pair and single-site effects. In general, if we wish to go to the nth cluster approximation we must simultaneously satisfy all CPA (m), $m \leq n$, conditions.

Finally, we have shown that this method can be easily extended to evaluate average two-particle Green's functions.

Note added in proof. The recent work of Cyrot-Lackmann and Ducastelle [Phys. Rev. Letters 27, 429 (1971)] is different from the diagrammatic expansion given above. In particular, a perturbation expansion of their equation (26) shows that beginning at order v^6 and c^3, their self-energy contains terms which correspond to *removing* pair renormalizations of the internal lines in $\Sigma^{(1)}$. The net result is that the $\langle \underline{G}_{ii} \rangle$ which appears in $\Sigma_{ii}^{(1)}$ is not the fully renormalized $\langle \underline{G} \rangle$ given by the solution of the Dyson equation (i.e., Eq. 6$'$ with Σ containing *both* single site and pair terms). There are other differences beginning at order v^8 and c^4 which do not appear to have any such simple explanation. A detailed comparison of the two methods has been made by Ducastelle. We wish to express our gratitude to Dr. Ducastelle for communicating these results to us prior to their publication.

ACKNOWLEDGMENTS

The authors would like to thank R. J. Elliott and P. L. Leath for valuable discussions and comments on this work.

---

*Work supported mainly by the U.S. Atomic Energy Commission through Contract AT(30-1)-3699, Technical Report No. NYO-3699-60.

[1] P. Lloyd, J. Phys. C 2, 1717 (1969).

[2] F. Yonezawa and T. Matsubara, Progr. Theoret. Phys. (Kyoto) 35, 357 (1966); 35, 759 (1966).

[3] F. Yonezawa, Progr. Theoret. Phys. (Kyoto) 40, 734 (1968).

[4] P. L. Leath, Phys. Rev. 171, 725 (1968).

[5] P. L. Leath and B. Goodman, Phys. Rev. 175, 963 (1968).

[6] P. Soven, Phys. Rev. 156, 809 (1967).

[7] D. W. Taylor, Phys. Rev. 156, 1017 (1967).

[8] Y. Onondera and Y. Toyozawa, J. Phys. Soc. Japan 24, 1341 (1968).

[9] F. Yonezawa and S. Homma, J. Phys. Soc. Japan Suppl. 26, 68 (1969).

[10] R. N. Aiyer, R. J. Elliott, J. A. Krumhansl, and P. L. Leath, Phys. Rev. 181, 1006 (1969).

[11] K. F. Freed and M. H. Cohen Phys. Rev. B 3, 3400 (1971).

[12] S. Takeno (unpublished).

[13] V. Capek, Phys. Status Solidi 43, 61 (1971).

[14] Γ only appears here as an intermediate step in the algebraic derivation; we have not attempted to interpret it "physically" to obtain an alternative derivation. See in this context the discussion given in Sec. V of Ref. 10.

[15] Note the different signs in Eqs. (23) and (15a). Also the self-energy in (23) is $\underline{\Sigma} \equiv \underline{\Sigma}\{\langle \underline{G} \rangle\}$; (15) involves $\underline{\Sigma}\{\underline{\Gamma}\}$.

[16] B. Velický, Phys. Rev. 184, 614 (1969).

PHYSICAL REVIEW B VOLUME 4, NUMBER 12 15 DECEMBER 1971

Electronic States in a Disordered Binary Alloy

M. P. Das and S. K. Joshi
Department of Physics, University of Roorkee, Roorkee, India

(Received 2 June 1971)

The electronic structure of a disordered binary alloy is discussed by using the method of Matsubara and Yonezawa. The self-energy is evaluated in a first-order approximation. The theory is applied to a model alloy where the host is assumed to possess a semicircular density of states. We also calculate the density of states for α-brass, by using the available density-of-states curve for copper.

I. INTRODUCTION

The behavior of electrons in disordered materials raises very complex problems, and recently this has been the subject of intensive investigations from many points of view. There have been several attempts to formulate a theory for alloys across the whole range of concentrations of solute atoms. Initially a number of simple but crude models were proposed.[1-3] The rigid-band approximation[1] is the earliest model and is based on a perturbative approach. In this approximation it is assumed that the constant energy surfaces and the density-of-states curve of the solvent remain unchanged on alloying, the only effect of the addition of solute atoms being, if its valency is greater than that of the solvent, to add electrons to the band, thus swelling the Fermi surface and filling the density-of-states curve to a higher energy.[2] Sometimes the virtual crystal approximation (VCA)[3] is used to interpret experimental results. In the VCA one approximates a disordered alloy by an equivalent ordered alloy wherein every site is assigned a potential equal to the concentration-weighted average of the potentials of the constituents. The VCA is also a perturbative approach, and this approximation has been extended to fourth order in perturbation,[4] resulting in a tailing of the density-of-states curve into the forbidden band. Stern[5] has used a tight-binding approach. However, the rigid-band approximation, the VCA, and the tight-binding method admit an energy–wave-vector dispersion relation for a disordered alloy and provide us with an oversimplified picture of such systems. The experimental study of electronic states in alloys is in an active stage of development.[6] Some of the methods used are the optical, photoemission, soft-x-ray, specific-heat, and positron-annihilation methods. These measurements have stimulated further efforts towards formulations of a reasonable theory.

Beeby and Edwards[7] used a multiple-scattering formulation in which the motion of electrons in a disordered system is viewed as a succession of collisions with the individual scattering centers. Such an approach had earlier been proposed as a possibility by Korringa.[8] The multiple-scattering theory has been applied to study the electronic states in dilute alloys by Jones[9] and by Dawber and Turner.[10] However, these theories based on perturbation expansions are not adequate for nondilute alloys, in which the constituents of the alloy are to be treated on an equal footing. Beeby[11] proposed the "averaged-T-matrix approximation," which is applicable to nondilute alloys too. But the unsatisfactory feature of this theory is that it leads to a spurious band gap in the density-of-states curve.[12,13] Among the existing approaches the coherent-potential approximation (CPA)[14] is the best approximation. The CPA entails an energy-dependent complex potential. The self-consistency condition requires that on the average there is no further scattering of electrons from the potential. The CPA is a single-site approximation which neglects all statistical correlations between the various lattice sites, such as the short-range ordering (cluster effect), and overlooks the multiple-scattering effects. The CPA has been applied to the case of binary alloys[15] and has yielded a wealth of information about the density of states. The CPA and some equivalent models have also been applied by Soven[16] to electrons, by Taylor and others[17] to phonons, by Roth[18] to magnons, and by Onedora and Toyozawa[19] to Frenkel excitons. More recently Freed and Cohen[20] have improved the single-site CPA to incorporate the cluster effects. They consider the response of an electron to a cluster of n atoms of definite composition and positions and treat the rest of the material in an averaged way.

