

# Electron spectrum of crystal in the presence of large-radius impurity states

M. A. Ivanov and Yu. G. Pogorelov

*Metal-Physics Institute, Ukrainian Academy of Sciences*

(Submitted 2 July 1978)

*Zh. Eksp. Teor. Fiz.* 76, 1010-1022 (March 1979)

The spectrum of the electronic states in a nonideal crystal is investigated within the framework of the hybrid  $s$ - $d$  model with the aid of group expansions of the diagonal Green's function in terms of complexes of interacting impurity centers. It is shown that in the presence of large-radius impurity states the system has a characteristic impurity concentration at which a qualitative restructuring of the crystal spectrum takes place. The conditions for the onset of an impurity zone, in which the states are characterized by a quasimomentum, are obtained. Crossing restructuring of the spectrum with production of a quasigap is also considered and the possibility of a phase transition in this case is discussed. The structure of the spectrum in various energy regions is analyzed at various ratios of such system parameters as the impurity concentration, energy of the impurity levels, and energy of the interaction between these levels. The limiting permissible values of the wave vector in the impurity band are determined and the question of the minimum metallic conductivity in this band is considered.

PACS numbers: 71.55.Dp, 71.10.+x, 72.15.Eb, 64.70.Kb

## 1. INTRODUCTION

A very important model for the description of the spectra of elementary excitations in a crystal with impurities is one in which the potential of the perturbation introduced by the impurity is assumed fixed and short-range, while the scatter of the energy levels is determined by the indirect interaction between the impurities. An investigation of the spectra of nonideal crystals within the framework of this model was initiated by Lifshitz. From among the large number of these systems, considerable interest attaches to crystals with impurity states whose energies lie near the edge of the unperturbed spectrum, so that the radius of these states is  $r_0 \ll v^{1/3}$ , where  $v$  is the volume of the unit cell.

An important property of a system with impurity states of large radius is the presence in it of a small parameter  $c_0 \sim 3v/4\pi r_0^3$ , which assumes the role of the characteristic relative concentration of the impurity centers. This has made it possible to develop a rather simple procedure for describing the spectra of elementary excitations in systems with non-Coulomb states, based on expansion of the diagonal Green's function in complexes of interacting impurity centers.<sup>3-7</sup> Since an important role is played in such a description by the interaction between impurities separated by large distances, the developed method turns out to be valid when the relative concentration of the impurities  $c$  is small ( $c \ll 1$ ). The energy levels corresponding to different pairs of interacting impurities fill in this case quite densely an extensive region of the spectrum, and we can confine ourselves in the group expansion to these pairs only. As a result, both at  $c \ll c_0$  and at  $c \gg c_0$  it is possible to obtain the density of states in a wide range of energies.

The restructuring of the spectrum was considered for different systems at relatively high concentrations,

$c \gg c_0$  (but  $c \ll 1$ ). This restructuring varied with the model: crossing splitting of the spectrum with onset of a quasigap could occur,<sup>3,4</sup> or an impurity band in which the states are characterized by a quasimomentum could<sup>5</sup> or did not<sup>6,7</sup> appear.

In all these cases, the simplest model of an impurity center was used, wherein the perturbation was characterized by a single parameter that determined both the energy of the impurity level and the interaction between the impurities. In the present paper we consider a more general case, when the energy of the impurity state and the interaction between the impurities are characterized by different parameters. This makes it possible to clarify the general picture of the restructuring of the spectrum of a nonideal crystal at high ( $c \gg c_0$ ) impurity concentrations, and makes it possible to find a criterion for production of the impurity band, while the states are described by a wave vector, and also of crossing restructuring with formation of a quasi-gap. To satisfy this criterion the interaction between the impurities at average distances  $\sim v^{1/3}c^{-1/3}$ , must be smaller than the difference between the energy of the impurity level and the renormalized edge of the band.

We shall use the hybrid  $s$ - $d$  model proposed by Anderson,<sup>8</sup> which describes, for example, the interaction of impurity  $d$  or  $f$  states with  $s$  electrons of the continuous spectrum. Such a model is used to describe the behavior of the impurities of transition and rare-earth elements both in metals<sup>9</sup> and in semiconductors.<sup>10</sup> We shall analyze the law within the framework of this model the character of the electron spectrum near the edge of an unfilled band (electron or hole) at different ratios of the impurity-system parameters. We discuss questions concerning the character of the Anderson transitions in the given system with minimum metallic electric conductivity in the impurity band.

## 2. SYSTEM HAMILTONIAN AND GREEN'S FUNCTION

Assume that near the edge of an unfilled electron band there is also an unfilled impurity level whose wave function is localized mainly on the impurity site (e.g.,  $d$  or  $f$  states), and the corresponding probabilities of jumps from the impurity sites to neighboring ones decrease exponentially with distance. The behavior of electron in such a system, as is well known, can be described within the framework of the Anderson Hamiltonian<sup>8</sup>

$$\mathcal{H} = \sum_{\mathbf{k}} \varepsilon_{\mathbf{k}} a_{\mathbf{k}}^{\dagger} a_{\mathbf{k}} + \varepsilon_0 \sum_p a_p^{\dagger} a_p + N^{-1/2} \sum_{\mathbf{k}, p} (\gamma_{\mathbf{k}} e^{i\mathbf{k}\mathbf{R}_p} a_{\mathbf{k}}^{\dagger} a_p + \text{H.c.}), \quad (1)$$

where  $a_{\mathbf{k}}^{\dagger}$  and  $a_{\mathbf{k}}$  are the Fermi operators of the band electrons with wave vector  $\mathbf{k}$  and energy  $\varepsilon_{\mathbf{k}}$  in the unperturbed crystal (we omit the spin indices throughout),  $\varepsilon_0$  is the unperturbed energy of the impurity state,  $a_p^{\dagger}$  and  $a_p$  are the operators for the creation and annihilation of an electron on the impurity sites  $p$ , and  $N$  is the number of sites in the lattice. The parameter  $\gamma_{\mathbf{k}}$  describes the hybridization of the band and impurity states and is determined by the integrals of the jumps from the impurity site to neighboring sites. These integrals decrease rapidly with distance, and for the low impurity concentrations considered by us ( $c \ll 1$ ) the direct jumps between the different impurity sites can be neglected. In addition, since not all the states are filled, we have left out of (1) the terms that describe the Coulomb correlation between the electrons (the parameter  $U$  of the Anderson model<sup>8</sup>). All the arguments that follow are valid also for the case of a completely filled ground-state band and an impurity level.

