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Spectral Density of States in Disordered Beta Brass

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The spectral density of states for electrons in disordered β brass has been determined by calculating the T matrix for the system. The geometric approximation introduced by Beeby has been invoked to sum the infinite series expressing the total T matrix in terms of the t matrices for the individual scatters. Beeby's procedure is extended to take account of the short-range order present in the alloy, and it results in the introduction of incomplete Green's functions of the form previously used by the authors in another approach for calculating the electronic spectrum of disordered alloys. Information about the short-range order obtained from neutron-scattering measurements is used to evaluate the incomplete Green's functions as well as the crystal potentials for the constituents. Model potentials of the form used by Soven are employed to facilitate the calculation of the t matrices. The distinction between the constituents is retained. We have computed the spectral density of states for β brass at the symmetry points Γ, H, P, and N of the Brillouin zone. The results are used to predict the flatness of the Fermi surface, which compares well with the speculative interpretation by Moss of the neutron-scattering data.

I. INTRODUCTION

THERE have recently been several attempts to calculate the electronic structure of disordered alloys. The simplest approximation, which has been applied to both α and β phases of brass (Cu-Zn)[1,2] as well as Ag-In alloys,[3] consists in replacing the disordered alloy by a hypothetical perfect crystal, wherein each site carries a potential equal to the average of the potentials of the constituents. The virtual-crystal approximation (VCA), as this is called, provides a qualitative explanation of results of optical-absorptivity measurements but fails to give a satisfactory detailed agreement. An attempt was made to see if the use of improved potentials, which took account of the occupation probabilities of the lattice sites by the two types of atoms in a binary alloy, could render the VCA more useful. It was found that this improvement in the potential destroyed the fortuitous agreement with optical data achieved before for α brass.[4] In another approach to the disordered-alloy problem, a generalization of the Green's-function method was proposed by the authors and applied to α brass[5] and the disordered Cu_3Au.[6] The model was found to give a fairly satisfactory description of both the conduction and the d bands. In default of any exact mathematical solution to the general problem, it was made plausible that the configurationally averaged wave function satisfies a Bloch-type condition. By making the further approximation of using the wave function for an averaged potential as the configurationally averaged wave function, one could obtain a secular determinant similar to that for the Kohn-Rostoker (KR) method[7] for the case of a diatomic lattice.

The above-mentioned approaches have the common weakness of associating a unique momentum with a given eigenstate, thus assigning to it an infinite lifetime. But it is clear that $\mathbf{k}$ is no longer a good quantum number for electrons in a disordered alloy. In such systems, the relevant and important physical quantity is the spectral density of states $\rho(E,\mathbf{k})$. For the case of perfect lattice, this has a δ-function peak. As a result of the disorder, the peak is broadened and its width would indicate the departure from the Bloch-wave character of the alloy wave function. An investigation which bears on this aspect has been made by Soven,[8] who has applied the averaged t-matrix approximation to α brass to calculate the spectral density for states of various symmetries.

The purpose of this paper is to present a t-matrix approach and apply it to the disordered substitutional binary alloy β brass. In this method, the distinction between the t matrices of the constituents is retained, and no hypothetical scatterer having an averaged t matrix need be assumed. The formalism relies heavily on the work of Beeby[9] and the calculation utilizes the model δ-function potential of Soven,[8] and the incomplete Green's functions of Pant and Joshi.[5] The method takes account of any short-range order present in the alloy, and uses the short-range-order parameters to calculate the potential at each site, as well as the incomplete Green's functions mentioned above. There are two basic approximations invoked in this analysis:

(1) The first approximation is the use of muffin-tin potentials where the potential at each site can be approximated by a spherically symmetric distribution is within nonoverlapping spheres around each ion, and assumed constant in the interstitial region. This approximation may be relaxed at the cost of increased computational effort. In a recent work, Rudge[10] has shown that the augmented-plane-wave (APW) method for band-

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[1] H. Amar, K. H. Johnson, and C. B. Sommers, Phys. Rev. **153**, 655 (1967).

[2] H. Amar, K. H. Johnson, and K. P. Wang, Phys. Rev. **148**, 672 (1966).

[3] M. M. Pant and S. K. Joshi, Phys. Letters **28A**, 556 (1969).

[4] M. M. Pant and S. K. Joshi, Phys. Rev. **184**, 639 (1969).

[5] M. M. Pant and S. K. Joshi, Phys. Rev. **186**, 675 (1969).

[6] M. M. Pant and S. K. Joshi, Phys. Rev. (to be published).

[7] W. Kohn and N. Rostoker, Phys. Rev. **94**, 1111 (1954).

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

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

[10] W. E. Rudge, Phys. Rev. **181**, 1024 (1969).

structure calculations, which was conventionally restricted to the muffin-tin potentials, can be extended to take account of the nonspherical contributions in the interior and nonconstant potentials in the interstitial regions. In a similar manner, the present method may also be extended beyond the muffin-tin approximation. It is known from band-structure calculations, that the muffin-tin approximation is quite satisfactory for most cases,[10,11] and therefore we decided to confine the present calculation to muffin-tin potentials.

(2) The second simplification introduced here is the "geometric approximation" discussed by Beeby.[9] This approximation enables us to sum the infinite series expresssing the T matrix for the system in terms of the t matrices for the individual scatterers. For an ordered alloy, this approximation yields the exact result, and for a disordered alloy, one could improve upon it by including higher-order terms.

