

Electron states in a crystal with impurity levels near the band edge

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The electron states in a crystal in the presence of impurity levels near the band edge are investigated. The density of states in various regions of the spectrum, including the transition region between the band and fluctuation states, are found by the method of group expansions of the Green functions with respect to the interacting impurity center complexes. The broadening of the individual two-particle levels determining the density of states near the band edge is investigated, and the criteria for the density of the fluctuation states in this region to be a smooth function or to possess a fine structure are obtained. The long-range interaction of the impurities is considered, and the question of localization of the fluctuation states, as well as the question of the mobility threshold, is discussed.

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INTRODUCTION

A large number of investigations have of late been devoted to the study of the essentially statistical energy spectrum of disordered systems (for greater details, see the review article by Elliot *et al.*^[1]). Important qualitative and quantitative results concerning the structure of such spectra as a whole have been obtained by Lifshitz.^[2,3] It is well known that there exist in disordered systems both band (current) states smeared out over the entire volume of the system and localized states whose wave function is concentrated in a finite volume. Anderson^[4] obtained for some model of a disordered system criteria for all the states in the system to be localized. For the case when not all the states are localized, Mott^[5] introduced, for the first time, the concept of mobility threshold as some critical energy separating the region of current states from the region of localized states, the electrical conductivity changing discontinuously when the Fermi level crosses the mobility threshold. At the same time the density of states (as well as any other quantity described by the averaged one-particle Green function) can remain a continuous and analytic function of the energy as the mobility threshold is crossed.^[1,6]

In the present paper we investigate the density of electron states in a crystal with impurity atoms that give rise to levels near the edge of the unperturbed spectrum. For such a system, we have available, besides the description of the band states, certain qualitative and, in individual cases, quantitative results^[2,7,8] pertaining to the localized states connected with the fluctuation-induced agglomeration of two or many impurity atoms. However, these theories did not describe the transition region between the band and fluctuation states.

With the aid of group expansions of the single-particle Green function with respect to the complexes of interacting impurity atoms, we compute below in a unique consistent manner—in much the same way as was done in Refs. 9–12—the density of states in a wide energy range near the edge of the unperturbed spectrum, including (in the case of not too high impurity concentrations) the transition region between the band and fluctu-

ation states. In contrast to our previous paper,^[11] where we solved a similar problem for the vibrational spectrum, here we find the conditions under which the density of states near the renormalized band edge is a smooth function of the energy. If these conditions are not fulfilled, then the density of states may exhibit individual peaks corresponding to pairs, triplets, etc., of impurity atoms located at distances smaller than the average. Furthermore, we find an expression for the unaveraged Green function which describes the interaction between the impurities and which is the analog of the electron wave function. For energies outside the band and transition regions, such a function at great distances decreases exponentially with increasing distance between the impurities, i.e., the states in this energy region are localized. As the transition region is approached, the group expansion for the unaveraged Green function becomes divergent, and it becomes impossible to infer whether or not the state is localized. On the other hand, inside the band, right up to the transition region, the attenuation of the band states over a wavelength is slight, and such states are current states. Consequently, the mobility threshold should, if it exists, be localized in the present model inside the narrow transition region.

1. GROUP EXPANSIONS FOR THE GREEN FUNCTIONS IN A CRYSTAL WITH IMPURITIES

We shall consider the simplest and often-used model for the electron subsystem of a crystal with randomly distributed impurity atoms, in which the change in the potential at an impurity site is taken into account, but the change in the overlap integrals is neglected. In such a model the principal characteristic features of the behavior of a disordered system are manifested. The Hamiltonian of the electron subsystem in the single-band approximation without allowance for the interelectron interaction has the form

$$H = H_0 + H_1, \quad H_0 = \sum_{k,\sigma} \epsilon_k a_{k,\sigma}^+ a_{k,\sigma}, \quad H_1 = V \sum_{i,\sigma} a_{i,\sigma}^+ a_{i,\sigma}. \quad (1)$$

Here

$$a_{i,\sigma} = \frac{1}{N^h} \sum_{\mathbf{k}} a_{\mathbf{k},\sigma} e^{i\mathbf{k}\mathbf{R}_i},$$

where $a_{\mathbf{k},\sigma}^+$, $a_{\mathbf{k},\sigma}$ are the Fermi operators for an electron with wave vector \mathbf{k} and spin σ (we drop the spin indices below), V is the matrix element of the perturbation, the index s runs over the sites occupied by the impurities, and the \mathbf{R}_s are their radius vectors. We shall assume, for simplicity, that the dispersion law obtaining near those extremal points, \mathbf{k}_{0j} , of the Brillouin zone that correspond to the lower band edge E_f has an isotropic character ($\hbar=1$):

$$\epsilon_{\mathbf{k}} = E_f + (\mathbf{k} - \mathbf{k}_{0j})^2 / 2m, \quad m > 0. \quad (2)$$