Matsubara and Toyozawa[21] (MT) have adopted a Green's-function approach to study the electronic states in disordered semiconductors. Later, Matsubara and Koneyoshi[22] reformulated the MT theory to include the effects of the clustering of impurities and the fluctuations of charges. Many of the above-mentioned studies[15–18] employ an expansion of the electron propagator for an alloy in a basis of Bloch functions, while the MT theory is based on an expansion in terms of the Wannier functions. Leath[23] and Matsubara[24] have shown that these two approaches are equivalent. Matsubara and Yonezawa[25] have developed in a systematic manner the Green's-function method[26] with Bloch functions of the perfect crystal as a basis of expansion combined with a perturbative approach. The method shows promise of yielding results which are much closer to reality than those derived by other methods mentioned above. As far as we know, this method of Matsubara and Yonezawa (MY) has not been exploited to examine the electronic states in a real three-dimensional disordered system. In this paper we apply the MY theory[27] to a topologically disordered binary alloy.

Very recently a good deal of information has become available on the localization of electronic states in disordered systems. Many people[28–33] have addressed themselves to a study of this important and challenging problem.

We describe in Sec. II the method of expansion of the Green's function relevant to a topologically disordered lattice. In Sec. III we configurationally average the Green's function. The self-energy is expanded in terms of semi-invariants and an approximate solution of the averaged Green's function is obtained. The problem of the localization of electronic states is discussed briefly in Sec. IV. We paraphrase the arguments of Cohen and coworkers[31] to obtain a criterion to demarcate the localized and extended states in the density-of-states curve. Section V is devoted to a discussion of the results of our numerical calculations (i) for the density of states of a model alloy when the solvent (host) possesses a semicircular density of states and (ii) for the density of states of a real disordered alloy–α-brass. Some concluding remarks follow in Sec. VI.

II. FORMALISM

We consider a completely disordered substitutional binary alloy of A-B type, where A represents the solute atoms and B the solvent atoms. c is the fractional concentration of the solute (A-type) atoms. If we associate a single atomiclike orbital with each site, we can write the Hamiltonian of the system as

$$H=\sum_{n} \epsilon_B^{(n)} a_n^\dagger a_n + \sum_{m\neq n} T_{mn} a_m^\dagger a_n + \sum_{l} (\epsilon_A^{(l)} - \epsilon_B^{(l)}) a_l^\dagger a_l \ . \tag{1}$$

Here ϵ_A and ϵ_B are the energies of the atomic levels of the A and B atoms, respectively, $a_n^\dagger$ (a_n) is the creation (destruction) operator for an electron in an atomic state at the lattice site n, l refers to the solute atom sites specified by $\vec{R}_l$, and T_{mn} is the tight-binding (hopping) integral. We shall assume that the hopping integral T_{mn} depends only on the relative positions of the lattice points m and n, and does not depend on the type of atoms occupying these sites. Under this assumption T_{mn} remains unchanged when the concentration of the solute atoms changes. The effects of alloying, like the changes in the lattice parameters, are ignored. If H_0 is the Hamiltonian for the pure host, we may regard the change H_1 in this Hamiltonian upon alloying as a perturbation. Obviously

$$H_1 = \sum_l [V_A(\vec{r} - \vec{R}_l) - V_B(\vec{r} - \vec{R}_l)] \equiv \sum_l W(\vec{r} - \vec{R}_l) , \tag{2}$$

where V_A and V_B are the static and superposable potentials of A- and B-type atoms, respectively. The l summation in (2) is over the solute atom sites only. For the pure host the Schrödinger equation reads

$$H_0 \phi_{bk}(\vec{r}) = \epsilon_{bk} \phi_{bk}(\vec{r}) , \tag{3}$$

where the Bloch functions

$$\phi_{bk}(\vec{r}) = u_{bk}(\vec{r})\, e^{-i\vec{k}\cdot\vec{r}}$$

are normalized to the volume of the crystal by

$$\int \phi_{bk}^*(\vec{r})\, \phi_{b'k'}(\vec{r})\, d\vec{r} = \delta_{bb'}\, \delta(\vec{k} - \vec{k}') \tag{4}$$

and ϵ_{bk} is the energy of the state $\vec{k}$ in the bth band. For the disordered alloy we have to solve the Schrödinger equation

$$(E - H)\psi(\vec{r}) = 0 . \tag{5}$$

We shall see later that the exact solution of this equation seems to be beyond our capabilities at this time. In the absence of the periodicity in the lattice in an alloy the Bloch states are no longer eigenstates. We expand $\psi(\vec{r})$ in terms of the orthogonal basis functions $\phi_{bk}(\vec{r})$,

$$\psi(\vec{r}) = \sum_{bk} B_{bk} \phi_{bk}(\vec{r}) ,$$

with B_{bk} as expansion coefficients. This gives

$$(E - \epsilon_{bk})\, B_{bk} = \sum_{b'k'} \langle bk | H_1 | b'k' \rangle B_{b'k'} , \tag{6}$$

where

$$\langle bk | H_1 | b'k' \rangle = \sum_l \int \phi_{bk}^*(\vec{r}) W(\vec{r} - \vec{R}_l) \phi_{br}(\vec{r})\, d\vec{r} . \tag{7}$$

On simplification we find

$$\langle bk | H_1 | bk \rangle = \rho(\vec{k} - \vec{k}')\, W_{kk'}^{bb'} , \tag{8}$$

where

$$\rho(\vec{k} - \vec{k}') = \sum_l e^{-i(\vec{k} - \vec{k}')\cdot\vec{R}_l} ,$$
$$W_{kk'}^{bb'} = \int u_{bk}^*(\vec{r})\, W(\vec{r})\, u_{b'k'}(\vec{r})\, e^{-i(\vec{k} - \vec{k}')\cdot\vec{r}}\, d\vec{r} . \tag{9}$$

The physical quantity we are interested in is the density-of-states function for the alloy. As we shall see, the density-of-states function can be obtained from the Green's function. The electron Green's function for the alloy is defined as

$$(G(E))_{kk'}^{bb'} = \langle 0 | a_{bk} \frac{1}{E - H} a_{b'k'}^\dagger | 0 \rangle , \tag{10}$$

where $|0\rangle$ represents the vacuum state. The Green's function for the host crystal is

$$(G_0(E))_{kk'}^{bb'} = \frac{1}{E - \epsilon_{bk}} \delta_{bb'}\, \delta(\vec{k} - \vec{k}') \equiv G_0^b(E, \vec{k}) . \tag{11}$$

