

*ENERGY SPECTRUM STRUCTURE AND QUANTUM
STATES OF DISORDERED CONDENSED SYSTEMS*

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1. INTRODUCTION. CHOICE OF MODEL

THE first question to be considered in an attempt to construct a quantum theory of a condensed system is the question of the energy spectrum of the system.

Everyone knows that the lowest energy state of any condensed system is either a crystal or a quantum liquid. For the ground state to be a crystal it is necessary that the zero-point energy be smaller than the energy of breaking up of the ordered lattice. Excited states of such a system can be regarded as a gas of separated elementary excitations called quasi-particles, whose nature and properties depend on the concrete characteristics of the system. For example, the simplest excitations, which are elastic waves (phonons), exist in all systems. The character of the other branches of the energy spectrum is essentially different for different materials such as metals, semiconductors, insulators, ferromagnetic and antiferromagnetic substances, and so on.

In all these cases, however, the "skeleton" of the solid body is an idealized periodic structure, the crystal lattice. But at low temperatures the relaxation times of a crystal lattice are enormous. Hence any fixed distribution of atoms in relative positions of equilibrium can be looked at as a ground state of the solid body (with respect to elementary excitations whose activation energies are significantly lower than the energy barrier involved in reconstructing the lattice). This applies to both amorphous, "glasslike" states and to solid solutions, in which disordered states are obtained by rapid cooling from high temperatures.

The existing theory of energy spectra was developed for ideal crystalline structures and is unsuitable for such disordered systems. In this article we study the energy spectrum of elementary excitations in dis-

ordered solid bodies, for which the random positions of equilibrium of the atoms are fixed.

It is well known that the systematics of the quantum states and of the energy spectrum for elementary excitations in a crystal possesses in certain respects a simple and universal structure, connected with the existence of the periodic translational symmetry of the crystal lattice. Translational symmetry leads to the existence and the conservation of quasi-momentum \mathbf{k} ($\hbar = 1$), and the energy spectrum of different kinds of elementary excitations in crystals is therefore determined by the dispersion relation $E = E(\mathbf{k})$ for the appropriate quasi-particle. Accordingly, the quantum state with quasi-momentum \mathbf{k} is described by a modulated plane wave with wave vector \mathbf{k} . This systematics makes very clear the statistical picture of elementary excitations and the mechanism of the kinetic phenomena connected with these excitations. For example, the concepts of particle collisions and free-path lengths are introduced into the kinetics relative to the variation of the quasi-momentum \mathbf{k} , and all the existing terminology is based on these concepts.

The features of the structure of the energy spectrum of elementary excitations in condensed systems without spatial periodicity are related to the absence of quasi-momentum in such systems, and hence to the different systematics of the states. On the other hand, kinetic phenomena in amorphous bodies often retain the same character as in crystalline media (e.g., the electric conductivities of liquid and solid metals are of the same order of magnitude at high temperatures). This means that the mechanism of those phenomena which are not specific to crystalline media with their characteristic anisotropy can be formulated in other ways.

Therefore the central question in the construction of a quantum theory of the condensed state of a sub-

stance without spatial periodicity is the study of the structure of the energy spectrum of elementary excitations and the explanation of the character of quantum states possible in such systems. In order to study this question in a simple case, it is natural to consider the one-particle approximation; that is to say, the movement of a test-particle in some random aperiodic "field" of atoms, forming a solid body. Alternatively one can consider the vibrations of coupled oscillators in an aperiodic structure. The first example is characteristic of the description of the states of a mobile electron in a solid body, and the second is used in the explanation of the structure of vibration (phonon) spectra, of spin-wave spectra, or of spectra of the different types of excitations in condensed systems.

In spite of the apparent physical difference of these problems, they possess a deep similarity in their mathematical nature and, as will be shown, they admit of a general formulation in terms of a unified mathematical model.