The group expansions of the equal-time (advanced) Green function

$$\langle\langle A|B \rangle\rangle^{\pm} = -i \int_{-\infty}^{\infty} \langle [A(t), B(0)]_{\pm} \rangle e^{iE t} dt \quad (3)$$

can be carried out in different representations. A completely renormalized representation and an unrenormalized one were constructed earlier^[11,12] which, for the diagonal function $\langle\langle a_{\mathbf{k}}|a_{\mathbf{k}}^+ \rangle\rangle^{\pm}$, respectively assume the forms

$$\langle\langle a_{\mathbf{k}}|a_{\mathbf{k}}^+ \rangle\rangle^{\pm} = (E - \epsilon_{\mathbf{k}} - R_{\mathbf{k}})^{-1}, \quad (4a)$$

$$\langle\langle a_{\mathbf{k}}|a_{\mathbf{k}}^+ \rangle\rangle^{\pm} = (E - \epsilon_{\mathbf{k}})^{-1} + \bar{R}_{\mathbf{k}} (E - \epsilon_{\mathbf{k}})^{-2}. \quad (4b)$$

Let us write down the group expansion of the polarization operator of the unrenormalized representation:

$$R_{\mathbf{k}} = \frac{V}{1 - V\mathcal{G}^0} \frac{1}{N} \sum_{s'} \left(1 + \sum_{s''} \frac{A_{s's'} e^{i\mathbf{k}\mathbf{R}_{s''}} + A_{s's''} A_{s''s'} + \dots \right), \quad (5)$$

$$A_{s's'}^0 = \frac{V}{1 - V\mathcal{G}^0} \mathcal{G}_{s's'}^0, \quad \mathcal{G}_{s's'}^0 = \frac{1}{N} \sum_{\mathbf{k}} \frac{e^{i\mathbf{k}\mathbf{R}_{s''}}}{E - \epsilon_{\mathbf{k}}}, \quad (6a)$$

$$R_{s's'} = R_s - R_{s'}, \quad \mathcal{G}^0 = \mathcal{G}_{s's}^0, \quad (6b)$$

and N is the number of sites in the lattice. In the expansion (5) the first term in the brackets corresponds to electron scattering by isolated impurity atoms; the second, to electron scattering by pairs of impurity atoms, etc. A similar structure is possessed by the group expansion of the renormalized polarization operator $R_{\mathbf{k}}$, where instead of the $\mathcal{G}_{s's}^0$, the components become

$$\mathcal{G}_{s's'} = \frac{1}{N} \sum_{\mathbf{k}} \frac{e^{i\mathbf{k}\mathbf{R}_{s''}}}{E - \epsilon_{\mathbf{k}} - R_{\mathbf{k}}}, \quad (7)$$

and in expressions of the type $A_{s's's''}, A_{s's''s'}, A_{s's's''s'},$ etc., the summation is performed over all the noncoincident wave vectors. In this case the first two terms of the group expansions of $R_{\mathbf{k}}$ and $\bar{R}_{\mathbf{k}}$ coincide in form.

As is well known, a number of physical quantities (the density of states, the cross section for light absorption, etc.) are determined by the diagonal Green function. For their determination, it is necessary to average the expressions (4) over the random distribution of the impurity centers, it being possible, on account of the self-averaging nature of the diagonal function, (4a), in the renormalized representation, to directly average the

polarization operator.^[10,12] As can be seen from (5), the group expansions are constructed in such a way that the summation in each term is performed over the noncoincident impurity states. As a result, the averaging amounts to the replacement of each sum over the impurity sites s by a sum, multiplied by the impurity concentration c ($c = n/N$, where n is the number of sites occupied by impurities), over all the sites l . It is convenient to transform the averaged renormalized representation in such a manner that we can neglect in it the limitations in the summation over the wave vectors. As a result, we have

$$\bar{R}_{\mathbf{k}} = \frac{cV}{1 - V\mathcal{G}} \left(1 - cA_{00} - cA_{00}^2 + c \sum_{l \neq 0} \frac{A_{0l} e^{i\mathbf{k}\mathbf{R}_{0l}} + A_{0l}^{\dagger}}{1 - A_{0l}^2} + \dots \right). \quad (8)$$