This is diagonal in the representation used. We shall always use the notation of Eq. (11) for representing a diagonal Green's function so that $G_0^b(E, \vec{k})$ will imply

$$\delta_{bb'}\, \delta(\vec{k} - \vec{k}')/(E - \epsilon_{bk}) .$$

Equation (10) may be rewritten as

$$(G(E)^{-1})_{kk'}^{bb'} = [(E - \epsilon_{bk})\delta_{bb'} (\vec{k} - \vec{k}') - (H_1)_{kk'}^{bb'}] , \tag{12}$$

where

$$(H_1)_{kk'}^{bb'} = \langle bk | H_1 | b'k' \rangle .$$

The Green's function can, therefore, be written as a perturbation expansion in terms of $(H_1)_{kk'}^{bb'}$:

$$\begin{aligned}(G(E))_{kk'}^{bb'} &= G_0^b(E, \vec{k}) + G_0^b(E, \vec{k})\, (H_1)_{kk'}^{bb'}\, G_0^{b'}(E, \vec{k}') + G_0^b(E, \vec{k}) \sum_{b_1 k_1} (H_1)_{kk_1}^{bb_1}\, G_0^{b_1}(E, \vec{k}_1) (H_1)_{k_1 k'}^{b_1 b'}\, G_0^{b'}(E, \vec{k}') + \cdots \\ &= G_0^b(E, \vec{k}) + \sum_{i=1}^{\infty} G_0^b(E, \vec{k}) \prod_{j=1}^{i} \left(\sum_{b_j k_j} (H_1)_{k_{j-1} k_j}^{b_{j-1} b_j}\, G_0^{b_j}(E, \vec{k}_j) \right) ,\end{aligned} \tag{13}$$

where

$b_{j-1} = b$, $\vec{k}_{j-1} = \vec{k}$ for $j = 1$,

$b_j = b'$, $\vec{k}_j = \vec{k}'$ for $j = i$.

Equation (13) is exact, but is too complicated to be of use in any analysis. One resorts to some suitable approximation to obtain a more manageable expression for the Green's function. If we glance at Eq. (8) for $(H_1)^{bb'}_{kk'}$ we find that Eq. (13) inherits a summation over all solute atom sites l for each H_1. This was (and still is) a great stumbling block in the progress of the theory because the only series that can be exactly summed has unrestricted summations. The restrictions that the summations are over the solute atom sites were removed by Yonezawa[27] by resorting to configurational averaging of (13), which we discuss in Sec. III.

III. APPROXIMATE SOLUTION OF DYSON EQUATIONS

The electronic properties of a disordered material, which are associated with the entire crystal, e.g., the density of states, contain within them a sampling of all the configurations in the system. In calculating such properties it is advisable to carry out averages over an ensemble of systems having all possible configurations. We have considered a completely disordered system; i.e., there is no correlation among the different solute atoms. For a random distribution every possible configuration occurs with equal weight in a configurational average. The perturbation term in the Hamiltonian is a random function and every site should contribute to it with equal probability. If we have an arbitrary random function $f(\ldots, R_{l_i} \ldots)$, where i denotes s variables of the function, the configurational averaging is effected by using a simple relation,[27]

$$\Big\langle \sum_{\{l_1, l_2, \ldots, l_s\}}{}' f(\vec{\mathrm{R}}_{l_1}, \vec{\mathrm{R}}_{l_2}, \ldots, \vec{\mathrm{R}}_{l_s}) \Big\rangle = c^s \sum_{\{n_1, n_2, \ldots, n_s\}}{}' f(\vec{\mathrm{R}}_{n_1}, \vec{\mathrm{R}}_{n_2}, \ldots, \vec{\mathrm{R}}_{n_s}) \;. \tag{14}$$

Here the summation of the left-hand side is over all the solute atom sites, while the summation on the right is over all the lattice sites. $\langle \cdots \rangle$ denotes the average over all possible configurations of solute atoms. A prime on the summation indicates that the summations are not completely unrestricted here, because all the terms where one or more summation indices repeat are excluded. This is known as the exclusion effect. Langer[34] was the first to point out that the exclusion effect must be considered in order for a formulation to be valid for a wide range of solute concentration. Yonezawa[27] has suggested a general scheme which enables us to incorporate the exclusion effect while performing the configurational averages. We use Eq. (8) in Eq. (13) and perform the configurational averaging according to the prescription (14); we get

$$\langle (G(E))^{bb'}_{kk'} \rangle = G^b_0(E, \vec{\mathrm{k}}) + G^b_0(E, \vec{\mathrm{k}}) \langle \rho_i(\vec{\mathrm{k}} - \vec{\mathrm{k}}') \rangle W^{bb'}_{kk'} G^{b'}_0(E, \vec{\mathrm{k}}') + G^b_0(E, \vec{\mathrm{k}}) \times \sum_{b_1 k_1} \langle \rho_{l_1}(\vec{\mathrm{k}} - \vec{\mathrm{k}}_1) \rho_{l_2}(\vec{\mathrm{k}}_1 - \vec{\mathrm{k}}') \rangle W^{bb_1}_{kk_1} G^{b_1}_0(E, \vec{\mathrm{k}}_1) W^{b_1 b'}_{k_1 k'} G^{b'}_0(E, \vec{\mathrm{k}}') + \cdots \;. \tag{15}$$

By a typical manipulation of the series (15) the configurationally averaged G can be written in the form

$$\langle (G(E))^{bb'}_{kk'} \rangle = G^b_0(E, \vec{\mathrm{k}}) + G^b_0(E, \vec{\mathrm{k}}) \times \sum_{b_1 k_1} (\Sigma_t)^{bb_1}_{kk_1} \langle (G(E))^{b_1 b'}_{k_1 k'} \rangle \;. \tag{16}$$

This can be written in a more compact form:

$$\langle G \rangle = G_0 + G_0 \Sigma_t \langle G \rangle \;. \tag{17}$$

The Green's-function method is essentially based upon constructing a proper self-energy Σ_t defined by the Dyson equation (17). The calculation of Σ_t is admittedly a difficult problem. In a first-order approximation the self-energy is represented by $\Sigma_1(E)$. This approximation is used with an intention of obtaining an expression which would be amenable to a calculation for the density of states of a real solid. Improvements over this approximation would demand huge computational efforts if we wish to apply the theory to a real system. The first-order approximation is obtained by retaining only terms associated with a single site in (15). This is a single-site approximation. We can write an expression for $\Sigma_1(E)$,

$$(\Sigma_1(E))^{bb'}_{kk'} = \langle \rho_l(\vec{\mathrm{k}} - \vec{\mathrm{k}}') \rangle W^{bb'}_{kk'} + \sum_{b_1 k_1} \langle \rho_{l_1}(\vec{\mathrm{k}} - \vec{\mathrm{k}}_1) \rho_{l_2}(\vec{\mathrm{k}}_1 - \vec{\mathrm{k}}') \rangle \times W^{bb_1}_{kk_1} G^{b_1}_0(E, \vec{\mathrm{k}}_1) W^{b_1 b'}_{k_1 k'} + (\text{higher-order terms}) \;. \tag{18}$$

The first-order self-energy has some spurious poles poles and the sum of the series is not convergent.[27] $\Sigma_1(E)$ is not defined in an analytic sense. The difficulty results from the fact that in deriving $\Sigma_1(E)$ proper attention has not been paid to the correction factors for exclusion effects which will vary from approximation to approximation. If only a small number of terms are included, a different correction factor is to be used.[27] If one follows such a "self-contained" treatment, the self-energy is found to be convergent. Yonezawa has emphasized the fact that in order to give the approximate self-energy a physical meaning, the correction factor to renormalize the cumulants must be chosen such that the self-containedness in the given stage of approximation is ensured.