The state density of the system described by the Hamiltonian (1) is expressed in terms of equal-time advanced Green's functions<sup>11</sup> as follows:

$$\rho(E) = \rho_1(E) + \rho_2(E), \quad (2)$$

where

$$\rho_1(E) = \frac{2}{\pi N} \text{Im} \lim_{\delta \rightarrow 0} \sum_{\mathbf{k}} \langle\langle a_{\mathbf{k}} | a_{\mathbf{k}}^{\dagger} \rangle\rangle^{E-i\delta}, \quad (3)$$

$$\rho_2(E) = \frac{2}{\pi} \text{Im} \lim_{\delta \rightarrow 0} G_{\text{imp}}(E-i\delta),$$

and

$$G_{\text{imp}} = \frac{1}{N} \sum_p \langle\langle a_p | a_p^{\dagger} \rangle\rangle^E, \quad (4)$$

where the factor 2 takes into account the spin degeneracy (the exponent  $E-i\delta$  will henceforth be omitted). Expression (4) contains the diagonal Green's functions  $\langle\langle a_{\mathbf{k}} | a_{\mathbf{k}}^{\dagger} \rangle\rangle$  and  $G_{\text{imp}}$ , which determine physically observable quantities and are therefore self-averaging. We shall consider henceforth just these functions.

Setting up a chain of equations of motion and confining ourselves in the virial expansion to groups of all possible pairs of impurities (neglecting triads, etc.), we obtain an analogy with Ref. 3-7 the following expression for the diagonal Green's functions averaged over the impurity configurations:

$$\langle\langle a_{\mathbf{k}} | a_{\mathbf{k}}^{\dagger} \rangle\rangle = (E - \varepsilon_{\mathbf{k}} - R_{\mathbf{k}})^{-1}, \quad (5)$$

where

$$R_{\mathbf{k}} = \frac{c |\gamma_{\mathbf{k}}|^2}{D(E)} (1 + c B_{\mathbf{k}} + \dots), \quad (6)$$

$$D(E) = E - \varepsilon_0 - \frac{1}{N} \sum_{\mathbf{k}' \neq \mathbf{k}} \frac{|\gamma_{\mathbf{k}'}|^2}{E - \varepsilon_{\mathbf{k}'} - R_{\mathbf{k}'}} \quad (6a)$$

$$B_{\mathbf{k}} = \sum_{l \neq 0} \frac{A_{0l} e^{-i\mathbf{k}\mathbf{R}_l} + A_{0l} A_{l0}}{1 - A_{0l} A_{l0}}, \quad (6b)$$

$$A_{0l} = \frac{1}{D(E)N} \sum_{\mathbf{k}' \neq \mathbf{k}} \frac{|\gamma_{\mathbf{k}'}|^2 e^{i\mathbf{k}'\mathbf{R}_l}}{E - \varepsilon_{\mathbf{k}'} - R_{\mathbf{k}'}} \quad (6c)$$

$$G_{\text{imp}} = \frac{c}{D(E)} (1 + c B + \dots), \quad (7)$$

$$B = \sum_{l \neq 0} \frac{A_{0l} A_{l0}}{1 - A_{0l} A_{l0}}.$$

The index  $l$  in (6) and (7) runs through all the lattice sites except the zeroth one. In the derivation of (5)-(7) we took into account the fact that the diagonal Green's functions  $\langle\langle a_{\mathbf{k}} | a_{\mathbf{k}}^{\dagger} \rangle\rangle$  and  $G_{\text{imp}}$  are self-averaging; this permits averaging over the random distribution of the impurities directly in the polarization operator  $R_{\mathbf{k}}$ , both in (5) and in the expressions for  $D(E)$  and  $A_{0l}$ . We note also that the summation in products of the type  $A_{0l} A_{l0}$  in (6) and (7) is over non-coinciding wave vectors.

The obtained representations of the Green's functions (5)-(7) are fully renormalized; they constitute self-consistent expressions, since they contain the polarization operator  $R$  in the quantities  $D(E)$  and  $A_{0l}$ . In  $R_{\mathbf{k}}$  and  $G_{\text{imp}}$  are taken into account, in any case, all the terms that are quadratic in the concentration. The quantities  $B_{\mathbf{k}}$  and  $B$  describe the effects of interaction of pairs of impurities located at arbitrary distances. If these are disregarded, then the expressions turn out to be similar to those that occur in the single-site approximation of the coherent-potential method<sup>12</sup> at  $c \ll 1$ . The terms omitted from (6) and (7) describe groups made up of three and more impurities.

Besides the fully renormalized representation, other representations of the diagonal Green's functions are also possible. For example, it is easy to obtain a non-renormalized representation, which takes for the function  $\langle\langle a_{\mathbf{k}} | a_{\mathbf{k}}^{\dagger} \rangle\rangle$  the form

$$\langle\langle a_{\mathbf{k}} | a_{\mathbf{k}}^{\dagger} \rangle\rangle = \frac{1}{E - \varepsilon_{\mathbf{k}}} + \frac{\bar{R}_{\mathbf{k}}}{(E - \varepsilon_{\mathbf{k}})^2}, \quad (8)$$

where the structure of  $\bar{R}_{\mathbf{k}}$  (as well as of the function  $G_{\text{imp}}$ ) remains the same as in the fully renormalized representation, except that  $D(E)$  and  $A_{0l}$  are respectively replaced by

$$D^{(0)}(E) = E - \varepsilon_0 - \frac{1}{N} \sum_{\mathbf{k}} \frac{|\gamma_{\mathbf{k}}|^2}{E - \varepsilon_{\mathbf{k}}}, \quad (9)$$

$$A_{0l}^{(0)}(E) = \frac{1}{D^{(0)}(E)N} \sum_{\mathbf{k}} \frac{|\gamma_{\mathbf{k}}|^2 e^{i\mathbf{k}\mathbf{R}_l}}{E - \varepsilon_{\mathbf{k}}}.$$

The restrictions on the summation over  $\mathbf{k}$  in the quantities of the type  $A_{0l}^{(0)} A_{l0}^{(0)}$  are then lifted. Expressions of the type (8) are direct expansions of the corresponding Green's functions in powers of  $c$ . It is more convenient to use this renormalized representation outside the region of states described by a wave vector, for

example in some vicinity of an impurity level.