The method has been applied to disordered β brass to determine the spectral density for states of various symmetries. The results of the experimental measurements of the short-range-order diffuse scattering are available for this alloy.[12] The band structures of the constituents are well known, and some theoretical studies have been made for the α phase.[1,4,5] However, β brass has been theoretically treated only by the virtual-crystal approximation.[2] These considerations prompted us to study the spectral density of states for disordered β brass at a few symmetry points.

In Sec. II we discuss the formalism which gives the expression for the spectral density of states by extending Beeby's work to take account of short-range order. Section III is concerned with the construction of the muffin-tin potentials and we also introduce there the model δ-function potentials to facilitate the calculation of the t matrices. The details concerning the application of the method to β brass are presented in Sec. IV. The results are discussed in Sec. V, which also relates this theory to other methods of exploring the one-electron spectrum in disordered alloys.

II. FORMALISM

The spectral density of states for noninteracting electrons in the presence of a system of potentials has been shown by Beeby and Edwards[13] to be

$$\rho(E,\mathbf{k})=-\frac{1}{(E-k^2)^2\pi\Omega}\,\mathrm{Im}\left\langle\int T(\mathbf{x},\mathbf{x}')e^{-i\mathbf{k}\cdot(\mathbf{x}-\mathbf{x}')}d\mathbf{x}d\mathbf{x}'\right\rangle,$$

which we write as

$$\rho(E,\mathbf{k})=-\frac{1}{(E-k^2)^2\pi\Omega}\,\mathrm{Im}\langle T(\mathbf{k})\rangle. \tag{1}$$

In these expressions, Ω is the volume of the assembly, the angular brackets denote an average over the disordered system of potentials, and Im indicates the imaginary part of the expression that follows it. The T function for the assembly is given by the series

$$T=\sum_{\alpha} t_\alpha+\sum_{\alpha\neq\beta} t_\alpha\mathcal{G}_0t_\beta+\sum_{\alpha\neq\beta,\beta\neq\gamma} t_\alpha\mathcal{G}_0t_\beta\mathcal{G}_0t_\gamma+\cdots, \tag{2}$$

where t_α is the t function corresponding to the potential V_α at the αth site and is defined by

$$t_\alpha(\mathbf{x},\mathbf{y})=V_\alpha(\mathbf{x})\delta(\mathbf{x}-\mathbf{y})+\int V_\alpha(\mathbf{x})\mathcal{G}_0(\mathbf{x}-\mathbf{z})t_\alpha(\mathbf{z},\mathbf{y})d\mathbf{z}.$$

$\mathcal{G}_0(\mathbf{x}-\mathbf{z})$ is the free-particle propagator. In order to obtain a matrix representation, we make angular-momentum expansions of the t functions. It is convenient to use the real spherical harmonics $Y_L(\hat{\mathbf{x}})$ of the angles of $\mathbf{x}$, where L is a compound subscript denoting both l and m, so that

$$t(\mathbf{x},\mathbf{y})=\sum_L t_l(x,y)Y_L(\hat{\mathbf{x}})Y_L(\mathbf{y}). \tag{3}$$

In the case of a disordered binary alloy, any site may be occupied by either of the two types of atoms. We use the superscripts 1 and 2 to denote the two types of atoms. The T matrix series may then be split into four parts, such that

$$T=\sum_{\mathcal{S}=1,2,\mathcal{S}'=1,2} T^{\mathcal{S}\mathcal{S}'}. \tag{4}$$

We have

$$\begin{aligned}
T^{11}&=\sum_{\alpha} t_\alpha{}^1+\sum_{\alpha\neq\beta} t_\alpha{}^1\mathcal{G}_0t_\beta{}^1+\sum_{\alpha\neq\beta,\beta\neq\gamma} t_\alpha{}^1\mathcal{G}_0t_\beta\mathcal{G}_0t_\gamma{}^1+\cdots,\\
T^{12}&=\sum_{\alpha\neq\beta} t_\alpha{}^1\mathcal{G}_0t_\beta{}^2+\sum_{\alpha\neq\beta,\beta\neq\gamma} t_\alpha{}^1\mathcal{G}_0t_\beta\mathcal{G}_0t_\gamma{}^2+\cdots,\\
T^{21}&=\sum_{\alpha\neq\beta} t_\alpha{}^2\mathcal{G}_0t_\beta{}^1+\sum_{\alpha\neq\beta,\beta\neq\gamma} t_\alpha{}^2\mathcal{G}_0t_\beta\mathcal{G}_0t_\gamma{}^1+\cdots,\\
T^{22}&=\sum_{\alpha} t_\alpha{}^2+\sum_{\alpha\neq\beta} t_\alpha{}^2\mathcal{G}_0t_\beta{}^2+\sum_{\alpha\neq\beta,\beta\neq\gamma} t_\alpha{}^2\mathcal{G}_0t_\beta\mathcal{G}_0t_\gamma{}^2+\cdots.
\end{aligned} \tag{5}$$

Here $t_\alpha{}^{\mathcal{S}}$ is the t function corresponding to the potential $V^{\mathcal{S}}$ at α. $T^{\mathcal{S}\mathcal{S}'}$ corresponds to that part of the total T function in which the electron scatters, first, off an atom of the $\mathcal{S}$th type, and lastly off one of the $\mathcal{S}'$th type. The intermediate scatterers may be of either type and are represented by t's without any superscript in the above series.