Besides the foregoing, other representations of the Green functions are also possible. Below we shall also use a representation that is renormalized to first order in the concentration:

$$\langle\langle a_{\mathbf{k}}|a_{\mathbf{k}}^+ \rangle\rangle^{\pm} = (E - \epsilon_{\mathbf{k}} - R^{\dagger})^{-1} + \bar{R}_{\mathbf{k}}^{\dagger} (E - \epsilon_{\mathbf{k}} - R^{\dagger})^{-2}; \quad (9)$$

$$\bar{R}_{\mathbf{k}}^{\dagger} = \frac{V}{1 - V\mathcal{G}^{\dagger}} \frac{1}{N} \sum_{s'} \frac{A_{s's'}^{\dagger} e^{i\mathbf{k}\mathbf{R}_{s''}} + A_{s's''}^{\dagger} A_{s''s'}^{\dagger} + \dots}{1 - A_{s's'}^{\dagger} A_{s's''}^{\dagger}}. \quad (10)$$

Here

$$R^{\dagger} = cV(1 - V\mathcal{G}^{\dagger})^{-1}, \quad \mathcal{G}^{\dagger} = \mathcal{G}_{s's'}^{\dagger}, \\ \mathcal{G}_{s's'}^{\dagger} = \frac{1}{N} \sum_{\mathbf{k}} \frac{e^{i\mathbf{k}\mathbf{R}_{s''}}}{E - \epsilon_{\mathbf{k}} - R^{\dagger}}, \quad A_{s's'}^{\dagger} = \frac{V}{1 - V\mathcal{G}^{\dagger}} \mathcal{G}_{s's'}^{\dagger},$$

where in expressions of the type $A_{s's'}^{\dagger}, A_{s's''}^{\dagger},$ etc., the wave vectors in neighboring cofactors do not coincide. After averaging, (10) assumes a form similar to (8), but with the first term in the brackets absent.

Notice that the regions of convergence of the group expansions of the various representations do not, generally speaking, coincide, and below one or another representation will be used, depending on the convergence of its group expansion.

2. CONVERGENCE OF THE GROUP EXPANSIONS AND THE DENSITY OF STATES IN THE NEIGHBORHOOD OF THE BAND EDGE

In the vicinity of the band edge, the resonance denominator, $1 - V\mathcal{G}^0$, entering into (5) and (6) can be represented in the form

$$1 - V\mathcal{G}^0 = \left(\frac{\pi}{2} \right)^{1/2} \frac{z_0 V}{E_1} (c_0 - \alpha); \quad (11)$$

$$\alpha = \left(\frac{E_f - E}{E_1} \right)^{1/2} \ll 1, \quad (12)$$

where the quantity E_1 is of the order of the band width (for a simple cubic lattice $E_1^{-1} = ma^2/\pi$), $a = v^{1/3}$, v being the volume of the unit cell, z_0 is the number of extreme points of the Brillouin zone that correspond to E_f . Below the parameter $|c_0|z_0$ plays the role of a characteristic impurity concentration.

Let the perturbation V be such that

$$|c_0| < 1. \quad (13)$$

In such a case an isolated impurity atom in the crystal creates a localized level whose energy lies near the band edge (when $c_0^{1/3} > 0$, a localized level with energy $E_0 = E_g - c_0^{2/3} E_1$ splits off from the band, while when $c_0^{1/3} < 0$, a virtual level exists within the band).

A complex spectral distribution arises at a finite impurity concentration, the band states being preserved and there arising fluctuation levels separated from the band states by a transition region. The density of electron states of such a disordered crystal can be found from the well-known relation

$$-g(E) = \frac{1}{\pi N} \text{Im Sp } \hat{G}(E) = \frac{2}{\pi N} \text{Im} \sum_{\mathbf{k}} \overline{\langle a_{\mathbf{k}} | a_{\mathbf{k}^+} \rangle^2}, \quad (14)$$

where the factor 2 takes account of the spin states. The averaged diagonal Green function

$$\overline{\langle a_{\mathbf{k}} | a_{\mathbf{k}^+} \rangle^2}$$

can be taken in any of the above-considered representations: In this case the completely renormalized representation (4a) turns out to be convergent within the band and the states can be described with the aid of plane waves.

A. Let us first consider the case when the impurity concentration is less than the characteristic quantity: $c \ll |c_0| z_0$. The band states are then described by the dispersion law

$$E_{\mathbf{k}} = \varepsilon_{\mathbf{k}} + \Delta_0 [1 + (\kappa(\varepsilon_{\mathbf{k}}))^2]^{-1/2} \quad (15)$$

and the decrement

$$\gamma_{\mathbf{k}} = \Delta_0 \kappa(\varepsilon_{\mathbf{k}}) [1 + (\kappa(\varepsilon_{\mathbf{k}}))^2]^{-1/2}; \quad (16)$$

$$\kappa(E) = \left(\frac{\pi}{2}\right)^{1/2} \frac{E_1 g(E)}{z_0 c_0^{1/2}}, \quad \Delta_0 = \left(\frac{2}{\pi}\right)^{1/2} \frac{c E_1}{z_0 c_0^{1/2}}. \quad (17)$$

The quantity Δ_0 determines the shift of the edge of the band states.