Some of the terms left out of (15) can be taken into account simply by replacing G_0 by the true Green's function $\langle G \rangle$ everywhere in (18).[27] The proper self-energy part calculated in this manner is denoted by $\Sigma(1)$. Therefore,

$$(\Sigma(1))^{bb'}_{kk'} = \langle \rho_l(\vec{k}-\vec{k}') \rangle W^{bb'}_{kk'} + \sum_{b_1k_1} \langle \rho_{l_1}(\vec{k}-\vec{k}_1)\rho_{l_2}(\vec{k}_1-\vec{k}') \rangle \times W^{bb_1}_{kk_1} \langle G^{b_1}(E,\vec{k}_1) \rangle W^{b_1b'}_{k_1k'} + (\text{higher-order terms}) . \tag{19}$$

The configurational averages $\langle \cdots \rho_{l_i} \cdots \rangle$ are known as semi-invariants denoted by S_s. Therefore, Eq. (19) can be alternatively written as

$$(\Sigma(1))^{bb'}_{kk'} = S_1(\vec{k}-\vec{k}')\, W^{bb'}_{kk'} + \sum_{b_1k_1} S_2(\vec{k}-\vec{k}_1, \vec{k}_1-\vec{k}') \times W^{bb_1}_{kk_1} \langle G^{b_1}(E,\vec{k}_1) \rangle W^{b_1b'}_{k_1k'} + (\text{higher-order terms}) . \tag{20}$$

The expressions for semi-invariants are obvious from a comparison of (19) and (20). We have used the cumulant expansion method of Kubo[35] to determine the semi-invariants. The evaluation of the first few semi-invariants in a self-contained first-order approximation for the proper self-energy is discussed in the Appendix.

Using the values of the semi-invariants given in the Appendix, we obtain $\Sigma(1)$ and retain terms up to fourth order only

$$\Sigma(1) = c(1-c)W_0^2 \left(\frac{1}{N} \sum_{b_1k_1} \langle G^{b_1}(E,\vec{k}_1) \rangle \right) + (c - 3c^2 + 2c^3) W_0^3 \left(\frac{1}{N^2} \sum_{b_1k_1} \sum_{b_2k_2} \langle G^{b_1}(E,\vec{k}_1) \rangle \langle G^{b_2}(E,\vec{k}_2) \rangle \right)$$
$$+ (c - 7c^2 + 12c^3 + 6c^4) W_0^4 \left(\frac{1}{N^3} \sum_{b_1k_1} \sum_{b_2k_2} \sum_{b_3k_3} \langle G^{b_1}(E,\vec{k}_1) \rangle \langle G^{b_2}(E,\vec{k}_2) \rangle \langle G^{b_3}(E,\vec{k}_3) \rangle \right) . \tag{21}$$

Here N is the total number of sites. We have replaced $W^{bb'}_{kk'}$ by W_0, which will be true if we are dealing with a δ-function potential. The coefficients of the cumulants, after the corrections for the cumulants to be self-contained have been applied, have been calculated by Yonezawa.[27] She finds that the corrected coefficients converge rapidly. The first three coefficients do not change, the fourth changes a little, and the remaining ones are quite small. The solute atom is not too grossly different from the solvent; therefore W or W_0 should be small. It is for these reasons that in (21) we have truncated the series for $\Sigma(1)$ at the fourth term. The magnitude of neglected terms is suspected to be small. It is not possible to obtain an analytic expression for the self-contained $\Sigma(1)$. We define

$$\mathcal{G}(E) = N^{-1} \sum_{bk} \langle G^b(E,\vec{k}) \rangle ; \tag{22}$$

then Eq. (21) could be written in the form

$$\Sigma(1) = c(1-c) W_0^2\, \mathcal{G}(E) [1 + (1-2c) W_0 G_t(E) + (1 - 6c + 6c^2) W_0^2\, \mathcal{G}^2(E)] . \tag{23}$$

We obtain in this scheme an approximate self-energy $\Sigma(1)$ that depends on E.

We write Eq. (16) in the form

$$\langle G(E,\vec{k}) \rangle = \frac{1}{G_0(E,\vec{k}) - \Sigma_t(E,\vec{k})} . \tag{24}$$

Here

$$G_0(E,\vec{k}) = (E - \epsilon - T_k)^{-1} ,$$

where T_k is the Fourier transform of the tight-binding integral and ϵ is the relevant eigenvalue for the solvent atom. Thus for a single nondegenerate band, we obtain

$$\mathcal{G}(E) = \frac{1}{N} \sum_k \frac{1}{E - \epsilon - T_k - \Sigma_t(E,\vec{k})} . \tag{25}$$

If we use the k-independent self-energy $\Sigma(1)$ given by (23), we have $\mathcal{G}(E)$ under the approximation implicit in the derivation of $\Sigma(1)$ above:

$$\mathcal{G}(E) = \frac{1}{N} \sum_k \frac{1}{E - \epsilon - T_k - \Sigma(1)} . \tag{26}$$

The coupled equations (23) and (26) for $\mathcal{G}(E)$ and $\Sigma(1)$ can now be solved self-consistently.

The function $\mathcal{G}(E)$ is of dominant importance in this problem. The energy density of the electronic state is obtained from the knowledge of $\mathcal{G}(E)$ via the relation

$$n(E) = -(\pi)^{-1} \operatorname{Im} \mathcal{G}(E) . \tag{27}$$

We may mention that nearly the same formulation with appropriate reinterpretation of parameters and variables can well describe the vibration of a disordered lattice, exciton propagation in molecular crystals, or spin waves in a ferromagnet.