The Fourier transformation $T(\mathbf{k})$ implied in Eq. (1) may now be carried out separately for each term of the series (5). The first term of T^{11} or T^{22} gives

$$\begin{aligned}
&\int\sum_{\alpha} t_\alpha{}^{\mathcal{S}}(\mathbf{x},\mathbf{y})e^{-i\mathbf{k}\cdot(\mathbf{x}-\mathbf{y})}d\mathbf{x}d\mathbf{y}\\
&\quad=(4\pi)^2N_{\mathcal{S}}\sum_L\int j_l(kx)j_l(ky)t_l{}^{\mathcal{S}}(x,y)x^2dx\\
&\qquad\qquad\times y^2dyY_L(\hat{\mathbf{k}})Y_L(\hat{\mathbf{k}}),
\end{aligned} \tag{6}$$

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[11] B. Segall, Phys. Rev. **124**, 1786 (1961).

[12] C. B. Walker and D. T. Keating, Phys. Rev. **130**, 1726 (1963); J. Als Nielsen and O. W. Dietrich, *ibid.* **153**, 706 (1967).

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

where $N_\mathcal{S}$ is the number of potentials of the type $\mathcal{S}$. The calculation of a general term involves angular integrations of the type

$$(S_{\alpha\beta}^{\mathcal{S}\mathcal{S}'})_{LL'}=i^{l'-l}\int Y_L(\hat{\mathbf{y}})\mathcal{G}_0(\mathbf{y}-\mathbf{z}+\mathbf{R}_\alpha-\mathbf{R}_\beta)\times e^{-i\mathbf{k}\cdot(\mathbf{R}_\alpha-\mathbf{R}_\beta)}Y_{L'}(\mathbf{z})d\mathbf{\Omega}_y d\mathbf{\Omega}_z\,, \tag{7}$$

besides the radial integrals involved in t_l and a summation over L. $\mathbf{R}_\alpha$, $\mathbf{R}_\beta$, etc., denote the positions of the α, β, and other sites. A typical term in series of Eq. (5) therefore contains products of the form

$$\Big(\sum_{\beta\neq\alpha}S_{\alpha\beta}^{\mathcal{S}\mathcal{S}'}\sum_{\gamma\neq\beta}S_{\beta\gamma}^{\mathcal{S}'\mathcal{S}''}\cdots\sum_{\omega\neq\psi}S_{\psi\omega}^{\mathcal{S}'''\mathcal{S}''''}\cdots\Big)_{LL'}\,,$$

where the superscripts on S take the values 1 and 2, depending on the type of atoms at locations specified by the subscripts. The problem is to sum an infinite series with terms of this nature, and then to average such sums over all configurations. Beeby presented a method of tackling this problem by replacing $S_\alpha^{\mathcal{S}\mathcal{S}'}=\sum_{\beta\neq\alpha}S_{\alpha\beta}^{\mathcal{S}\mathcal{S}'}$ by some $S^{\mathcal{S}\mathcal{S}'}$ which does not depend on α. The series in Eq. (5) then become a geometric series. This approximation is therefore referred to as the "geometric approximation" and may be readily seen to be exactly true for a perfectly ordered alloy. We then have

$$(S^{\mathcal{S}\mathcal{S}'})_{LL'}=\frac{1}{N_\mathcal{S}}\sum_{\beta\neq\alpha}(S_{\alpha\beta}^{\mathcal{S}\mathcal{S}'})_{LL'}$$

$$=\frac{1}{N_{\mathcal{S}'}}\sum_{\beta\neq\alpha}\int i^{l'-l}Y_L(\hat{\mathbf{y}})\mathcal{G}_0(\mathbf{y}-\mathbf{z}+\mathbf{R}_\alpha-\mathbf{R}_\beta)\times e^{-i\mathbf{k}\cdot(\mathbf{R}_\alpha-\mathbf{R}_\beta)}Y_{L'}(\hat{\mathbf{z}})d\mathbf{\Omega}_y d\mathbf{\Omega}_z\,. \tag{8}$$

Our formalism up to this stage is essentially identical to that of Beeby. Beeby proceeds further by relating the lattice sums to the Kohn-Rostoker Green's functions. In this paper we take account of the short-range order while summing over the lattice sites. We can identify $\sum_{\beta\neq\alpha}\mathcal{G}_0(\mathbf{y}-\mathbf{z}+\mathbf{R}_\alpha-\mathbf{R}_\beta)e^{-i\mathbf{k}\cdot(\mathbf{R}_\alpha-\mathbf{R}_\beta)}$ in Eq. (8) as the incomplete Green's function of Ref. 5, with the $\beta=\alpha$ term omitted. This may therefore be expanded in terms of the spherical Bessel functions j_l as done in Eq. (16) of Ref. 5,

$$\sum_{\beta\neq\alpha}\mathcal{G}_0(\mathbf{y}-\mathbf{z}+\mathbf{R}_\alpha-\mathbf{R}_\beta)e^{-i\mathbf{k}\cdot(\mathbf{R}_\alpha-\mathbf{R}_\beta)}=\sum_{LL'}i^{l'-l}G_{LL'}^{\mathcal{S}\mathcal{S}'}j_l(\kappa y)j_{l'}(\kappa z)Y_L(\hat{\mathbf{y}})Y_{L'}(\hat{\mathbf{z}})\,.$$