On the other hand we should remember the limited applicability of such models; whereas in a periodic structure, translational and point symmetry can itself provide a significant amount of information about systematics of the quantum states and the spectrum (irrespective of the model), for a disordered system we have a much larger choice of models. Therefore there is no reason to assume that the properties and structure of the spectrum, given by some model, possess a fully universal character. Nevertheless, the generality of such models is sufficiently wide and many of the laws derived from them are, in principle, important.

In the last ten years there has been much work devoted to the study of the energy spectrum of disordered systems, using a similar approach^[12-25]. In most of this work, however, only one-dimensional problems of a very specialized form are considered. In particular the beautiful solution of Dyson^[12] for one special case of a linear chain of oscillators does not hold out any possibility of generalization to the general problem. In the majority of other papers methods of approximation are used which are not applicable to those regions of the spectrum where singularities occur; that is, just where the main interest of the problem lies. The solution of this important problem is therefore still far from completion.

The present article is based on the results of the author's own work in this field^[1-11]. It makes no use of results by others on this subject, which are therefore not reported. Some of the results in this paper have been already published by the author but a significant portion of the paper (in particular Secs. 3 and 5) is published for the first time. Besides, some new considerations and also a formulation of the problem based on the study of the singular points of the spectral density allow us to give a more finished and general character to these results.

For a qualitative picture of a solid body without

spatial periodicity we look at a disordered solid solution. In such a system the Hamiltonian of the quasi-particles, in both the cases referred to above, can be written in the single form

$$\hat{H} = \hat{H}_0 + \sum_j \hat{U}_j, \quad (1.1)$$

where \hat{H}_0 is the Hamiltonian of the quasi-particles in an ideal crystal and U_j is the Hamiltonian of a local perturbation (an impurity atom) at the point \mathbf{r}_j .

Thus, for example, the equation for an electron in this very simple model of a disordered system is

$$\hat{H}_0 \psi + \sum_j U(\mathbf{r} - \mathbf{r}_j) \psi = E \psi, \quad (1.2)$$

where

$$\hat{H}_0 = -\frac{1}{2m} \Delta + V(\mathbf{r})$$

($V(\mathbf{r})$ is the periodic potential), i.e.,

$$-\frac{1}{2m} \Delta \psi + V(\mathbf{r}) \psi + \sum_j U(\mathbf{r} - \mathbf{r}_j) \psi = E \psi.$$

In the \mathbf{k} -representation $\hat{H}_0 = E_s(\mathbf{k})$, i.e.,

$$E_s(\mathbf{k}) \psi + \sum_j U(\mathbf{r} - \mathbf{r}_j) \psi = E \psi.$$

As always, $E_s(\mathbf{k})$ is a periodic function of \mathbf{k} with the period of the reciprocal lattice, s is the band number, and the perturbation $U(\mathbf{r})$ acts over distances of the order of atomic dimensions. The points \mathbf{r}_j are randomly distributed, their mean density being determined by the impurity concentration c .

In the study of vibration spectra the equations for the elastic displacement of the atoms in a simple atomic lattice (i.e., without impurities) are

$$\hat{L} \mathbf{u} + \sum_j \hat{\Lambda}_j \mathbf{u} = \omega^2 \mathbf{u},$$

$$\mathbf{u} = u_{\mathbf{r}}^{\mathbf{x}}, \quad \hat{L} = L_{\mathbf{r}\mathbf{r}'}^{\mathbf{x}\mathbf{x}'}; \quad \hat{\Lambda}_j = \Lambda_{\mathbf{r}-\mathbf{r}_j, \mathbf{r}'-\mathbf{r}_j}^{\mathbf{x}\mathbf{x}'}, \quad (1.3)$$

i.e., in coordinate form,

$$\sum_{\mathbf{x}, \mathbf{r}'} L_{\mathbf{r}-\mathbf{r}', \mathbf{r}'}^{\mathbf{x}\mathbf{x}'} u_{\mathbf{r}'}^{\mathbf{x}'} + \sum_j \sum_{\mathbf{x}', \mathbf{r}'} \Lambda_{\mathbf{r}-\mathbf{r}_j, \mathbf{r}'-\mathbf{r}_j}^{\mathbf{x}\mathbf{x}'} u_{\mathbf{r}'}^{\mathbf{x}'} = \omega^2 u_{\mathbf{r}}^{\mathbf{x}}.$$