The expressions (15) and (16) are valid as long as $|\mathbf{k} - \mathbf{k}_{\text{min}}| \gg k_{\text{min}}$, where $k_{\text{min}} = c / (a z_0 c_0^{2/3})$; the attenuation over a wavelength is then slight. The minimum wave-vector value k_{min} allows us to estimate the width of the transition region, which width turns out to be of the order of Δ_1 , where

$$\Delta_1 = \frac{c^2 E_1}{2\pi z_0^2 c_0^{1/2}} \ll \Delta_0. \quad (18)$$

The density of states $g(E)$ within the band is, up to terms of higher order in $c / (|c_0| z_0)$, equal to

$$g(E) = g_0 \left(E + \Delta_1 - \frac{\Delta_0 c_0^{1/2}}{c^{1/2} + |\bar{\alpha}|} \right). \quad (19)$$

Here $\bar{\alpha}^2 = (E_g + \Delta_0 - E) / E_1$, while

$$g_0(E) = \left(\frac{2}{\pi}\right)^{1/2} \frac{z_0}{E_1} \left(\frac{E - E_g}{E_1}\right)^{1/2}$$

is the density of states in the unperturbed crystal.

The fluctuation states arise as a result of the random agglomeration of the impurity atoms. Their energy spectrum is, generally speaking, a collection of δ -function peaks corresponding to the poles of the individual terms of the group expansion. Since $|c_0| \ll 1$, the repulsion of the levels in pairs of impurities located at distances considerably greater than the interatomic distances, leads to a situation in which the corresponding two-center levels fairly densely fill the fluctuation spectral region adjoining the edge of the band states (such pairs produce virtual levels inside the band). It is convenient to describe the density of states in this region ($\bar{\alpha}^2 > 0$) with the aid of the representation (9), which takes account of the shift of the edge of the band states. Replacing in the corresponding averaged group expansion the summation over the discrete sites l by integration, we obtain the density of states averaged over an energy interval greater than the distance between the individual two-center levels. In this case, when $\bar{\alpha}^2 \gg \Delta_1 / E_1$, the group expansion turns out to be convergent, and the density of states is determined by the contribution from the two-center levels. Taking into account the fact that the quantity A_{0l}^1 has, for $\bar{\alpha}^2 > 0$, the form

$$A_{0l}^1 = \frac{\sigma_{0l} a \exp(-\bar{\alpha} (2\pi)^{1/2} R_{0l} / a)}{(2\pi)^{1/2} R_{0l} (\bar{\alpha} - c_0^{1/2})}, \quad (20)$$

where

$$\sigma_{0l} = \frac{1}{z} \sum_{j=1}^{z_0} \exp(ik_{0j} R_{0l}),$$

we obtain

$$g(E) = \frac{c^2}{(2\pi)^{1/2} E_1 \bar{\alpha} |\bar{\alpha} - c_0^{1/2}|} \sum_l n_l(R_l) \frac{1 - |\sigma_l| \exp(-\bar{\alpha} R_l) \text{sign}(c_0^{1/2} - \bar{\alpha})}{1 + \bar{\alpha} R_l}. \quad (21)$$

Here n_l is the relative number of the l sites, where the quantity σ_{0l} assumes the value σ_l and R_l is determined by the equation

$$R_l = |\sigma_l| |\bar{\alpha} - c_0^{1/2}|^{-1} \exp(-\bar{\alpha} R_l). \quad (22)$$

Let the structural factor

$$\chi = \frac{z_0}{2} \sum_l n_l |\sigma_l|^2 (1 - |\sigma_l| \text{sign } c_0^{1/2}) \quad (23)$$

be nonzero (in the general case $\chi \geq 0$, since $|\sigma_l| \leq 1$). Then near the band edge the expression (21) becomes equal to $(2/\pi)^{1/2} c^2 \chi / (z_0 E_1 c_0^{4/3} \bar{\alpha})$; it is valid, as has already been noted, when $\bar{\alpha}^2 \gg \Delta_1 / E_1$, and diverges as $\bar{\alpha} \rightarrow 0$.