Therefore,

$$[S^{\mathcal{S}\mathcal{S}'}]_{LL'}=G_{LL'}^{\mathcal{S}\mathcal{S}'}j_l(\kappa y)j_{l'}(\kappa z)\,, \tag{9}$$

where $\kappa=\sqrt{E}$ if $E>0$ and $i\sqrt{-E}$ if $E<0$; and $G_{LL'}^{\mathcal{S}\mathcal{S}'}$ are related to the $B_{LL'}^{\mathcal{S}\mathcal{S}'}$ of Ref. 5. The $G_{LL'}^{\mathcal{S}\mathcal{S}'}$ are independent of y and z and are collectively denoted by $G^{\mathcal{S}\mathcal{S}'}$. The radial y and z integrals now involve only Bessel functions and the radial t_l functions. Their most general form is

$$t_l^\mathcal{S}(p,q)=\int j_l(px)t_l^\mathcal{S}(x,y)j_l(qy)x^2dxy^2dy\,, \tag{10}$$

with p and q taking values of k or κ. We use $\tau^\mathcal{S}$ to denote $t_l^\mathcal{S}(\kappa,\kappa)$. In this notation, we have for the series of Eq. (5)

$$T^{11}=(4\pi)^2N_1\sum_{LL'}Y_L(\hat{\mathbf{k}})Y_{L'}(\hat{\mathbf{k}})\Big\{t_l^1(k,k)\delta_{LL'}+\Big[t^1(k,\kappa)\times\Big(G^{11}+\sum_{\mathcal{S}=1,2}G^{1\mathcal{S}}\tau^\mathcal{S}G^{\mathcal{S}1}+\sum_{\mathcal{S}=1,2,\mathcal{S}'=1,2}G^{1\mathcal{S}}\tau^\mathcal{S}G^{\mathcal{S}\mathcal{S}'}\tau^{\mathcal{S}'}G^{\mathcal{S}'1}+\cdots\Big)t^1(\kappa,k)\Big]_{LL'}\Big\}\,,$$

$$T^{12}=(4\pi)^2N_1\sum_{LL'}Y_L(\hat{\mathbf{k}})Y_{L'}(\hat{\mathbf{k}})\Big[t^1(k,\kappa)\Big(G^{12}+\sum_{\mathcal{S}=1,2}G^{1\mathcal{S}}\tau^\mathcal{S}G^{\mathcal{S}2}+\sum_{\mathcal{S}=1,2,\mathcal{S}'=1,2}G^{1\mathcal{S}}\tau^\mathcal{S}G^{\mathcal{S}\mathcal{S}'}\tau^{\mathcal{S}'}G^{\mathcal{S}'2}+\cdots\Big)t^2(\kappa,k)\Big]_{LL'}\,, \tag{11}$$

with similar expressions for T^{21} and T^{22}. On performing the summations, we get

$$T^{11}=(4\pi)^2N_1\sum_{LL'}Y_L(\hat{\mathbf{k}})Y_{L'}(\hat{\mathbf{k}})\big[t_l^1(k,k)\delta_{LL'}+\{t^1(k,\kappa)M_1^{-1}[G^{21}+(1-G^{22}\tau^2)(G^{12}\tau^2)^{-1}G^{11}]t^1(\kappa,k)\}_{LL'}\big]\,,$$

$$T^{12}=(4\pi)^2N_1\sum_{LL'}Y_L(\hat{\mathbf{k}})Y_{L'}(\hat{\mathbf{k}})\{t^1(k,\kappa)M_1^{-1}[G^{22}+(1-G^{22}\tau^2)(G^{12}\tau^2)^{-1}G^{12}]t^2(\kappa,k)\}_{LL'}\,. \tag{12}$$

T^{22} and T^{21} are obtained by interchanging the superscripts 1 and 2 in the above expressions. M_1 and M_2 are defined by the following expressions:

$$\begin{aligned}M_1&=(1-G^{22}\tau^2)(G^{12}\tau^2)^{-1}(1-G^{11}\tau^1)-G^{21}\tau^1\,,\\M_2&=(1-G^{11}\tau^1)(G^{21}\tau^1)^{-1}(1-G^{22}\tau^2)-G^{12}\tau^2\,.\end{aligned} \tag{13}$$

The above set of Eqs. (10), (12), and (13) enable us to determine the spectral density of states. The only problems we face at this stage are the calculation of the matrix elements of $G^{\mathcal{S}\mathcal{S}'}$ and of the evaluation of the t matrices. It is clear that the calculation of $G^{\mathcal{S}\mathcal{S}'}$ requires a detailed knowledge of the relative positions of the atoms. In the case of a disordered alloy, the short-range-order parameters may be used to estimate an average distribution pattern of the constituents, thus enabling us to calculate the $G^{\mathcal{S}\mathcal{S}'}$. A complete discussion of the use of the short-range-order parameters to determine the matrix elements of $G^{\mathcal{S}\mathcal{S}'}$ has been given in Ref. 6. The approximation introduced in order to calculate these matrix elements is that the short-range order extends only up to a certain neighborhood, beyond which the occupation probabilities are those of a randomly occupied lattice. In terms of the Cowley short-range-order parameters α_i this means that $\alpha_i=0$ for i greater than a certain value, say σ. Then this σ is referred to as the "order of significant neighborhood." The matrix elements of $G^{\mathcal{S}\mathcal{S}'}$ are given by

$$G_{LL'}{}^{\mathcal{S}\mathcal{S}'}=4\pi\sum_{L''}D_{L''}{}^{\mathcal{S}\mathcal{S}'}C_{LL'L''}. \qquad (14)$$