Next, in analogy with Refs. 3-7, we analyze the convergence of the different group expansions and obtain on the basis of this analysis the spectrum of the electronic states in different energy regions and at different impurity concentrations.

### 3. SPECTRUM OF ELECTRONIC STATES AT LOW IMPURITY CONCENTRATIONS

At sufficiently low impurity concentrations, for which a criterion will be given below, the spectrum remains in the main the same as that for isolated impurity centers. It is known that in the one-dimensional approximation the Green's function  $G_{\text{imp}}$  has a pole that determines the energy  $\varepsilon_L$  of the localized impurity state and corresponds to the root of the equation

$$D^{(0)}(\varepsilon_L) = 0. \quad (10)$$

Near the edge of the band, where the dispersion law takes the form  $\varepsilon_k = k^2/2m$ , ( $\hbar=1$ ), the resonant denominator  $D^{(0)}(E)$  turns out to be

$$D^{(0)}(E) = E - \varepsilon_0 - \frac{\gamma^2}{E} (-E)^{1/2}, \quad (11)$$

$$\varepsilon_k = \varepsilon_0 - \frac{1}{N} \text{Re} \sum_k \frac{|\gamma_k|^2}{\varepsilon_k}, \quad E_L = \frac{(4\pi)^{1/2}}{2m\nu^{1/2}},$$

$$\gamma^2 = |\gamma_{k=0}|^2.$$

Inasmuch as the large-radius impurity states considered here must satisfy the condition

$$|\varepsilon_k| \ll E_1, \quad (12)$$

we have left out of (11) terms of higher order of smallness in the parameter  $E/E_1$  ( $E_1$  is of the order of the width of the  $s$  band). Taking (11) into account, the solution of (10) takes the form

$$\varepsilon_L = \varepsilon_0 \left[ 1 - \frac{1}{2\delta} + \frac{1}{2\delta} (1 - 4\delta)^{1/2} \right], \quad \delta = \varepsilon_0 E_1^2 / \gamma^4. \quad (13)$$

It lies on the physical sheet at  $\delta < 0$  or  $\delta > \frac{1}{4}$ . The values  $\bar{\varepsilon}_0 < 0$  correspond to the local impurity level ( $\varepsilon_L$  is real), while  $\bar{\varepsilon}_0 > 0$  correspond to a virtual level. a) Assume initially that  $\bar{\varepsilon}_0 < 0$ . The wave function of the impurity state with energy  $\varepsilon_L$  in a crystal with isolated impurity atom at the site  $p=0$  can be represented in the form

$$|\psi\rangle = \varphi_0 |a_0\rangle + \sum_{i \neq 0} \varphi_i |a_i\rangle, \quad a_i = N^{-1/2} \sum_k e^{-ikR_i} a_k,$$

$$\varphi_i = \varphi_0 G_{0i}, \quad G_{0i} = \frac{1}{N} \sum_k \frac{\gamma_k e^{ikR_i}}{\varepsilon_k - \varepsilon_L} = \frac{\gamma \nu^{1/2} \exp(-R_i/r_0)}{(4\pi)^{1/2} E_1 R_i}, \quad (14)$$

$$r_0 = \left( \frac{\nu}{4\pi} \right)^{1/2} \left| \frac{E_1}{\varepsilon_L} \right|^{1/2} = (2m|\varepsilon_L|)^{-1/2},$$

so that the probability of finding the electron in this state at the site  $p=0$  is

$$P_0 = |\varphi_0|^2 = \left( 1 + \frac{\gamma^2}{2|\varepsilon_L|^{1/2} E_1^{1/2}} \right)^{-1} \approx \begin{cases} 1 - 1/2|\delta|^{1/2}, & |\delta| \gg 1, \\ 2|\delta|, & |\delta| \ll 1. \end{cases} \quad (15)$$

As seen from (14) and (15), at  $|\delta| \gg 1$  the wave functions of the impurity state is localized mainly on the impurity site, and only a small fraction  $\sim (2|\delta|)^{-1/2}$  of the wave function is distributed in a volume with the radius  $r_0$  of the impurity state. At the same time, at

$|\delta| \ll 1$  practically the entire wave function is distributed in this volume.

The characteristic impurity concentration at which one can expect a substantial restructuring of the spectrum of the system is

$$c_0 = \nu / 4\pi r_0^3 = |\varepsilon_L / E_1|^{1/2}. \quad (16)$$

In accordance with the difference in the behavior of the wave function, the restructuring of the spectrum of a nonideal crystal at  $c \gg c_0$  should be qualitatively different at  $|\delta| \ll 1$  and  $|\delta| \gg 1$ .