In the case of the appearance of a localized level, the group expansion (9) ceases to converge in the vicinity of this level, where $|E - E_0| \sim c^{1/2} c_0^{-1/6} E_1$. At the same time the unrenormalized representation (4b) converges here, the density of states being described, as before, by the formula (21), where we need only replace $\bar{\alpha}$ by α . In this case, when $|\alpha - c_0^{1/3}| \ll c_0^{1/3}$, the density of states assumes, according to (21) and (22), the form^[2]

$$g(E) = \frac{c^2(1-n_0)}{(2\pi)^{1/2} E_1 c_0^{1/2} (\bar{\alpha} - c^{1/2})} \ln^2 \left| \frac{c_0^{1/2}}{\alpha - c_0^{1/2}} \right|, \quad (24)$$

where n_0 corresponds to $\sigma_0 = 0$. The expression (24) is applicable outside a narrow neighborhood (of width of the order of the concentration broadening, Δ_2 , of the local level) of the energy E_0 , where none of the group expansions converges. In the $c \ll |c_0|z_0$ case under consideration, we can show that

$$\Delta_2 \sim (cc_0)^{1/2} \exp[-\gamma(c_0/c)^{1/2}], \quad \gamma \sim 1.$$

Notice that the performed analysis is, when $\bar{\alpha}^2 \sim 1$, also inapplicable far from the band edge, where the density of states is determined by the agglomeration of a large number of impurities.

If in the region adjoining the band edge the broadening of the two-center fluctuation levels is greater than the level spacing, then the replacement of the summation over l by integration can be justified also in the case of the completely renormalized representation (4a). The corresponding group expansion (8) turns out to be convergent with respect to the small parameter $c/|c_0|z_0$ both inside the band and in the transition and fluctuation regions (but not too close to a local level). Substituting (4a) and (8) into (14), we obtain, similar to what was obtained in Ref. 12, a self-consistent equation for the determination of the density of states. It is not difficult to show by solving this equation with allowance for the two-impurity clusters that, for $\chi > 0$, the density of states near the band edge ($|\bar{\alpha}| \ll c_0^{1/3}$) can be represented up to terms of higher order in smallness in the parameter $c/|c_0|z_0$ in the form

$$g(E) = \left(\frac{2\Delta_1}{\pi E_1} \right)^{1/2} \frac{z_0}{E_1} f\left(\bar{\alpha}^2 \frac{E_1}{\Delta_1}\right), \quad (25)$$

where $f(x)$ is a universal function not depending on the impurity concentration and being the only real and positive root of the equation

$$f^4 + xf^2 - (f + 2\pi\chi)^2 = 0. \quad (26)$$

For $-\bar{\alpha}^2 \gg \Delta_1/E_1$ the expression (25) goes over into (19) while for $\bar{\alpha}^2 \gg \Delta_1/E_1$ it goes over into (21). In the intermediate region, $f(x)$ can easily be tabulated for a given χ . The plot of $f(-x)$ for $\chi = 1$ is shown in Ref. 12.

A distinct case is the $\chi = 0$ case, which obtains when to the band edge E_* corresponds the only extremal point $k_0 = 0$, while the impurity is such that $c_0^{1/3} > 0$. In this case the density of states is described inside the band and in the transition region (except at the outer edge) by the expression (19) and in the fluctuation region ($\bar{\alpha}^2 > 0$) by the expression (21), which in this case remains finite as $\bar{\alpha} \rightarrow 0$. If we can replace the summation over the sites by integration, then there also exists for the $\chi = 0$ case a systematic procedure, similar to the one described earlier in Ref. 12, with the aid of which the density of states can be obtained in the form of a continuous function in the entire energy region under consideration. Whereas for $\chi \neq 0$ it was sufficient to take account of only the two-impurity clusters, for $\chi = 0$ we should also consider the three-impurity clusters. How-

ever, the latter clusters turn out to be important only at the edge of the transition region, where the expressions (19) and (21) join smoothly onto each other. Notice that the thus obtained density of states cannot be represented near the band edge with the aid of a universal function like (25).

B. At high impurity concentrations, when $c \gg |c_0|z_0$, the region, Δ_2 , of the concentration broadening of an impurity level, where every group expansion diverges, turns out to be of the order of $(c/z_0)^{2/3} E_1$, and exceeds both the width of the transition region and the distance from the level to the band edge. Inside the band, allowance for the group expansions leads to small corrections to the density of states, corrections which were given earlier in Ref. 12. In the fluctuation region of the spectrum, where $\bar{\alpha}^2 \gg \Delta_2/E_1$, the density of states is described, as before, by the formula (21), and is equal to

$$g(E) = \frac{c^2}{(2\pi)^{1/2} E_1 \bar{\alpha}^3} \sum_i n_i \xi_i^2, \quad \xi_i = |\sigma_i| e^{-\xi_i}. \quad (27)$$

The expression (27) coincides in form with the one obtained in Ref. 8.

3. BROADENING OF THE TWO-CENTER LEVELS AND THE CRITERIA FOR THE RESOLVABILITY OF THE FINE STRUCTURE IN THE DENSITY OF STATES

To derive for $c \ll |c_0|z_0$ the density of states (25), which is continuous in the vicinity of the band edge, we assumed that the broadening of the individual two-center levels was greater than the level spacing. If these conditions are not fulfilled, then the density of states in the transition region cannot be derived with the aid of the above-considered group expansions. Nevertheless, the representation (9) can be used in the fluctuation region in this case, and in the density of states can be resolved peaks that correspond to the individual levels. The expression (21) is then proportional to the probability for the appearance at the given energy of the most intense (two-center) fluctuation levels, and describes the energy-averaged density of states.