Here $C_{LL'L''}$ are related to the Clebsch-Gordan coefficients and

$$D_L{}^{\mathcal{S}\mathcal{S}'}=m_{\mathcal{S}'}D_L+i\kappa(4\pi)^{-1/2}m_{\mathcal{S}'}\delta_{L0}+\kappa i^{-l}\sum_{\gamma<\sigma}{}' e^{i\mathbf{k}\cdot\mathbf{R}_\gamma}$$
$$\times[n_l(\kappa R_\gamma)-ij_l(\kappa R_\gamma)]Y_L(\hat{\mathbf{R}}_\gamma)[P^{\mathcal{S}\mathcal{S}'}(\mathbf{R}_\gamma)-m_{\mathcal{S}'}]. \qquad (15)$$

In this expression, $m_{\mathcal{S}'}$ is the atomic concentration of atoms of $\mathcal{S}'$th type, and the D_L without superscripts are the familiar structure constants of the ordered crystal which occur in the KR method. n_l is the spherical Neumann function. $P^{\mathcal{S}\mathcal{S}'}(\mathbf{R}_\gamma)$ denotes the probability of finding an atom of the $\mathcal{S}'$th type at a position $\mathbf{R}_\gamma$ with respect to an atom of the $\mathcal{S}$th type. This probability can be expressed in terms of the short-range-order parameters as discussed in Ref. 5. The summation in Eq. (15) runs through a neighborhood σ in the direct space, and the prime on the summation indicates that the term with $\gamma=0$ is to be omitted. The δ_{L0} term is introduced to compensate for the fact that the calculation of D_L for the perfect lattice does not exclude this term. The matrix elements of $G^{\mathcal{S}\mathcal{S}'}$ are then directly obtained from Eqs. (14) and (15). We discuss the calculation of the t matrix in the following section.

III. POTENTIALS AND EVALUATION OF t MATRIX

It was shown in Ref. 5 that the muffin-tin potentials $\langle V^{\mathcal{S}}(r)\rangle$ for the constituents in the alloy could be obtained by overlapping the atomic potentials from neighboring sites, taking due account of the probability of the occupation of a site by a given type of atom. In order to facilitate the calculation of the t matrix, Soven[8] suggested the use of model δ-function potentials in place of the muffin-tin potentials. The δ-function potentials were chosen to be of the form

$$\langle V^{\mathcal{S}}(\mathbf{x},\mathbf{x}')\rangle=\sum_L Y_L(\hat{\mathbf{x}})\frac{\delta(x-r_{mt})}{r_{mt}{}^2}v_l{}^{\mathcal{S}}\frac{\delta(x'-r_{mt})}{r_{mt}{}^2}Y_L(\hat{\mathbf{x}}'), \qquad (16)$$

where r_{mt} is the radius of the muffin-tin sphere and $v_l{}^{\mathcal{S}}$ are energy-dependent potential amplitudes. The use of such potentials in the ordered lattice has been previously discussed by Slater.[14] We know from the formalisms of the APW and KR methods for the perfect lattice and the extension of the KR method to disordered alloys,[5] that the potential enters the final formulas only via the logarithmic derivatives of the radial wave function at the radius of the muffin-tin sphere. A suitable method for determining $v_l{}^{\mathcal{S}}(E)$ is then to require it to yield the same logarithmic derivatives as generated by the actual potential. We then have

$$v_l{}^{\mathcal{S}}(E)=r_{mt}{}^2[\gamma_l{}^{\mathcal{S}}(E)-\kappa j_l'(\kappa r_{mt})/j_l(\kappa r_{mt})], \qquad (17)$$

where j_l' is the derivative of the Bessel function and $\gamma_l{}^{\mathcal{S}}(E)$ is the logarithmic derivative of the radial wave function (for angular momentum l and energy E at the sphere radius r_{mt}) engendered by the actual muffin-tin potential $\langle V^{\mathcal{S}}(r)\rangle$. The angular momentum components of the t matrix can then be written as

$$t_l(x,x')=t_l\frac{\delta(x-r_{mt})}{r_{mt}{}^2}\frac{\delta(x'-r_{mt})}{r_{mt}{}^2}, \qquad (18)$$

so that

$$t_l=v_l(1-v_lg_l)^{-1}, \qquad (19)$$

where $g_l=G_l(r_{mt},r_{mt})$ is the lth component in the angular momentum representation of $G(\mathbf{x}-\mathbf{x}')$,

$$G_l(x,x')=\kappa j_l(\kappa x_<)[n_l(\kappa x_>)-ij_l(\kappa x_>)].$$

Here $x_<$ is the lesser and $x_>$ is the greater of x and x'. The introduction of the δ-function model potentials, then leads to the following simple expression for the matrix elements (10) of t

$$t_l(p,q)=t_lj_l(pr_{mt})j_l(qr_{mt}). \qquad (20)$$

These expressions completely define $T^{\mathcal{S}\mathcal{S}'}(\mathbf{k})$ in terms of $G^{\mathcal{S}\mathcal{S}'}$ and the logarithmic derivatives of the radial functions at the muffin-tin radius. The spectral density of states is then obtained from

$$\rho(E,\mathbf{k})=-\frac{1}{(E-k^2)^2\pi\Omega}\operatorname{Im}\sum_{\mathcal{S}=1,2,\mathcal{S}'=1,2}T^{\mathcal{S}\mathcal{S}'}(\mathbf{k}). \qquad (21)$$