At small impurity concentrations, when  $c \ll c_0$ , the average distance between impurities  $r_{\text{av}} \sim (\nu/c)^{1/3}$  is much larger than the impurity-state radius  $r_0$ , and no coherent restructuring of the spectrum takes place. Inside the band, the renormalized representation is convergent and the states retain their current character with a dispersion law  $\bar{\varepsilon}_k$  determined from the solution of the equation

$$E - \varepsilon_k - \text{Re} \frac{c|\gamma_k|^2}{D^{(0)}(E)} = 0. \quad (17)$$

It is seen from (17) and (11) that the edge of the band states shifts by an amount

$$\Delta = \frac{c\gamma^2}{\varepsilon_0} = \begin{cases} -cE_1/c_0^{1/2}, & |\delta| \ll 1, \\ -cE_1/c_0^{1/2}|\delta|^{1/2}, & |\delta| \gg 1. \end{cases} \quad (18)$$

The dispersion law (17) is valid so long as the damping over the wavelength is small, and this condition is satisfied at  $k \gg k_{\text{min}}$ , where

$$k_{\text{min}} \sim cE_1\nu^{-1/2}/\varepsilon_0\delta. \quad (19)$$

In a transition region between the current and fluctuation states, having a width

$$\Delta_1 \sim \bar{\varepsilon}_{k_{\text{min}}} - \bar{\varepsilon}_{k=0} \sim \frac{c^2 E_1^2}{\varepsilon_0^2 \delta^2} \approx \begin{cases} c^2 E_1 / c_0^{1/2}, & |\delta| \ll 1, \\ c^2 E_1 / c_0^{1/2} \delta^2, & |\delta| \gg 1, \end{cases} \quad \Delta_1 \ll \Delta, \quad (20)$$

we can expect the presence of a mobility threshold.<sup>7</sup>

As shown previously<sup>5,7</sup> at  $c \ll c_0$ , in the vicinity of the local impurity level and far from the region of the band states, better convergence is obtained in the nonrenormalized representation (8), in which the expansions are in terms of the parameter  $cr^3(E)/\nu$ , where

$$r(E) = \frac{\gamma^2 \nu^{1/2} \exp[-(2m|E|)^{1/2} r(E)]}{(4\pi)^{1/2} |D^{(0)}(E)| E_1}. \quad (21)$$

This group expansion diverges in a narrow vicinity of  $\varepsilon_L$  where  $r(E) \approx (\nu/c)^{1/3} \sim r_{\text{av}}$ . This region, whose width is

$$\Delta_2 \sim \frac{|\varepsilon_L|}{1 + 2(\varepsilon_L |\delta| / \varepsilon_0)^{1/2}} \exp \left[ -\eta \left( \frac{c_0}{c} \right)^{1/2} \right], \quad \eta \sim 1 \quad (22)$$

can be identified with the concentration width of the impurity level.

In the region  $\gamma^2/E_1 \gg |E - \varepsilon_L| \gg \Delta_2$ , outside the band states, the main contribution to the state density is made by fluctuation clusters of impurity pairs separated by distances  $\nu^{1/3} \ll r(E) \ll r_{\text{av}}$ . As a result we have

$$\rho(E) = \frac{4\pi c^2 r^2(E) [1 + (\varepsilon_0/|E\delta|)^{1/2} (1 - (\text{sign } D^{(0)}(E)) \exp[-(2m|E|)^{1/2} r(E)]]}{|D^{(0)}(E)| [1 + r(E) (2m|E|)^{1/2}]} \quad (23)$$

As seen from (23), the state density in the considered

fluctuation region is proportional to the square of the concentration. At  $|\delta| \gg 1$  the main contribution to (23) is made by the first term in the square brackets, which is due to the quantity  $\rho_2(E)$ , while at  $|\delta| \ll 1$  the dominant term in (23) is the second, which results from  $\rho_4(E)$ , and this case was considered in detail previously.<sup>6,7</sup> In an impurity-level neighborhood defined by the condition

$$|E - \epsilon_L| \ll \frac{|\epsilon_L|}{1 + |\epsilon_L|^{1/2} E_1^{1/2} / \gamma^2}, \quad (24)$$

the state density increases like<sup>2,6,7</sup>  $|D^{(0)}(E)|^{-1} \ln^2 |D^{(0)}(E)|$  when  $\epsilon_L$  is approached.

If the condition  $\gamma^2/E_1 \gg |\epsilon_L|$  is satisfied, then the energy levels due to the pairs of impurities fill the spectral region adjacent to the edge of the band, and virtual states are produced inside the band. In this case, using the renormalized representation, it becomes possible to describe the state density in the entire vicinity of the edge of the band, including the transition region between the band and fluctuation states.<sup>6,7</sup>

b) We consider now a case when we have in (11)  $\bar{\epsilon}_0 > 0$ . The characteristic concentrations is described here as before by expression (16) with the  $\epsilon_L$  defined in (13), even when this solution is on an unphysical sheet.

If the characteristic parameter of the considered model is  $\delta \gg 1$ , then in the region of the energies  $E \approx \epsilon_L$  ( $\epsilon_L \approx \bar{\epsilon}_0$  at  $\delta \gg 1$ ) the state density  $\rho(E)$  has a maximum with a Lorentz shape

$$\Delta\rho(E) = \rho_2(E) = \frac{2}{\pi} \frac{c\Gamma}{(E - \bar{\epsilon}_0)^2 + \Gamma^2}, \quad (25)$$

corresponding to a quasilocal level. The half-width of this maximum  $\Gamma = \bar{\epsilon}_0/\delta^{1/2} \ll \bar{\epsilon}_0$  is connected with the decay of the quasilocal state into continuous-spectrum states. When  $c > c_0/\delta^{1/2}$  the value of  $\Delta\rho(\bar{\epsilon}_0)$  exceeds the state density of the unperturbed crystal. At these concentrations, coherent restructuring of the spectrum sets in and consists at  $c \ll c_0$  in the fact that in some vicinity of  $k_0$  ( $\epsilon_{k_0} = \bar{\epsilon}_0$ ,  $k_0 = (4\pi c_0/\nu)^{1/3}$ ) with width  $|k - k_0| < k_0 c/4c_0$  there are three solutions of the dispersion equation (17); these solutions are shown in Fig. 1. Two of them have a normal dispersion, and the third has an anomalous dispersion ( $\partial \bar{\epsilon}_k/\partial k < 0$ ). Nonetheless, at  $c \ll c_0$  the renormalized representation, even in the most unfavorable case near  $\bar{\epsilon}_0$ , where  $|E - \bar{\epsilon}_0| \leq \Gamma$ , remains convergent in terms of the parameter  $c/c_0 \ll 1$  and accordingly the damping of all the states is small over the wavelength. Therefore the states in the vicinity of the impurity level remain current states.