IV. LOCALIZATION IN DISORDERED ALLOYS

The localization of the electronic states has been found to be a general feature of a disordered system. If an electron moves in a rigid lattice, where the fluctuations in the potential satisfy certain conditions, the state of the electron becomes localized. Here we are dealing with random quantities; therefore localizability is a matter of probability. Anderson[28] has, therefore, studied this process from a probability point of view. Anderson's basic condition for the localizability of a state of energy E is related to the convergence of a renormalized perturbation series for the self-energy. He has deduced a criterion for the onset of localization in a topologically disordered lattice. Later Mott[33] interpreted Anderson's localization criterion in the language of the transport theory and showed that in the density of states there exist mobility edges. A mobility edge is specified by a critical energy at which there is a sharp transition from the localized states in the band tails to the extended states in the interior of the band. The complete disappearance of extended states from the system as the randomness exceeds a certain critical value is known as the Anderson transition. Various electronic properties of the disordered materials such as switching phenomena and the metal-nonmetal transition are direct consequences of the localization of electrons.

Let us consider the motion of a particle in a three-dimensional periodic lattice such that at each site n the particle of energy $\epsilon(n)$ can occupy a Wannier state $|n\rangle$. The disorder is introduced into the system by regarding the single-site energies $\epsilon(n)$ as random variables. Suppose we consider the state associated with the origin $n=0$. Anderson's criterion for the existence of localized states at this site is that the diffusion of the particle from this site is not complete. We may use the symbol $p_{(00)}$ to denote the probability of finding a particle in the state $|0\rangle$ at $t=\infty$ if initially (at $t=0$) it was in $|0\rangle$. Anderson's criterion is $p_{(00)} \neq 0$.

Cohen and co-workers[31] have studied the problem of localization by analyzing the self-energy,

$$\Sigma_{(0)}(E) = E - \epsilon_{(0)} - G^{-1}_{(0)}(E) .$$

$G_{(0)}(E)$ is the (0, 0) matrix element of the Green's function $(E-H)^{-1}$. The subscript (0) denotes that we are concerned with site 0. It can be easily shown that when there is no long-range statistical correlation among the variables $\{\epsilon_{(n)}\}$ for the eigenstate of energy E overlapping with $|0\rangle$ to be localized, i.e., $p_{(00)} \neq 0$, $\Sigma_{(0)}(E)$ should be analytic across the real axis. By writing a renormalized perturbation series (RPS) for $\Sigma_{(0)}(E)$ Cohen and co-workers show that there exists a non-negative function $L(E)$ such that when $L(E)<1$ the RPS converges for all sets of values $\epsilon_{(n)}$ and when $L(E)>1$ the series for $\Sigma_{(0)}(E)$ diverges for all values of $\epsilon_{(n)}$. Therefore, the region for which $L(E)<1$ consists only of localized states, and when $L(E)>1$ the region will have extended states. Thus the equation $L(E_c)=1$, will demarcate the mobility edges. Cohen and co-workers have deduced from plausibility arguments an expression for the localization function in the general case where the self-energy is k dependent:

$$L(E) = \frac{\max_k\{E(\vec{k})\}}{|E - \Sigma(E, \vec{k})|} . \tag{28}$$

When the self-energy is $\vec{k}$ independent, the localization function in (28) is given by

$$L(E) = \frac{\max_k\{E(\vec{k})\}}{|E - \Sigma(E)|} . \tag{29}$$

As we have mentioned, $L(E)=1$ corresponds to the mobility edges, and the regions of localized and extended states are obtained for $L(E)<1$ and $L(E)>1$, respectively. It is worth pointing out here that we cannot make any reliable predictions concerning the localization of states merely on the basis of the modified single-site theory that we have discussed in Sec. III.

V. APPLICATIONS TO MODEL ALLOY AND α-BRASS

The method outlined above is applied to calculate the density of states of a somewhat artificial model of an alloy as well as the density of states of α-brass We shall first present our results for the model alloy.

A. Model Alloy

We consider a model alloy for which the pure host crystal has a semicircular density of states,[36]

$$n^{(0)}(E) = (2/\pi B^2)(B^2 - E^2)^{1/2} , \quad |E| < B$$
$$= 0 , \quad \text{otherwise} . \tag{30}$$

$n^{(0)}(E)$ is centered at $E=0$. B is the half-width of the band. This density-of-states function has the desired singularities at the edges. The model density of the host is used to solve the coupled equations (23) and (26) self-consistently following the procedure described by Onedora and Toyozawa.[19] The density of states defined by Eq. (27) is calculated for various values of B and atomic concentrations of the solute atoms. The results are presented in Figs. 1–3. The localization function $L(E)$ of Eq. (29) is calculated using the same set of parameters B and c. Following Economou *et al.*, we take $E(\vec{k})$ to be symmetric about the zero of energy and also choose $\max_k\{E(\vec{k})\} = B$. We have used three values of B, and for each value of B we use three values of c (0.1, 0.2, and 0.3). In Figs. 1–3 the mobility edges are shown by the vertical arrows in each density-of-states curve. The region in which the states are localized because of $L(E)<1$ are shaded. The unshaded regions correspond to

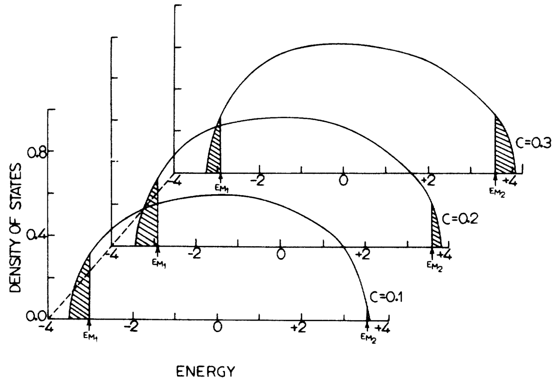

FIG. 1. Density of states for the model alloy calculated for $(\epsilon_A - \epsilon_B)/B = 0.25$ and $c = 0.1$, 0.2, and 0.3, respectively. E_{M_1} and E_{M_2} are the mobility edges shown by the vertical arrows.

extended states. In Fig. 1 (corresponding to the largest value of B used by us) the density-of-states curve shifts towards the higher energy with an increase in the concentration of solute atoms. In Fig. 2 (corresponding to the medium value of B) the density-of-states curve is split into two subbands for $c = 0.1$ and a small gap shows up for this concentration. The two subbands merge into each other at a higher concentration. A narrow extended band has developed for $c = 0.3$. In Fig. 3 (corresponding to the lowest value of B used by us) two subbands separated by a gap are obtained over a wide range of concentration. The gap increases with an increase in the concentration. We notice that these findings about the density of states for the model alloy agree qualitatively with the results of Velický *et al.*[15] in the rigid-band and split-band limits.