Soven[8] has shown that the use of energy-dependent model potentials necessitates the use of a correction factor

$$\left|1-\sum_{\mathcal{S}=1,2}m_{\mathcal{S}}\frac{dv_l{}^{\mathcal{S}}(E)}{dE}\right|$$

with Eq. (21). When we compared the results with and without the use of this correction factor we found that the shapes of the $\rho(E,\mathbf{k})$-versus-E curves, do not change perceptibly and there is no noticeable difference in the peak positions. However, all results presented or discussed here are for $\rho(\mathrm{E},\mathbf{k})$ calculated with the correction factor.

IV. APPLICATION TO β BRASS

The x-ray diffuse scattering from β brass has not been observed experimentally, because of the similarity in

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[14] J. C. Slater, Phys. Rev. **145**, 599 (1966).

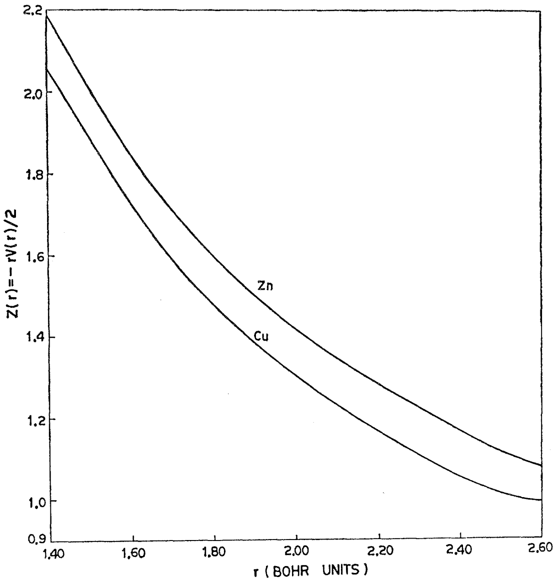

FIG. 1. Charge $Z(r)=-rV(r)/2$ for copper and zinc in disordered β brass at 75°C above the transition temperature.

the x-ray scattering factors of the constituents. The neutron-diffraction technique has been successfully employed to observe the short-range-order diffuse scattering in this alloy. Walker and Keating[12] found that it was not possible to assign unique values to the short-range-order parameters in β brass, because of the long-range nature of the short-range order. They therefore compared the measured scattering with its values calculated from various theoretical approaches and showed that (for 75°C above the critical transition temperature) the short-range-order parameters could be given by a Zernike-type expression

$$|\alpha(r)|=0.540e^{-0.400r'}/r', \tag{22}$$

where $r'=2r/a$, and a is the lattice constant. We have used this expression to calculate the short-range-order parameters employed in the calculation. The calculation of the muffin-tin potentials for the constituents and the matrices $G^{\mathrm{SS}'}$ are easily carried out as discussed in Refs. 5 and 6. Although the disordered β phase is found for a range of Zn concentrations in the vicinity of the 50-50 stoichiometry, we have chosen the concentrations of Cu and Zn atoms to be equal. The lattice parameter was taken to be 2.9907 Å [15] or 5.6514 in atomic units. The radii of the muffin-tin spheres for Cu and Zn were chosen to be equal, and slightly less than the radius of the inscribed sphere. The radius of the inscribed sphere is 2.44724 and the radii of the muffin-tin spheres were both chosen to be 2.41484 in atomic units. The constant part of the muffin-tin potential was chosen to be the average of the Cu and Zn potentials at the sphere radii. We found this value to be -0.9152 Ry. In order to determine the muffin-tin potentials for Cu and Zn, the required overlap was carried through tenth neighbors. While calculating the $G^{\mathrm{SS}'}$, the order of significant neighborhood σ was also set equal to 10. The actual potentials for Cu and Zn employed in the calculation are plotted in Fig. 1.

We have carried out numerical calculations of the spectral densities for states at the symmetry points Γ, H, P, and N of the Brillouin zone. We have chosen to calculate what Soven calls the reduced spectral density,

$$\tilde{\rho}(E,\mathbf{k})=\sum_{K}\rho(E,\mathbf{k}+\mathbf{K}),$$

where $\mathbf{K}$ is a reciprocal-lattice vector, and $\mathbf{k}$ is confined to the first Brillouin zone. This reduced spectral density should be convenient for comparison with the energy-versus-momentum curves of an ordered crystal, which are also defined modulo a reciprocal-lattice vector. The curves for the reduced spectral density $\tilde{\rho}(E,\mathbf{k})$ plotted against E for some of the states are shown in Figs. 2 and 3 and the peak positions in $\tilde{\rho}(E,\mathbf{k})$ for states at the symmetry points Γ, H, P and N are tabulated in Table I. The abscissa in these curves is a dimensionless parameter ϵ in terms of which, the energy is given by $E=(4\pi^2/a^2)\epsilon$. The ordinates give $\tilde{\rho}(E,\mathbf{k})a^3/(4\pi)^2$.