In the energy region  $E + \Delta < \Delta_1$  the states are of fluctuation origin, and at  $\bar{\epsilon}_0 \ll \gamma^2/E_1$  the main contribution to the state density near the edge of the band is made by groups of two impurities, so that it is possible to describe in continuous fashion, as previously,<sup>6,7</sup> the transition region of region  $\Delta_1$  between the band and fluctuation states. In the region  $|E + \Delta| \ll \gamma^4/E_1^2$  the main contribution to the density of both the band and

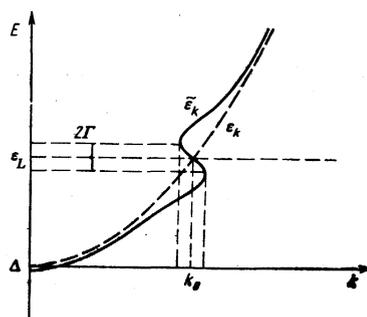


FIG. 1. Dispersion law of the band states at  $c_0/\delta^{1/2} < c \ll c_0$ ,  $\epsilon_0 > 0$ ,  $\delta \gg 1$ .

fluctuation states is made by the quantity  $\rho_1(E)$ , which is described here with the aid of a concentration-independent universal function  $f(E)$  defined previously in Refs. 6 and 7.

If  $\delta \ll 1$ , then the energy  $\bar{\epsilon}_0$  falls inside a nearthreshold region of width  $\gamma^4/E_1^2$  at the band edge. The equation  $D^{(0)}(E) = 0$  has in this case no solution on the physical sheet and there is no maximum in the state density. This is precisely the case considered in detail in the preceding papers,<sup>6,7</sup> and the expressions for the state density obtained there at  $c \ll c_0$  remain valid also in the present problem if the quantity  $c_0$  in these expressions is replaced by  $(2/\pi)^{1/2}(\bar{\epsilon}_0 \delta/E_1)^{3/2}$ .

#### 4. RESTRUCTURING OF THE ELECTRON SPECTRUM OF CRYSTALS AT HIGH CONCENTRATION OF THE IMPURITY CENTERS

We proceed now to consider the spectrum of the system at relatively high impurity concentrations  $c \gg c_0$  (but  $c \ll 1$ ), i.e.,  $r_{av} \ll r_0$ , when a large number of impurities is contained on the average in the volume with impurity-state radius  $r_0$ . The interaction between the impurities leads to a qualitative restructuring of the spectrum, and the character of this restructuring, as already noted, depends substantially on the parameter  $|\delta|$ .

a) We consider first the case when  $|\delta| \gg 1$  and  $\bar{\epsilon}_0 < 0$ , i.e., an impurity level exists outside the unperturbed band and has a wave function concentrated mainly on the impurity site. At  $c \gg c_0$  the region about  $\epsilon_L$  in which the nonrenormalized representation diverges becomes wider and its order of magnitude is not (22) but  $c\gamma^2/|\epsilon_L|$ . At the same time, for the renormalized representation (5), (7), the expansion parameter is  $c(\gamma^2/E_1|E - \epsilon_L|)^3$ . As a result, this representation diverges in a narrower region of width

$$|E - \epsilon_L| \ll \Delta_2 \sim c^{1/3} \gamma^2/E_1. \quad (26)$$

At  $c \gg c_0$  we shall therefore use the renormalized representation to investigate the spectrum. The concentration broadening of the impurity level is determined in this case by expression (26).

In the region of convergence of the renormalized representation, the states can be either localized or of the current type. The self-energies of the current (band) states, which are characterized by a wave

vector, are determined by the solution of the dispersion equation (17) and take the form

$$\varepsilon_{1,2}(k) = \frac{\varepsilon_L + \varepsilon_k}{2} \pm \left( \frac{(\varepsilon_L - \varepsilon_k)^2}{4} + c\gamma^2 \right)^{1/2}. \quad (27)$$

The damping of these states, due to scattering by the impurities that are considered here, is

$$\Gamma_{1,2}(k) = \frac{\left| \frac{\varepsilon_{1,2}(k) - \varepsilon_L}{\varepsilon_1(k) - \varepsilon_2(k)} \right| \text{Im} R_k(\varepsilon_{1,2}(k))}{c\gamma^2 \varepsilon_k^{1/2}} = \frac{E_1^{1/2} |(\varepsilon_{1,2}(k) - \varepsilon_L)(\varepsilon_1(k) - \varepsilon_2(k))|}{c\gamma^2 \varepsilon_k^{1/2}}. \quad (28)$$

States with energy  $\varepsilon_2(k)$  form an impurity band in which the states are described by a wave vector; this band is detached from the ground band and its width  $\Delta_0$  greatly exceeds the concentration broadening of the impurity level  $\varepsilon_2$ . If the impurity concentration satisfies the condition  $c_0 \ll c \ll c_1 = c_0 |\delta|^{1/2}$ , then the energy  $\varepsilon_2(k)$  takes the form

$$\varepsilon_2(k) = \varepsilon_L + \frac{c\gamma^2}{\varepsilon_L - \varepsilon_k}. \quad (29)$$

The dispersion law of the band states is shown for this case in Fig. 2.