B. α-Brass

We chose α-brass for our calculation because the neutron scattering experiments[37] have shown that this system does not possess any detectable short-range order. Our theory is also applicable to the systems where there is no short-range order. In the formulation we have tacitly assumed that the lattice spacing is unchanged by alloying, allowing for a sensible definition of a rigid, periodic empty lattice. In α-brass with 11.4% of zinc the lattice parameter has been found to change only by 1.4% from its value for pure copper.[38] This is quite a small change. Therefore the α-brass system is well within the framework of assumptions implicit in the formalism. The band structures of copper[39,40] and zinc[41] are well understood. The d band in zinc is, to a considerable extent, atomic in character. Moreover, some band-structure calculations are available for α-brass.[42,43]

We adopted the method described by Kirkpatrick *et al.*[44] to calculate the density of states. These authors have calculated the density of states of Ni-Cu alloys using an interpolation scheme.[45] In this scheme the density of states $n^{(0)}(E)$ of the solvent, which is known for various values of energy, is used as the base of the calculation. These data are then interpolated throughout the energy range by a straight-line interpolation. The present calculation uses the density of states of pure copper derived from a Korringa-Kohn-Rostoker-method band-structure calculation by Faulkner *et al.*[40] The atomic eigenvalues are taken from the tabulation of Herman and Skillman,[46] which are based on the self-consistent Hartree-Fock-Slater method. Using these

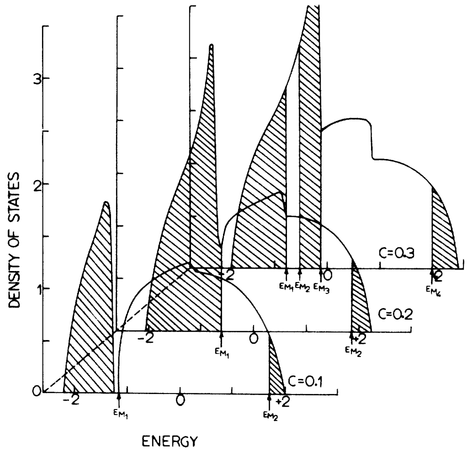

FIG. 2. Density of states for the model alloy calculated for $(\epsilon_A - \epsilon_B)/B = 0.50$ and $c = 0.1$, 0.2, and 0.3, respectively. E_{M_1}, E_{M_2}, E_{M_3}, and E_{M_4} are the mobility edges shown by the vertical arrows.

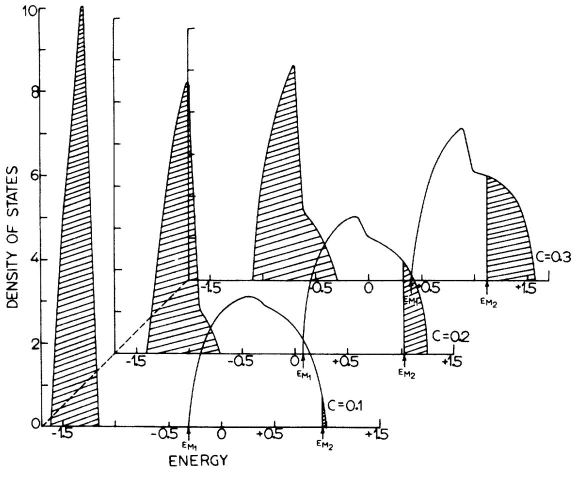

FIG. 3. Density of states for the model alloy calculated for $(\epsilon_A - \epsilon_B)/B = 1.25$ and $c = 0.1$, 0.2, and 0.3, respectively. E_{M_1} and E_{M_2} are the mobility edges shown by the vertical arrows.

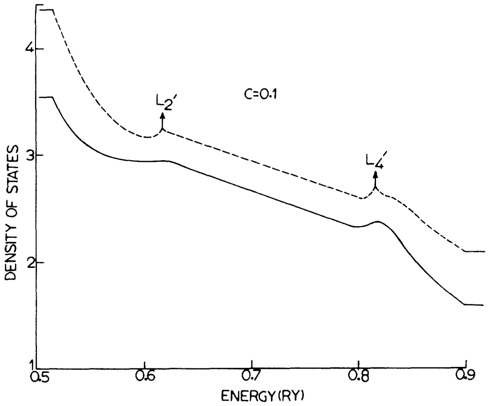

FIG. 4. Interpolated density of states of α-brass with $c = 0.1$. The dashed curve is for pure copper and the full curve for the alloy.

values, we solve for the Green's function, and $n(E)$ is determined as in the preceding example. The interpolated density of states for α-$\text{Cu}_{0.90}\text{Zn}_{0.10}$ is shown in Fig. 4. There are two peaks at 0.616 and 0.814 Ry for pure copper corresponding to the symmetry points $L_{2'}$ and $X_{4'}$, respectively. As one should expect, these peaks are smoothed in the alloy. However, we notice that there is the tendency of the peaks in the density-of-states curve to shift towards higher energy on alloying. Amar *et al.*[42] have calculated the band structure of α-$\text{Cu}_{0.70}\text{Zn}_{0.30}$ within the VCA and from this they extracted the density of states in a semiquantitative manner. They shift towards lower energies.

The optical data of Biondi and Rayne[47] could be analyzed in terms of the interband absorption processes and could be used to provide information concerning the electronic states in alloys.[48] The optical-absorption edge which occurs at 0.154 Ry in copper is seen to move to higher energies with increasing zinc concentrations, while the secondary absorption peak which is initially at 0.309 Ry moves to lower energies. The absorption edge of 0.154 Ry in copper is associated with an $L_{2'}$-E_f (Fermi energy) transition. The secondary peak is attributed to an X_5-$X_{4'}$ transition. With this assignment the data of Biondi and Rayne suggest that the states at $X_{4'}$ will shift downwards in energy as the concentration of zinc is increased. Our calculation therefore fails to explain the optical data. The band-structure results based on VCA show surprisingly good agreement with the optical data. The low-temperature specific-heat measurements[49] reveal that the density of states at the Fermi level falls on alloying and this agrees with our findings. However, no direct measurements of the total density-of-states function are available to date and it would be very desirable for evaluating any theory if some definitive measurements of the density of states could be made on α-brass by using the optical, photoemission, or soft-x-ray techniques. The modified single-site formulation that we have used here has some resemblance to the CPA. The CPA underemphasizes the randomness in the way it replaces the potential on each site by an effective potential. In the CPA we assume that we know the solution of Eq. (17) with a diagonal unit matrix for Σ. This solution we call G_e. There are now solute atoms at all sites with potential $v_s - \Sigma$ at the old solute atom (potential v_s) site and Σ at the old host site. It is ensured that on the average the total scattering from this system is zero, as it must be if Σ is the correct self-energy. Clustering effects have been completely ignored in the CPA and in our calculation. A general approach for incorporating the cluster effects in the MY-type theory has been indicated by Yonezawa.[27] The cluster effects are to be included in order to explain the fine structure of the density of states.

