20) for the Yukawa potential.

Note added in proof. It has been stated by some that, in comparing experiment and theory, the present authors should have selected "better" low-temperature data which contains little thermal resistivity. A number

of works have been cited as qualifying in this respect. It would require a lengthy discussion to explain why each of the suggested works on the Cu-Au system has been rejected, but one example may help. The suggested data of Pasaglia and Love [Phys. Rev. **98**, 1006 (1955)] for the rapidly quenched Cu-Au system appears to exhibit a nonrandom character for 50–50 concentrations. Further, they do not report measurements on the pure metals for their sample sizes and histories.

More complicated systems pose a problem of the determination of the effective number of conduction electrons as a function of concentration. Nevertheless, with A. H. Wilson's suggestion of 0.3–0.6 for the effective valence of Pd and with the use of Eq. (2.34), it is possible to obtain a good theoretical fit to the low-temperature data of Schindler, Smith, and Salkovitz [J. Phys. Chem. Solids **1**, 39 (1956)] for the Ni-Pd system. The values of the other parameters required are: $V_{Ni}=2.0$, $q=1.5-2.0$, $C=1.83 \times 10^{-2}$, and $\Delta Z=18$.

PHYSICAL REVIEW

VOLUME 132, NUMBER 3

1 NOVEMBER 1963

Magnetic Susceptibility of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ at Low Temperature*

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 (Received 24 June 1963)

The magnetic susceptibility of cupric nitrate "trihydrate" $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ has been measured on the powder and on single crystals in the 14–20 and 0.4–4.2°K ranges of temperature. The susceptibility of the powder has a rounded maximum at 3.2°K, where it is equal to 0.065 cgs/mole, and drops very rapidly towards zero below this temperature. This behavior differs from that of a typical antiferromagnet. The experimental data have been compared with existing theoretical calculations for antiferromagnetic linear chains or binary clusters. In the single crystal, the susceptibility measured in a direction parallel to the monoclinic axis is always larger by 20% than the susceptibility in the perpendicular directions. This is probably due to a uniaxial anisotropy of the g factor.

INTRODUCTION

THE study of the cupric salts provides one of the most convenient experimental tests for the theories of interacting paramagnetic ions. The Cu^{++} ion has a spin $S=\frac{1}{2}$, value for which the largest amount of theoretical work has been done. Moreover, the relatively small value of the magnetocrystalline anisotropy simplifies comparisons between experiments and theory.

Very little is known about the magnetic properties of cupric nitrate trihydrate, which is one of the most common cupric salts. The magnetic susceptibility has been measured¹ only above 78°K. The paramagnetic resonance has been observed at room temperature on the powder.²

We have measured the susceptibility of this salt in both powder and single crystal forms, in the liquid helium and in the liquid-hydrogen ranges of temperature. The measurements on the powder have been extended down to 0.4°K, using a He_3 cryostat.

DESCRIPTION OF THE SAMPLES

The salt obtained above 26°C by cooling a saturated solution of cupric nitrate in water is usually referred to

as the trihydrate³ $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$. According to Schreinemakers, Berkhoff, and Posthumus,⁴ and also to Wilcox and Bailey,⁵ this salt is rather $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$. In a short note⁶ on the x-ray determination of the structure, Dornberger-Schiff and Leciejewicz give a projection of the electron density on a plane perpendicular to the monoclinic axis, from which one may infer that the formula is $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$.

The material used in the present investigations was obtained from the J. T. Baker Chemical Company, in the "Baker Analyzed Reagent" grade. All samples were recrystallized, by cooling a saturated solution down to 40 or 30°C, in order to insure the proper degree of hydration. Solutions of cupric nitrate should not be heated to more than 70°C, as a white powder precipitates slowly above this temperature. Care should also be exercised to prevent organic materials from coming into contact with this strongly oxidizing salt. Sheets of filter paper catch fire spontaneously when soaked with

³ J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry* (Longmans Green and Company, Ltd., London, 1923), Vol. 3, p. 280.

⁴ F. A. H. Schreinemakers, G. Berkhoff, and K. Posthumus, *Rec. Trav. Chim.* **43**, 508 (1924).

⁵ K. W. Wilcox and C. R. Bailey, *J. Chem. Soc. (London)* **150** (1927).

⁶ K. Dornberger-Schiff and J. Leciejewicz, *Acta Cryst.* **11**, 825 (1958). According to a private communication from these authors, the formula $\text{Cu}(\text{NO}_3)_2 \cdot 1.5\text{H}_2\text{O}$ given in their note should read $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$.

* Work supported in part by the Office of Naval Research, and the National Science Foundation.

¹ P. Escoffier and J. Gauthier, *Compt. Rend.* **252**, 271 (1961).

² Z. Miduno, O. Matumura, K. Hukuda, K. Horai, *Mem. Fac. Sci., Kyusyu Univ. Ser. B* **2**, 13 (1956).