The width of the impurity band turns out to be

$$\Delta_0 = c\gamma^2 / |\varepsilon_L| \ll |\varepsilon_L|, \quad (30)$$

and the effective mass of the impurity states with  $k \ll c_0^{1/2} v^{-1/3}$  is

$$m^* = m\varepsilon_L^2 / c\gamma^2 = mc_0 / c \gg m. \quad (31)$$

The limiting values of the wave vector in this band are determined from the condition that the damping over the wavelength be small

$$k \left| \frac{\partial \varepsilon_2(k)}{\partial k} \right| \gg \Gamma_2(k) \quad (32)$$

and are of the order of

$$k_{\min} \sim \frac{c_0^{1/2}}{c} v^{-1/3}, \quad k_{\max} \sim c^{1/2} v^{-1/3}. \quad (33)$$

As  $k \rightarrow k_{\max}$  the energy of the band states approaches the region of the concentration width of the impurity level. Below the impurity band, the states are of fluctuation origin. The width  $\Delta_1'$  of the transition region is determined here by the quantity  $\varepsilon_2(k_{\min})$ :

$$\Delta_1' = \varepsilon_2(k_{\min}) - \varepsilon_2(0) \sim \Delta_0 (c_0/c)^2. \quad (34)$$

The quantities  $k_{\min}$  and  $k_{\max}$  defined in (33) limit the region of energies corresponding to the current impur-

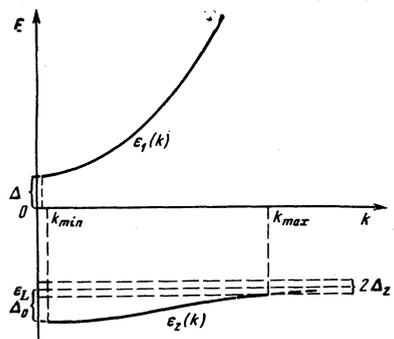


FIG. 2. States in the ground and impurity bands at  $c_0 \ll c \ll c_0 |\delta|^{1/2}$ ,  $\varepsilon_0 < 0$ ,  $|\delta| \gg 1$ .

ity states. The energies corresponding to these values of the wave vector coincide in order of magnitude with the thresholds of the mobilities in this band. It can be assumed that there exists (just as in the simplest Anderson model<sup>13</sup> with diagonal disorder) a critical concentration  $c_{cr}$  at which the current states in the impurity band first appear. The value of  $c_{cr}$  differs from  $c_0$  by a certain numerical factor  $\sim 1$ , the determination of which calls for different analysis methods. We note that, in contrast to the ordinary Anderson transition, in this model with nondiagonal disorder the mobility thresholds  $k_{\min}$  and  $k_{\max}$  are on the same side of the maximum of the state density in the impurity band.

As noted in the preceding section, the density of the fluctuation states in the region  $\gamma^2/E_1 \gg |E - \varepsilon_L| \gg \Delta_2$  is determined mainly by impurity pairs and is described by expression (23). They can therefore be used at  $\gamma^2/E_1 \gg \Delta_0$  near the lower edge of the impurity band, and at  $\gamma^2/E_1 \gg |\varepsilon_L|$  near the lower edge of the ground band characterized by the dispersion law  $\varepsilon_1(k)$ .

With increasing impurity-center concentration, when  $c \gg c_0 |\delta|^{1/2}$ , the width  $\Delta_0$  of the impurity band [as follows from (27)], as well as the gap between the bands  $\varepsilon_1(k)$  and  $\varepsilon_2(k)$ , becomes equal to  $c^{1/2}\gamma$  and greatly exceeds the energy  $|\varepsilon_L|$  of the impurity level. The effective mass of the states becomes equalized as  $k \rightarrow 0$  for the upper and lower bands:  $m_1 = m_2 = 2m$ . The minimum values of the wave vector for both branches do not depend on the concentration of the impurity centers and are of the order of

$$k_{\min} \sim \gamma^2/E_1^2 v^{1/3}, \quad (35)$$

while the widths  $\varepsilon_{1,2}(k_{\min}) - \varepsilon_{1,2}(0)$  of the transition regions coincide with the near-threshold region  $\sim \gamma^4/E_1^3$ . At the same time, the concentration width of the impurity level and the maximum value of the wave vector for the lower branch are determined as before by expressions (26) and (33). The character of the spectrum at different impurity concentrations and in different energy regions is shown schematically in Fig. 3.

b) If  $\varepsilon_0 > 0$  and  $\delta \gg 1$ , i.e., a well defined quasilocal level with energy  $\varepsilon_L \approx \varepsilon_0$  exists, then the crossing restructuring of the spectrum, as already noted above,

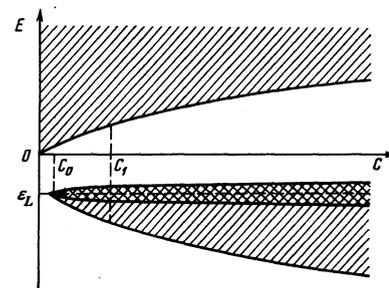


FIG. 3. Restructuring of the spectrum and character of electronic states in different energy regions as functions of the concentrations of the impurity centers. The case  $\varepsilon_0 < 0$ ,  $|\delta| \gg 1$ . The singly hatched region is that of the band states, and the doubly hatched region is that of the concentration broadening of the impurity level.

begins when  $c > c_0/\delta^{1/2}$ . At high impurity concentrations, when  $c \gg c_0$ , a region of width  $\Delta_2$  (26), in which the renormalized representation becomes divergent, appears near the energy  $\varepsilon_L$ . Outside this region the states in the vicinity of  $\varepsilon_L$  can be either in a band or localized.

The energies of the band states are determined as before by expressions (27), have a normal dispersion ( $\partial \varepsilon_{1,2}(k)/\partial k > 0$ ), and their dependence on the wave vector for the case  $c_0 \ll c \ll c_0 \delta^{1/2}$  is shown in Fig. 4. In place of the anomalous-dispersion region which is obtained when  $c_0/\delta^{1/2} < c \ll c_0$ , at  $c \gg c_0$  a forbidden band (quasigap) of width  $\Delta_0 = c\gamma^2/\bar{\varepsilon}_0 \gg \Delta_2$ , appears at  $c_0$  between the energy  $\bar{\varepsilon}_0$  and the new limiting energy  $\varepsilon_1 = \bar{\varepsilon}_0 + \Delta_0$ . In this band the states are not described by a quasimomentum. Inside the forbidden region the states are localized and the state density is determined by the fluctuation clusters of the pairs of impurities (if  $\Delta_0 \ll \gamma^2/E_1$ ). The minimum value of the wave vector for the upper band and the maximum value for the lower band are determined by expressions (33). Thus, the picture of the restructuring of the spectrum of the quasilocal level at  $c_0 \ll c \ll c_0 \delta^{1/2}$  is in a certain sense dual with respect to the onset of the impurity band near the local level.