VI. CONCLUSION

We have been able to apply the formulation to a real three-dimensional system. There are insufficient experimental results to prove or disprove the theory presented here. The most definitive test would be provided by a measurement of the density of states. The approach is a perturbative one and we have used the first-order approximation for the self-energy, retaining only a few terms in the Eq. (19). This approach should be applicable only where the difference of potentials of the constituents of the alloy is small. Our treatment does not give a correct description of clusters. By neglecting the $\vec{k}$ dependence of self-energy, we obtained a smoothed-out spectrum without fine structures due to clusters. We have assumed that the transfer energies do not depend on the type of atoms. Physical realism demands that the hopping integrals vary from pair to pair, but this makes the whole calculation very much more complicated. Berk[50] and Shiba[51] have analyzed this problem independently for a random binary alloy. We have not taken into account the d bands and the s-d hybridization.

There is a pressing need for careful experiments and more incisive theoretical treatments. Our results are specific to the model and assumptions which have been made therein. Nevertheless, they should be indicative of the type of behavior which can be expected from a more sophisticated approximation to this complicated problem.

ACKNOWLEDGMENTS

We are grateful to the authorities of the Indian Institute of Technology, Kanpur, for allowing us the use of their computer facilities. We acknowledge useful correspondence with Dr. M. M. Pant and Dr. S. Kirkpatrick. The financial assistance from the Council of Scientific and Industrial Research, India, and State Council of Scientific and Industrial Research U. P. is gratefully acknowledged.

APPENDIX

The semi-invariants or moments are the averages of the products of ρ's

$$S_s = \left\langle \sum_{l_1} \cdots \sum_{l_s} e^{-i(\vec{k}-\vec{k}_1)\cdot\vec{R}_{l_1}} \cdots e^{-i(\vec{k}_{s-1}-\vec{k}_s)\cdot\vec{R}_{l_s}} \right\rangle$$

$$= \langle \rho_{l_1}(\vec{k}-\vec{k}_1) \cdots \rho_{l_s}(\vec{k}_{s-1}-\vec{k}_s) \rangle \ . \qquad \text{(A1)}$$

These are calculated by using an expansion in terms of cumulants. The advantage of using cumulants is that the cumulant of the product of statistically independent variables vanishes identically. If we write

$$\vec{k}-\vec{k}' = \vec{q}\ , \quad \vec{k}-\vec{k}_1 = \vec{q}_1\ , \quad \vec{k}_1-\vec{k}_2 = \vec{q}_2, \ldots,$$

$$\vec{k}_{s-1}-\vec{k}_s = \vec{k}_{s-1}-\vec{k}' = \vec{q}_s\ ,$$

then the sth semi-invariant is

$$S_s = \left\langle \prod_{j=1}^{s} \sum_{\{l_j\}} e^{-i\vec{q}_j\cdot\vec{R}_{l_j}} \right\rangle$$

$$= \left\langle \prod_{j=1}^{s} \rho_{l_j}(\vec{q}_j) \right\rangle \ . \qquad \text{(A2)}$$

Following Yonezawa,[27] S_s's are written in terms of cumulant C_s's:

$$S_1(\vec{q}_1) = C_1(\vec{q}_1)\ ,$$

$$S_2(\vec{q}_1, \vec{q}_2) = C_1(\vec{q}_1)C_1(\vec{q}_2) + C_2(\vec{q}_1, \vec{q}_2)\ ,$$

$$S_3(\vec{q}_1, \vec{q}_2, \vec{q}_3) = C_1(\vec{q}_1)C_1(\vec{q}_2)C_1(\vec{q}_3)$$

$$+ C_2(\vec{q}_1, \vec{q}_2)C_1(\vec{q}_3) + C_1(\vec{q}_1)C_2(\vec{q}_2, \vec{q}_3)$$

$$+ C_2(\vec{q}_1, \vec{q}_3)C_1(\vec{q}_2) + C_3(\vec{q}_1, \vec{q}_2, \vec{q}_3)\ ,$$

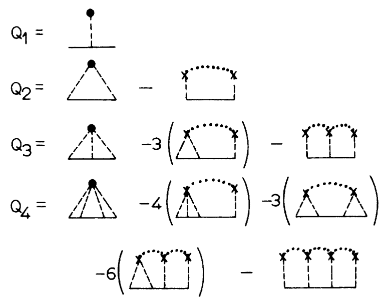

FIG. 5. Diagrammatic representation used in evaluating the semi-invariants up to fourth order.

and so on. The values of C_s's are obtained from

$$C_s(\vec{q}_1, \vec{q}_2, \ldots, \vec{q}_s) = NQ_s(c)\delta(\vec{q}_1 + \cdots + \vec{q}_s)\ . \qquad \text{(A3)}$$

We use a diagrammatic representation[27] for the cumulants. In Fig. 5 the cumulant diagrams to fourth order in c are shown. A heavy dot denotes an unrestricted vertex and a cross is a cumulant vertex. The dotted line is used for the summation restriction. The dashed lines are interaction lines and a factor N is assigned to each proper part. If we work in the self-contained first-order approximation for Σ, we get

$$Q_1(c) = c\ ,$$

$$Q_2(c) = c - Q_1(c)Q_1(c)$$

$$= c - c^2\ ,$$

$$Q_3(c) = c - 3Q_1(c)Q_2(c) - Q_1^3(c)$$

$$= c - 3c^2 + 2c^3\ ,$$

$$Q_4(c) = c - 4Q_3(c) - 3Q_2^2(c) - 6Q_2(c)Q_1^2(c) - Q_1^4(c)$$

$$= c - 7c^2 + 12c^3 - 6c^4\ ,$$

and so on. These values for Q_s will enable us to determine S_s.

---

[1] N. F. Mott and H. Jones, *The Theory of Properties of Metals and Alloys* (Dover, New York, 1958), pp. 170–174.

[2] J. Friedel, Advan. Phys. 3, 446 (1954).

[3] L. Nordheim, Ann. Phys. 9, 607 (1931); M. H. Cohen and V. Heine, *ibid.* 7, 396 (1958).

[4] R. H. Paramenter, Phys. Rev. 97, 587 (1955); 99, 1759 (1955).

[5] E. A. Stern, Physics 1, 255 (1965).

[6] *Optical Properties and Electronic Structure of Metals and Alloys*, edited by F. Abelès (North-Holland, Amsterdam, 1966); *Soft X-Rays Band Spectra and the Electronic Structure of Metals and Materials*, edited by D. J. Fabian (Academic, New York, 1968); Proceedings of the Electronic Density of States Conference, Gaithersburg, Md., 1969 (unpublished).

[7] J. L. Beeby and S. F. Edwards, Proc. Roy. Soc. (London) A274, 395 (1963).