The two-center level energy E_{ss} , can, as can be seen, for example, from (5) and (8), be determined from the condition $\Delta_{ss}(E_{ss}) = 0$, where

$$\Delta_{ss}(E) = 1 - A_{ss}^1 A_{ss}^1, \quad (28)$$

and is a function of R_{ss} and σ_{ss} . To the levels adjoining the band edge correspond such distances, R_{ss} , between the impurities that

$$R_{ss} \cdot \text{sign } c_0^{1/2} \geq a |\sigma_{ss}| c_0^{-1/2} (2\pi)^{-1/2}. \quad (29)$$

The possible values of R_{ss} in the lattice have a discreteness $\Delta R_{ss} \sim a^2/2R_{ss}$ ($R_{ss} \gg a$). The corresponding discreteness of the energy levels is equal to $\Delta E_{ss} = (\partial E_{ss}/\partial R_{ss}) \Delta R_{ss}$, where in the region $0 < \bar{\alpha}^2 \ll c_0^{2/3}$

$$\frac{\partial E_{ss}}{\partial R_{ss}} = c_0^{1/2} E_1 / a (2\pi)^{1/2} \quad (30a)$$

for a) $\chi = 0$, b) $\chi \neq 0$, $|\sigma_{ss}| \text{sign } c_0^{1/3} = 1$ and

$$\frac{\partial E_{ss'}}{\partial R_{ss'}} = \frac{c_0^{1/2} E_1 (c_0^{1/2} - a |\sigma_{ss'}| (2\pi)^{1/2} R_{ss'} \text{sign } c_0^{1/2})}{R_{ss'} (1 - |\sigma_{ss'}| \text{sign } c_0^{1/2})} \quad (30b)$$

for $\chi \neq 0$, $|\sigma_{ss'}| \text{sign } c_0^{1/2} \neq 1$.

If we allow for the interaction of the impurity pair s and s' with distant impurities s'' , then the line shape of the two-center level E_{ss} is determined by the expression $f_{ss'}(\Delta_{ss'}(E))$, where

$$f_{ss'}(\Delta) = \frac{1}{\pi} \text{Im} \left(\Delta - \sum_{s'' \neq s, s'} F_{ss''} \right)^{-1} \quad (31)$$

Here

$$F_{ss''} = A_{ss''} A_{s's''} + A_{s's''} A_{ss''} + 2A_{ss''} A_{s's''} A_{s's''}$$

and the bar denotes averaging over the random distribution of the impurities s'' . Carrying out this averaging for $c \ll 1$, we obtain

$$f_{ss'}(\Delta) = \int_{-\infty}^{\infty} \exp(it\Delta - \varphi_{ss'}(t)) dt, \quad (32)$$

where

$$\varphi_{ss'}(t) = c \sum_{l=s, s'} (1 - \exp(itF_{ss'l})).$$

Taking into account the fact that the dominant contribution to the line broadening is due to the impurities s'' , located at distances R from the sites s and s' of the order of the mean interimpurity distance \bar{r} ($\bar{r} = (4\pi/3)^{1/3} c^{-1/3} a \gg R_{ss'}$), and that F is a smooth function of R , we can go over in (32) from summation over l to integration (with allowance for the discrete values of σ_{ls} , $\sigma_{s'l}$). As a result, we obtain for $\bar{\alpha} < c^{1/3}$

$$f(\Delta) = \frac{2}{\Gamma_1} \int_0^{\infty} \cos\left(\frac{\Delta}{\Gamma_1} t\right) \exp(-t^{1/\chi}) dt, \quad \Gamma_1 \approx 3.06\lambda(\chi) \left(\frac{c}{c_0}\right)^{1/\chi}, \quad \chi \neq 0, \quad (33)$$

$$f(\Delta) = \frac{2}{\Gamma_2} \int_0^{\infty} \cos\left(\frac{\Delta}{\Gamma_2} t\right) \exp(-t^{1/4}) dt, \quad \Gamma_2 \approx 0.44 \left(\frac{c}{c_0}\right)^{1/4}, \quad \chi = 0.$$