Here ω is the frequency, and the displacement vector $\mathbf{u} = u_{\mathbf{r}}^{\mathbf{x}}$ depends on the discrete coordinate \mathbf{r} of the lattice sites; the unperturbed matrix of the elastic coupling \hat{L} is a function of the difference of the coordinates \mathbf{r} and \mathbf{r}' , and the matrix of the local perturbation $\hat{\Lambda}_j$ acts only in the immediate surroundings of the given site \mathbf{r}_j . In \mathbf{k} -space the unperturbed matrix \hat{L} is diagonal, just as in the case of the electron,

$$\hat{L} = \lambda_s(\mathbf{k}) = \omega_s^2(\mathbf{k}), \quad s = 1, 2, 3. \quad (1.4)$$

The equations for spin waves can be put in an analogous form; in this case the role of the matrices of elastic coefficients \hat{L} , $\hat{\Lambda}$ is played by the matrices of exchange integrals \hat{I} , \hat{I}' . Equations of the type (1.3) thus represent a discrete analog of (1.2), in which we have in place of the energy E the square of the fre-

quency ω^2 [correspondingly, $E(\mathbf{k})$ is replaced by $\lambda(\mathbf{k}) = \omega^2(\mathbf{k})$].

We should emphasize that the true energy of a phonon is, of course, $\epsilon(\mathbf{k}) = \hbar\omega(\mathbf{k})$. But in order to put the equation for the characteristic frequencies into the form (1.2) we must replace the Hamiltonian H_0 in (1.2) by the matrix of elastic coefficients \hat{L} , and the energy E by the square of the frequency ω^2 . In all the following formulae the results are fully applicable to the phonon spectrum, but with the substitution $E \rightarrow \omega^2$.

For the study of the basic qualitative characteristics and the singularities of the energy spectrum it is convenient to simplify the model further, freeing it of unnecessary cumbersome details which are not of principal importance while, as far as possible, preserving those properties which allow the results derived to be correct and reasonable. With this goal we limit ourselves to cases where the unperturbed operator for the ideal crystal possesses only one branch (one band) in its spectrum. In the general case this corresponds to the neglect of transitions between bands; however the reasonableness of such a model is confirmed by concrete examples of systems with this spectral structure.

Thus, for example, in (1.2) we would write now $\hat{H}_0 = -\nabla^2/2m$, just as for free electrons (i.e., $V(\mathbf{r}) = 0$) $E(\mathbf{k}) = k^2/2m$). For lattice vibrations (i.e., for systems of coupled oscillators) this case corresponds to the absence of interaction between displacements in perpendicular directions. Here elastic coupling exists only for identically "polarized" displacements (or vibrations); for the general case it is possible to consider that elastic forces arise not only on account of relative displacements (i.e., the differences $\mathbf{u}_{\mathbf{r}} - \mathbf{u}_{\mathbf{r}'}$) but that there exist direct couplings between each atom and its "absolute" equilibrium position. Such a situation leads to the non-zero limiting frequencies $\omega(0) \neq 0$ characteristic of the optical branches in many-atom crystals. It is evident that within the limits of a model with one branch of vibrations the existence of "absolute" equilibrium positions must ensure very heavy atoms of a second kind, practically creating the immovable "skeleton" of the ideal lattice.