V. DISCUSSION

Beeby[16], and later Ziman[17] also, have shown that for a perfect lattice, the T-matrix approach yields the same

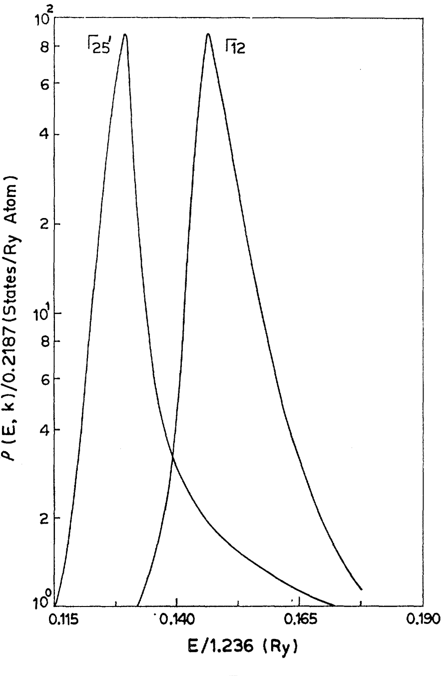

FIG. 2. Spectral density of states for $\Gamma_{25'}$ and Γ_{12} (d-like) states in β brass, plotted as a function of energy.

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[15] W. B. Pearson, *A Handbook of Lattice Spacings in Metals and Alloys* (Pergamon Press, Ltd., London, 1958), p. 177.

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relationship between E and $\mathbf{k}$ as the KR method. It was therefore felt that it may be possible to find a connection between the method of the present paper and the extension of the Kohn-Rostoker method to disordered alloys[5] (PJ). In particular this would indicate the validity of some of the assumptions which were simply "made plausible" in that paper. Of course, the PJ method cannot be compared to the present T-matrix approach in so far as the former neglects the diffuseness in the eigenstates. But we could correlate the peaks in $\tilde{\rho}(E,\mathbf{k})$-versus-$E$ curves and the eigenvalues determined by the PJ method. The sharpness in the spectral density for β brass from this calculation and in α brass from Soven's work, indicates that talking in terms of Bloch-type states is not entirely meaningless. We may therefore regard $\mathbf{k}$ as a fairly good quantum number and deal in terms of eigenstates of PJ method, provided we do not attempt a very detailed interpretation of experimental observations. Examination of Eqs. (12), (13), and (15) shows that, in general, the peak of $\tilde{\rho}(E,\mathbf{k})$ and the zero of $D(E,\mathbf{k})$, the secular determinant of the PJ method are not correlated. However, in the particular case of a randomly occupied lattice, the peak in the $\rho(E,\mathbf{k})$ would be given by $\det|M_1|=0$, which turns out to be the same as $D(E,\mathbf{k})=0$. In other words, the PJ method and the present method are equivalent for the case of randomly occupied lattice. We also know that for such a system, the geometric approximation reduces to the averaged t-matrix approximation employed by Soven. This accounts for the similarity in the results[18] obtained by PJ and Soven for the case of α brass, for which there is no short-range order. The small discrepancies that do exist may be attributed to the differences in the potentials employed in the two calculations.

We now compare the results of the present calculation with the experimental data. Most of the experimental techniques employed for probing the electronic states in the ordered lattices require long electron relaxation times and are therefore not applicable to the disordered alloys. Recourse has therefore been taken to indirect methods such as optical properties, positron annihilation, and the short-range-order diffuse scattering. In a recent work, Moss[19] has conjectured that nonspherical pieces of the Fermi surface may give rise to a detectable singularity in the intensity of diffusely scattered x rays, electrons, or neutrons. He applied the idea to the neutron-scattering curves for β brass, measured by Walker and Keating,[12] and concluded that along $\langle 111\rangle$, $k_F=0.74$ of the Γ-P distance. In order to estimate k_F from our limited calculation we use the Cohen-Heine model,[20] characterizing the band structure in terms of the states Γ_1, N_1, and $N_{1'}$. An effective mass can be defined for the $\Gamma_1-N_{1'}$ band and the Fermi energy obtained. The intersection of E_F with the Γ_1-P_4 band gives $k_F=0.75$ of the $\Gamma-P$ distance. The free-electron value for the ratio is 0.82, and the virtual-crystal approximation gives the value[2] 0.78. Our calculations thus indicate that the Fermi surface normal to $\langle 111\rangle$ is flatter than that given by the VCA. The flatness calculated by us compares surprisingly well with Moss's analysis of the neutron scattering data. We cannot give much credence to Moss's value, as his result is subject to a number of uncertainties. The diffuseness in the Fermi surface as a result of the disorder should erode the singularity and render its observation difficult. It is known[21] that eigenfunction for

TABLE I. Positions of peaks in $\tilde{\rho}(E,\mathbf{k})$-versus-$E$ curves for states of various symmetries in β brass. All energies are in Ry and relative to the muffin-tin zero, $\langle V_c\rangle=-0.9152$ Ry.