The principal difference between the cases of small ( $c \ll c_0$ ) and large ( $c \gg c_0$ ) concentrations of the impurity centers is here that when the concentration reaches a certain critical value  $c_{cr} \sim c_0$  a phase transition takes place in the electronic subsystem. This transition, which has the character of the inverse Anderson transition, consists in the fact that near the energy  $\varepsilon_L$  a region of localized states (quasigap) is produced jumpwise.

When the concentration of the impurities becomes so large that  $c \gg c_0 \delta^{1/2}$ , the width of the forbidden band  $\Delta_0 = c^{1/2}\gamma$  exceeds the energy of the quasilocal level  $\varepsilon_L$ , and in this case there is no substantial difference between the character of the coherent restructuring for the local and quasilocal states.

c) In the case when the parameter  $|\delta| = |\bar{\varepsilon}_0|E_1^3/\gamma^4 \ll 1$ , i.e., the wave functions of the impurity states are distributed mainly in a volume of radius  $r_0$ , no coherent restructuring of the spectrum takes place at

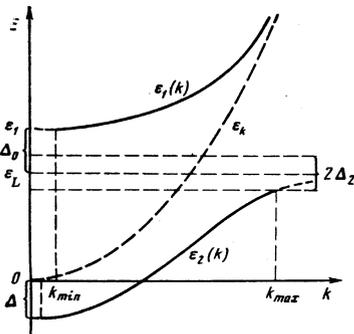


FIG. 4. Dispersional law when a quasigap is produced near a quasilocal level.  $\varepsilon_0 > 0$ ,  $\delta \gg 1$ ,  $c_0 \ll c \ll c_0 \delta^{1/2}$ .

$c \gg c_0$  (but  $c \ll c_0/|\delta|^3$ ). The reason is that at these concentrations all the characteristic energies of the impurity subsystem turn out to be less than the width of the threshold region  $\sim \gamma^4/E_1^3$ , where the term proportional to the square root of  $E$  in  $D^{(0)}(E)$  (11) predominates over the linear term and the indicated restructuring of the spectrum is impossible. The concentration broadening of the impurity state (the region of divergence of the group expansion) is the same as for the cases considered previously<sup>6,7</sup> is of the order of

$$\Delta_0' \sim c^{1/2} E_1 \ll \gamma^4/E_1^3 \quad (36)$$

regardless of the sign of  $\bar{\varepsilon}_0$ , and greatly exceeds the impurity-level energy  $\varepsilon_L$  ( $\varepsilon_L \approx \bar{\varepsilon}_0|\delta|$  at  $\bar{\varepsilon}_0 < 0$ ,  $|\delta| \ll 1$ ). The lower edge of the band states is determined by the concentration broadening of  $\Delta_2'$ , and the minimum value of the wave vector turns out to be of the order of  $k_{\min} \sim c^{1/3}v^{-1/3}$ . The state density outside the region  $\Delta_2'$  (36) can be obtained with the aid of the expressions given in Ref. 6 and 7.

On the other hand, if the concentration of the impurities becomes so large that  $c \gg c_2 = c_0/|\delta|^3 = \gamma^6/E_1^6$ , then a coherent restructuring of the spectrum takes place at  $|\delta| \ll 1$ , and an additional band appears (at a certain critical concentration  $c_{cr} \sim c_2$ ), in which the states are described by the wave vector. The character of the spectrum turns out to be the same as considered in item a) of the present section at  $c \gg c_0|\delta|^{1/2}$ , i.e., the dispersion law is determined by expression (28), the widths of the quasigap and of the lower band are equal to  $c^{1/2}\gamma$ , the concentration width of the impurity level is  $\Delta_2' \sim c^{1/3}\gamma^2/E_1 \ll c^{1/2}\gamma$ , the minimum value of the wave vector for both branches of the spectrum is  $k_{\min} \sim (\gamma^2/E_1^2)v^{-1/3} = c_2^{1/3}v^{-1/3}$ , and the maximum for the lower branch is  $k_{\max} \sim c^{1/3}v^{-1/3}$ . This restructuring of the spectrum is due to the fact that at  $c \gg c_2$  the concentration width of the impurity level  $\Delta_2'$  and other parameters of the coherent restructuring of the spectrum become larger than the width of the near-threshold region  $\gamma^4/E_1^3$ , and the term linear in  $E$  predominates in the expression for  $D^{(0)}(E)$ .

## 5. CONCLUSION

The here-considered crystal-spectrum restructuring at relatively large concentrations of the large-radius impurity centers ( $c_0 \ll c \ll 1$ ) is connected primarily with the fact that a volume with impurity-state radius  $r_0 \sim (v/c_0)^{1/3}$  contains on the average a large number of such centers, and partial averaging of the fluctuations takes place. In addition, for coherent restructuring of the spectrum it is necessary that the characteristic dimensions of the region of this restructuring exceed the dimensions of the region of the concentration broadening. This condition is equivalent to the requirement that the energy of the indirect interaction of the impurities at average distances  $E_{av} \sim c^{1/3}\gamma^2/E_1$  be shorter than the distance from the impurity level to the renormalized edge of the band:

$$|E_{av}| \ll |e_1(k=0) - e_l|. \quad (37)$$

This condition is always satisfied for  $c \gg c_0$  if the hybridization energy is not too high, so that  $|\delta| \gg 1$ . On

the other hand, if  $|\delta| \ll 1$ , then the condition (37) is satisfied at  $c \gg c_2 = c_0/|\delta|^3$ . As a result, the criterion for coherent restructuring of the spectrum can be represented in the form

$$c \gg c_0 \max\{1, |\delta|^{-3}\}. \quad (38)$$

At  $\gamma \sim E_1$  this criterion cannot be satisfied at any value  $c \ll 1$ , and this is why no coherent restructuring of the spectrum was observed in the previously considered cases.<sup>6,7</sup> We note that in the case when the singularity of the edge of the band is not of the van Hove type, coherent restructuring can take place at  $c \sim c_0$  even if the parameter  $|\delta|$  is small.