The factor $\lambda(\chi) = 1$ when $\chi = 1$. The quantities Γ_1 and Γ_2 play the role of distribution widths on the scale of $\Delta_{ss'}(E)$. Their power dependence on c stems from the fact that, when $\bar{\alpha} < c^{1/3}$, the expression for F when $R \sim \bar{r}$ is a power function of R , i.e., is $\propto \bar{R}^{-2}$ when $\chi \neq 0$ and $\propto R^{-4}$ for $\chi = 0$. If, on the other hand, $\bar{\alpha} > c^{1/3}$, then the behavior of F becomes, when $R \sim \bar{r}$, exponential, and the distribution width is of the order of

$$\Gamma \sim F(\bar{r}) = \frac{c^{1/\chi}}{(\bar{\alpha} - c^{1/\chi})^{1/\chi}} \exp\left(-\frac{\bar{\alpha}}{c^{1/\chi}} \left(24 \sqrt{\frac{\pi}{2}}\right)^{1/\chi}\right), \quad \chi \neq 0, \quad (34)$$

$$\Gamma \sim F(\bar{r}) = \frac{\bar{\alpha}^2 c^{1/4}}{c^{1/4}} \exp\left(-\frac{\bar{\alpha}}{c^{1/4}} \left(24 \sqrt{\frac{\pi}{2}}\right)^{1/4}\right), \quad \chi = 0.$$

Notice that, for the model under consideration, the inhomogeneous broadening, which is described by the expression (31), predominates outside the region, Δ_2 , of concentration broadening of the local level, exceeding the broadening due to the other mechanisms (for example, due to the resonance two-pair interaction).

Comparing the broadenings Γ_1 and Γ_2 with the level discreteness on the scale of $\Delta_{ss'}(E)$, which is equal to

$$\frac{2\Delta R_{ss'}}{R_{ss'}} \left(1 + \frac{\bar{\alpha} R_{ss'}}{a} (2\pi)^{1/2}\right),$$

we can easily see that, when $\bar{\alpha} \leq c^{1/3}$, the broadening of the two-center levels is greater than their discreteness if the impurity concentration satisfies the conditions

$$\begin{aligned} c \gg c_0^2, \quad \chi \neq 0, \\ c \gg c_0^{1/2}, \quad \chi = 0. \end{aligned} \quad (35)$$

This result will also be valid in this case for the higher-order fluctuation levels. As a result, any arbitrarily slight bare broadening guarantees a smearing out of the fine structure in the density of states in this energy region. In this case, as has already been noted, we can go over from summation over the discrete indices l to integration in the completely renormalized representation (4a), and the density of states in the transition region is described by the expression (25) (or by the analogous expression for $\chi = 0$).

As can be seen from (34), the broadening of the fluctuation levels decreases as we go away from the band edge, and in the region where

$$\begin{aligned} \bar{\alpha} \gg c^{1/2} \ln(c/c_0^2), \quad \chi \neq 0, \\ \bar{\alpha} \gg c^{1/2} \ln(c/c_0^{1/2}), \quad \chi = 0, \end{aligned} \quad (36)$$

the density of states ceases to be a smooth function of the energy and the peaks corresponding to the individual levels get resolved. If the conditions (35) are not fulfilled, then the individual levels are resolved in the entire fluctuation region (with the exception of a narrow neighborhood, $\Delta_2(cc_0)^{-1/6} \gg \Delta_2$, of the local level), and the transition region cannot be described with the aid of the considered group expansions. A similar consideration for high concentrations ($c \gg |c_0|z_0$) shows that the individual two-center levels are resolved when

$$E_c - E > c^{1/2} E_1 \ln^2(1/c) \quad (37)$$

(it can be seen that this difference exceeds the concentration broadening ($\sim c^{2/3} E_1$) of a localized level).

4. INTERACTION OF THE IMPURITY CENTERS AND THE CONDITIONS FOR THE LOCALIZATION OF THE FLUCTUATION STATES

Let us consider the unaveraged, nondiagonal Green function $\langle\langle a_s | a_{s'}^+ \rangle\rangle^E$, which describes the amplitude of the probability that an electron in a state with energy E is located at time $t = \infty$ at the site s' if at $t = 0$ it was located at the site s . According to Anderson,^[4] the behavior of such a function at great distances $R_{ss'}$, determines whether or not the state with energy E is localized.

Using, for example, the representation that is renormalized to first order in the concentration, we can derive for the function $\langle\langle a_s | a_{s'}^+ \rangle\rangle^E$ the following group expansion:

$$\langle a_s | a_{s'} \rangle^E = \frac{1}{V(1-V\mathcal{G}^1)} \left(\frac{A_{ss'}}{\Delta_{ss'}} + \sum_{s'' \neq s, s'} \frac{A_{ss''} F_{ss''} / \Delta_{ss''} + A_{s''s'} A_{s''s'}}{\Delta_{ss''} - F_{ss''}} + \dots \right) \quad (38)$$