[8] J. Korringa, J. Phys. Chem. Solids 7, 252 (1958).

[9] H. Jones, Proc. Roy. Soc. (London) A285, 416 (1965); A294, 405 (1966).

[10] P. G. Dawber and R. E. Turner, Proc. Phys. Soc. (London) 88, 217 (1966).

[11] J. L. Beeby, Phys. Rev. 135, A130 (1964).

[12] J. L. Beeby, J. Res. Natl. Bur. Std. (U.S.) 74A, 281 (1970).

[13] P. Soven, Phys. Rev. 151, 539 (1966).

[14] P. Soven, Phys. Rev. 156, 809 (1967).

[15] B. Velický, S. Kirkpatrick, and H. Ehrenreich, Phys. Rev. 175, 747 (1968).

[16] P. Soven, Phys. Rev. 178, 1126 (1969).

[17] D. W. Taylor, Phys. Rev. 156, 1017 (1967); P. L.

Leath, *ibid.* 171, 725 (1968).
[18] L. M. Roth, Phys. Letters 31A, 440 (1970).
[19] Y. Onedora and Y. Toyozawa, J. Phys. Soc. Japan 24, 341 (1968).
[20] K. Freed and M. H. Cohen, Phys. Rev. B 3, 3400 (1971).
[21] T. Matsubara and Y. Toyozawa, Progr. Theoret. Phys. (Kyoto) 26, 739 (1961).
[22] T. Matsubara and T. Koneyoshi, Progr. Theoret. Phys. (Kyoto) 36, 695 (1966).
[23] P. L. Leath, Phys. Rev. B 2, 3078 (1970).
[24] T. Matsubara, Progr. Theoret. Phys. (Kyoto) 44, 1116 (1971).
[25] F. Yonezawa, Progr. Theoret. Phys. (Kyoto) 31, 357 (1964); F. Yonezawa and T. Matsubara, *ibid.* 35, 357 (1966); T. Matsubara and F. Yonezawa, *ibid.* 37, 1346 (1966).
[26] S. F. Edwards, Phil. Mag. 3, 1020 (1958).
[27] F. Yonezawa, Progr. Theoret. Phys. (Kyoto) 40, 734 (1969).
[28] P. W. Anderson, Phys. Rev. 109, 1492 (1958); Comments Solid State Phys. 2, 193 (1970), and references cited therein.
[29] S. F. Edwards, J. Non-Cryst. Solids 4, 417 (1970).
[30] M. H. Cohen, J. Non-Cryst. Solids 4, 391 (1970).
[31] E. N. Economou and M. H. Cohen, Mater. Res. Bull. 5, 577 (1970); Phys. Rev. Letters 25, 1445 (1970); E. N. Economou, S. Kirkpatrick, M. H. Cohen, and T. P. Eggartar, *ibid.* 25, 520 (1970).
[32] I. M. Lifshitz, Usp. Fiz. Nauk 83, 617 (1964) [Sov. Phys. Usp. 7, 549 (1965)].
[33] N. F. Mott, Phil. Mag. 22, 1 (1970), and references cited therein.
[34] J. S. Langer, J. Math. Phys. 2, 584 (1961).
[35] R. Kubo, J. Phys. Soc. Japan 12, 570 (1957).
[36] J. Hubbard, Proc. Roy. Soc. (London) A281, 401 (1964).
[37] D. T. Keating, Acta Met. 2, 885 (1954).
[38] W. B. Pearson, *A Handbook of Lattice Spacing and Structure of Metals and Alloys* (Pergamon, New York, 1967), Vol. 2, p. 892.
[39] B. Segall, Phys. Rev. 125, 109 (1962).
[40] J. S. Faulkner, H. L. Davis, and H. W. Joy, Phys. Rev. 161, 656 (1967).
[41] W. E. Loy, Jr. and H. Amar, Bull. Am. Phys. Soc. 16, 637 (1971).
[42] H. Amar and K. H. Johnson, in *Optical Properties and Electronic Structures of Metals and Alloys*, edited by F. Abelès (North-Holland, Amsterdam, 1966).
[43] M. M. Pant and S. K. Joshi, Phys. Rev. 184, 635 (1969); 186, 675 (1969).
[44] S. Kirkpatrick, B. Velický, and H. Ehrenreich, Phys. Rev. B 1, 3250 (1970).
[45] K. Lieberman, B. Velický, and H. Ehrenreich, Bull. Am. Phys. Soc. 14, 320 (1969).
[46] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, N.J., 1963).
[47] M. A. Biondi and R. A. Rayne, Phys. Rev. 115, 1522 (1959).
[48] A. H. Lettington, Phil. Mag. 11, 863 (1965).
[49] L. L. Isaacs and T. B. Massalski, Phys. Rev. 138, A134 (1965).
[50] N. F. Berk, Phys. Rev. B 1, 1336 (1970).
[51] H. Shiba (unpublished).

PHYSICAL REVIEW B VOLUME 4, NUMBER 12 15 DECEMBER 1971

Magnetoacoustic Attenuation by Bragg-Reflected Electrons[*]

Casio R. Oré-Oré[†] and Leonard Kleinman
Department of Physics, University of Texas, Austin, Texas 78712

(Received 21 June 1971)

We discuss the difficulties associated with the jellium model and the validity of the deformation-potential method of calculating magnetoacoustic attenuation in metals when the electrons are Bragg reflected. We then calculate the attenuation of a transverse acoustic wave propagating along the magnetic field in a metal whose Fermi surface consists of a free-electron sphere truncated by the six Bragg planes of a simple-cubic Brillouin zone. The attenuation-vs-magnetic-field curves show considerable structure which depends strongly on the ratio $K/2k_F$ where K is the separation between Bragg planes.

I. INTRODUCTION

The jellium theory of magnetoacoustic attenuation[1,2] was extended to nonspherical Fermi surfaces by Eckstein.[3] She was attempting to reproduce peaks found by Boyd and Gavenda[4] in the magnetic field dependence of the attenuation of transverse acoustic waves propagating parallel to the magnetic field along the [100] direction in copper. They attributed these peaks to singularities in the $v_H = \partial E/\partial p_H$ density of states on the Fermi surface. Eckstein chose a dumbbell-shaped model Fermi surface with such singularities and found a peak in the conductivity which leads to a *dip* in the attenuation. Thinking this might be a consequence of the jellium theory, which strictly speaking could be valid only for spherical Fermi surfaces, we recalculated[5] the attenuation using a free-electron deformation-potential (FED) approximation to the exact deformation potential.[6,7] We found, however, that the FED approximation gave exactly Eckstein's jellium result for her Fermi surface and for more complicated dumbbell-shaped Fermi surfaces gave results more compli-