Let us dwell briefly on the electric conductivity via the impurity current states. Under certain conditions the Fermi level  $\varepsilon_F$  of the considered system can be located inside the impurity band:

$$\varepsilon_2(k_{\min}) < \varepsilon_F < \varepsilon_2(k_{\max}), \quad (39)$$

and as a result the states on the Fermi surface are of the current type and lead to metallic conductivity at low temperatures. This situation can occur, for example, in a semiconductor with a sufficiently large dielectric constant  $\kappa$  doped with a transition element. The unfilled impurity level should then lie near the conduction band (or the filled one near the edge of the valence band), so that its energy reckoned from the edge of the band exceeds the effective Rydberg value  $\varepsilon_R = me^4/2\kappa^2$ . The number of fluctuation states with energy lower than  $\varepsilon_2(0)$  is, as seen from (23), of the order of  $Nc_0^2/c$  (if  $c_0 \ll c \ll \min(c_0^{2/3}, c_1)$ ). By additionally doping the semiconductor with ordinary donors (acceptors) of concentration  $\sim c_0^2/c \ll c$  we can fill all these localized states and ensure satisfaction of the condition (39). It is easy to show in this case that if  $c \gg c_0(|\delta|\varepsilon_R/|\varepsilon_L|)^{3/4}$ , then the scatter of the levels due to the random Coulomb potential of the donors turns out to be less than the width  $\Delta_0$  of the impurity band and the diagonal disorder does not upset the coherence in the impurity band.

Inside the impurity band we have in accord with (32)

$$kl \gg 1, \quad (40)$$

where the mean free path is defined by the expression

$$l = \left| \frac{\partial \varepsilon_2(\mathbf{k})}{\partial k} \right| \Gamma_2^{-1}(\mathbf{k}). \quad (41)$$

Therefore, if the condition (39) is satisfied, it is possible to show in the usual manner<sup>14</sup> that the kinetic equation is valid, and the static conductivity via the impurity band turns out to be

$$\sigma = e^2 l k_F^2 / 3\pi^2, \quad (42)$$

where  $k_F$  is the Fermi momentum. Equation (42) takes account of the fact that the scattering of the electrons in the impurity band is isotropic, so that the transport mean free path  $l_{tr}$  coincides with (41).

It follows from (32) and (41) that the  $lk_F \sim 1$  when the Fermi momentum becomes of the order of  $k_{\min}$  or  $k_{\max}$ , and this condition determines the limits of applicability of expression (42). On the upper edge of the impurity band the limiting value of this metallic conductivity can then be assumed to be of the order of

$$\sigma \sim \frac{1}{3\pi^2} c^2 e^2 v^{-1/2}, \quad (43)$$

i.e., of the same order as the minimum value of the metallic conductivity  $\sigma_{\min} = 0.06e^2/\gamma_{cp}$  estimated by Mott.<sup>15</sup> On the lower edge of the impurity band, however, the corresponding limiting value can reach

$$\sigma_0 \sim \frac{1}{3\pi^2} e^2 k_{\min} \sim \frac{1}{3\pi^2} e^2 v^{-1/2} \begin{cases} c_0^{2/3}/c, & c_1 \gg c \gg c_0, \\ \gamma^2/E_1, & c \gg c_1, \end{cases} \quad (44)$$

and the minimal metallic conductivity via the impurity band is thus much less than the Mott estimate. When  $c \gg c_1$ , the value of  $\sigma_0$  no longer depends on the concentration of the impurity centers.

In conclusion we thank I. M. Lifshitz, M. A. Krivoglaз, É. I. Rashba, and A. L. Éfros for useful discussion of the results.

<sup>1</sup>I. M. Lifshitz, Nuovo Cimento Suppl. 3, 716 (1956).

<sup>2</sup>I. M. Lifshitz, Usp. Fiz. Nauk 83, 617 (1964) [Sov. Phys. Usp. 7, 549 (1965)].

<sup>3</sup>M. A. Ivanov, Fiz. Tverd. Tela (Leningrad) 12, 1895 (1970) [Sov. Phys. Solid State 12, 1508 (1971)].

<sup>4</sup>M. A. Ivanov and Yu. G. Pogorelov, Fiz. Tverd. Tela (Leningrad) 16, 3294 (1974) [Sov. Phys. Solid State 16, 2140 (1975)].

<sup>5</sup>M. A. Ivanov and M. N. Botvinko, Phys. Stat. Solidi B 76, 797 (1976).

<sup>6</sup>M. A. Ivanov, Yu. G. Pogorelov, and M. N. Botvinko, Zh. Eksp. Teor. Fiz. 70, 610 (1976) [Sov. Phys. JETP 43, 317 (1976)].

<sup>7</sup>M. A. Ivanov and Yu. G. Pogorelov, Zh. Eksp. Teor. Fiz. 72, 2198 (1977) [Sov. Phys. JETP 45, 1155 (1977)].

<sup>8</sup>P. W. Anderson, Phys. Rev. 124, 41 (1961).

<sup>9</sup>C. Kittel, Quantum Theory of Solids, Wiley, 1963, Ch. 18.

<sup>10</sup>K. A. Kikoin and V. N. Flerov, J. Phys. C 9, 1673 (1976).

<sup>11</sup>D. N. Zubarev, Usp. Fiz. Nauk 71, 71 (1960) [Sov. Phys. Usp. 3, 320 (1960)].

<sup>12</sup>R. J. Elliott, J. A. Krumhansl, and P. L. Leath, Rev. Mod. Phys. 46, 465 (1974).

<sup>13</sup>P. W. Anderson, Phys. Rev. 109, 1492 (1958).

<sup>14</sup>A. A. Abrikosov, L. P. Gor'kov, and I. E. Dzyaloshinskiĭ, Metody kvantovoi teorii polya v statisticheskoi fizike (Quantum Field Theoretical Methods in Statistical Physics), 1962, Ch. VII, pg. 39 [Pergamon, 1965].

<sup>15</sup>N. F. Mott, Adv. Phys. 16, 49 (1967).

Translated by J. G. Adashko