The expression (38) is a complex function of $R_{ss'}$ and E , and each term in it, starting from the second, is a random quantity which depends on the random arrangement of the impurities with respect to the selected sites s, s' . If the first term exceeds both the mean values and the mean fluctuations of the subsequent terms, then the series (38) is convergent in the statistical sense, and it can be approximated by the expression (for $|A_{ss'}^1| \ll 1$)

$$\langle a_s | a_{s'} \rangle^E = \frac{A_{ss'}}{V(1-V\mathcal{G}^1)} = \left(\frac{\pi}{2} \right)^{1/2} \frac{E_i (\text{Re } \mathcal{G}^0(E_i))^2 \exp(-\bar{\alpha} R_{ss'} (2\pi)^{1/2} / a)}{R_{ss'} (\bar{\alpha} - c_0^h)^2} \quad (39)$$

Let us consider the region of the spectrum where $\bar{\alpha} > 0$ and, for simplicity, let us restrict ourselves to the case $z_0 = 1$. We can show, with allowance for the limitations in the summation over k in quantities of the type $A_{ss''}^1, A_{s''s'}^1$, that at sufficiently large distances $R_{ss'}$, such that $|A_{ss'}^1| \ll 1$, the mean value of the random quantities from (38) in the given region are small, and therefore we should estimate their fluctuations. The greatest contribution is made by the fluctuations in the quantity

$$X_{ss'} = \sum_{s''} A_{ss''}^1 A_{s''s'}^1 \quad (40)$$

Here we should, generally speaking, drop in the sum over s'' , the terms for which $|F_{ss''s''}| \geq 1$, but these limitations will not be important below. The probability distribution for the quantity $X_{ss'}$ has the form

$$P(X) = \int_{-\infty}^{\infty} \exp(iXt - \psi_{ss'}(t)) dt \quad (41)$$

where

$$\psi_{ss'}(t) = c \sum_i (1 - \exp(-itA_{ii}^1 A_{ii}^1))$$

Bearing in mind that $\bar{X}_{ss'} \ll A_{ss'}^1$, let us compare $A_{ss'}^1$ with the width, $\Gamma_{ss'}$, of the distribution $P(X_{ss'})$, which width can be estimated from the condition $\psi_{ss'}(\Gamma_{ss'}^{-1}) \sim 1$. In the expression (39), the characteristic decay range of the function $\langle \langle a_s | a_{s'} \rangle \rangle^E$ is $a/\bar{\alpha}$; therefore, we shall consider the values of $R_{ss'} \gg a/\bar{\alpha}$. It can be shown that at sufficiently large $R_{ss'}$, the width of the distribution (41) is of the order of

$$\Gamma_{ss'} \sim A_{ss'} \left(\frac{c}{\bar{\alpha}(\bar{\alpha} - c_0^h)^2} \ln \frac{\bar{\alpha} R_{ss'}}{a} \right)^{1/2} \quad (42)$$

It can be seen from this that, for the group expansion (38) to converge, it is necessary that

$$\bar{\alpha} \gg c/c_0^{1/2}, \quad |\bar{\alpha} - c_0^h| \gg c^h/c_0^{-1/2} \quad (43a)$$

when $c \ll |c_0|$, which is valid outside the transition region and outside some neighborhood of the local level, or that

$$\bar{\alpha} \gg c^h \quad (43b)$$

when $c \gg |c_0|$. Furthermore, the condition $R_{ss'} < R_{11m}$, where

$$R_{11m} = \frac{a}{\bar{\alpha}} \exp \left(\frac{\bar{\alpha}(\bar{\alpha} - c_0^h)^2}{c} \right) \quad (44)$$

should be fulfilled.

At greater distances the "direct" interaction of the impurities, which is described by the expression (39), is replaced by an "indirect" interaction via intermediate impurity centers.

Thus, in the above-indicated regions of the spectrum the Green function $\langle \langle a_s | a_{s'} \rangle \rangle^E$, which is the analog of the wave function of an electron with energy E , is described by the expression (39) for $R_{ss'} < R_{11m}$. Since here $R_{11m} \gg a/\bar{\alpha}$, there exists a fairly broad region of $R_{ss'}$ values where the wave function falls off exponentially with the range $a/\bar{\alpha}$. Therefore, in accordance with Anderson's analysis,^[4] the states with such an energy are localized states. This is also corroborated by the fact that, as shown above, the width of the individual levels is determined by the inhomogeneous broadening.

As the transition region is approached, the localization radius increases like $(E - E_g - \Delta_0)^{-1/2}$, attaining a value $\sim ac_0^{2/3}/c$. On the other hand, inside the band (outside the region Δ_1), the states are current states and, as can be seen from (15) and (16), the mean free path, as the transition region is approached, is also of the order of $ac_0^{2/3}/c = 1/k_{\min}$. Thus, in the present model, in which an impurity level is located near the band edge and other electron-level broadening mechanisms are not considered, the transition from current states to localized states occurs inside the transition region Δ_1 , where the mobility threshold introduced by Mott^[5] may, consequently, be located.

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