State	Energy	State	Energy
Γ_1	0.018	P_4	0.158
$\Gamma_{25'}$	0.160	P_3	0.162
Γ_{12}	0.180	P_4	0.896
H_{12}	0.124	P_1	0.985
$H_{25'}$	0.198	N_1	0.120
H_{15}	1.051	N_2	0.141
H_{12}	1.333	N_1	0.165
H_1	1.693	N_4	0.183
E_F (Cohen-Heine method)	0.511	N_3	0.204
		$N_{1'}$	0.404
		N_1	0.571

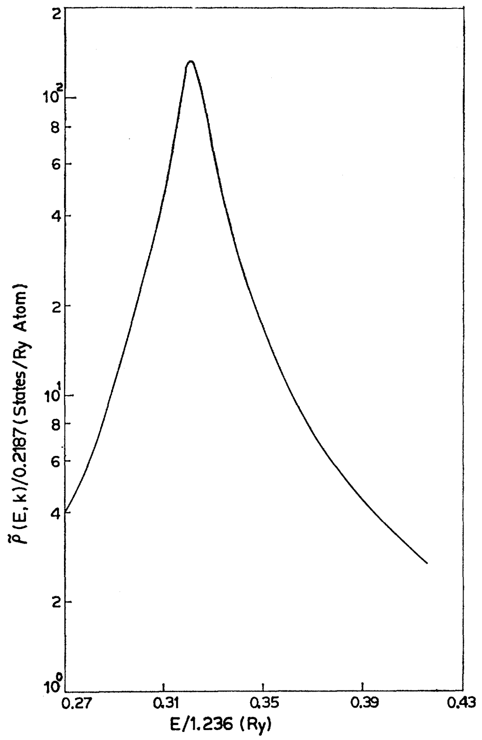

FIG. 3. Spectral density of states for $N_{1'}$ (p-like) state in β brass, plotted as a function of energy.

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wave vectors about half way to the zone edge depart seriously from Bloch waves and the Fermi surface would appear to be a concept of limited utility in this region. Besides, the experimental data used by Moss is of uncertain accuracy near the region of interest. We find the $N_{1'}-N_1$ gap to be 2.2 eV, whereas the value due to Amar, Johnson, and Wang for this gap is 1.5 eV. Thus, our calculation gives a Fermi surface for which the departure from sphericity is greater than that given by the virtual-crystal approximation. In order to carry this comparison further we have calculated the $N_{1'}-N_1$ gap following the method presented in this paper but using atomic potentials for copper and zinc. These were the potentials used by Amar, Johnson, and Wang[2] in their VCA calculation. Our calculation gives a value 2.4 eV for the $N_{1'}-N_1$ gap. Thus the energy gap for the disordered alloy also is sensitive to the choice of potential, but it is clear that striking difference in the values of $N_{1'}-N_1$ gap given by the present method and by the VCA approach originates from the differences in the formalisms. The virtual-crystal approximation is an over simplification of the alloy problem and the present approach may be regarded as in improvement in the sense that it recognizes the distinction between the constituents, takes account of the short-range order, and incorporates the lifetime effects for the electronic states.

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Critique of Current Theories of Akhieser Damping in Solids

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There are two widely used theories of ultrasonic attenuation in the Akhieser ($\Omega\tau\ll1$) regime. Woodruff and Ehrenreich used the Boltzmann equation and found that the attenuation was a function of the specific heat of the thermal phonons. Mason and Bateman obtained the fundamentally different result that the attenuation also involved the thermal energy. It is shown here that the Mason-Bateman theory contains both mathematical and conceptual errors and that its apparent agreement with experimental data on Si and Ge is fortuitous.

I. INTRODUCTION

ULTRASONIC attenuation in dielectric single crystals is usually dominated by interaction of the ultrasonic wave with thermal phonons. If $\Omega\tau<1$ (where Ω is the radian frequency of the ultrasonic wave and τ is a typical thermal-phonon relaxation time), the attenuation occurs via a mechanism first described by Akhieser.[1] Because of the anharmonicity of the medium, the strain produced by the sound wave modulates the frequencies of the thermal-phonon modes. The equilibrium populations of these modes are therefore modulated also. However, the *actual* populations, since they require a time τ to readjust to the new equilibrium conditions, lag in phase behind the driving sound wave. The reestablishment of equilibrium is an entropy-producing process with a consequent absorption of energy from the sound wave.

There have been a number of theoretical treatments of Akhieser damping.[1–8] The most thorough is the work of Woodruff and Ehrenreich[2] who obtain an expression for the attenuation A (on a Debye model with $\Omega\tau\ll1$) in the form

$$A=\beta C_V T\gamma_{\mathrm{av}}^2\Omega^2\tau/3\rho v^3 \quad \text{(nepers/unit length)}, \qquad (1)$$

where C_V is the specific heat per unit volume, T is the absolute temperature, γ_{av} is some average Grüneisen constant, ρ is the mass density, v is the ultrasonic velocity, and β is a numerical factor of order unity which depends on the form assumed for the local equilibrium distribution of thermal phonons.[2] The precise value of β is usually not important since γ_{av} is usually treated as an adjustable parameter.

A different result was obtained by Mason and Bateman,[7] who made the important contribution of considering the anisotropy of the Grüneisen tensor as

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