The vibrations of an ideal lattice in this case can thus be described by equations for the displacements $\mathbf{u}_{\mathbf{r}} = \chi_{\mathbf{k}}(\mathbf{r})$, (\mathbf{r} is the discrete lattice-site vector)

$$\sum L_{\mathbf{r}-\mathbf{r}'}\chi_{\mathbf{k}}(\mathbf{r}') = \lambda\chi_{\mathbf{k}}(\mathbf{r}), \quad \lambda = \omega^2(\mathbf{k}), \quad (1.5)$$

whence

$$\chi_{\mathbf{k}}(\mathbf{r}) \sim e^{i\mathbf{k}\cdot\mathbf{r}}; \quad \omega^2(\mathbf{k}) = \sum L_{\mathbf{r}}e^{i\mathbf{k}\cdot\mathbf{r}}, \quad (1.6)$$

and in the general case $\omega^2(0) = \sum L_{\mathbf{r}} \neq 0$. In this approximation it is natural to regard the eigenfunctions $\chi_{\mathbf{k}}(\mathbf{r})$ for the ideal crystal as unmodulated plane waves $\chi_{\mathbf{k}} \sim e^{i\mathbf{k}\cdot\mathbf{r}}$ not only in the case of discrete but also of continuous \mathbf{r} .

The operator for the local perturbation \hat{U}_0 in the electron case can be taken, as we have already seen,

in the natural form of a potential $\hat{U}_0 = U_0(\mathbf{r})$. When \mathbf{r} is discrete (e.g., for lattice vibrations) the diagonal form $(U_0)_{\mathbf{r}\mathbf{r}'} = U(\mathbf{r})\delta_{\mathbf{r}\mathbf{r}'}$ is, in general, not possible. In particular, considering the acoustic vibration branch ($\omega^2(0) = \sum L_{\mathbf{r}} = 0$) we have on equating to zero the forces and torques upon displacement and rotation of the crystal the equations

$$\sum_{\mathbf{r}'} (U_0)_{\mathbf{r}\mathbf{r}'} = 0, \quad \sum_{\mathbf{r}'} (U_0)_{\mathbf{r}\mathbf{r}'} \mathbf{r}' = 0, \quad (1.7)$$

which are incompatible with diagonal U_0 in the \mathbf{r} -representation. From (1.7) it follows for long waves in the \mathbf{k} -representation that

$$(\hat{U}_0)_{\mathbf{k}\mathbf{k}'} \sim k^2 k'^2, \quad (\hat{U}_j)_{\mathbf{k}\mathbf{k}'} \sim e^{i\mathbf{r}_j(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}_j} k^2 k'^2. \quad (1.8)$$

This means that as $\mathbf{k} \rightarrow 0$ the perturbation does not change the systematics of the wave functions, which remain plane waves. In the limiting case of long acoustic waves the medium can be regarded as continuous and the order of arrangement of the impurities does not play any role.

However, such considerations apply only for the acoustic branch [as a result of (1.7)]. For the optical branch and for electrons, condition (1.7) does not hold and plane waves do not satisfy the equations (1.2) and (1.3) even as $\mathbf{k} \rightarrow 0$. Therefore the perturbation \hat{U}_0 can be regarded qualitatively as a delta-function and we write the potential $U_0(\mathbf{r}) = U_0\delta_{\mathbf{r}\mathbf{r}_0}$. In the \mathbf{k} -representation

$$(\hat{U}_0)_{\mathbf{k}\mathbf{k}'} = U_0, \quad (U_j)_{\mathbf{k}\mathbf{k}'} = U_0 e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}_j}. \quad (1.9)$$

This corresponds for lattice vibrations to the situation wherein each impurity atom has a modified elastic coupling with its position of equilibrium; an analogous form results also from a change in mass of the impurity atom (8):

$$(U_0)_{\mathbf{k}\mathbf{k}'} = \frac{m'-m}{m} \omega(\mathbf{k}) \omega(\mathbf{k}'), \\ (U_j)_{\mathbf{k}\mathbf{k}'} = \frac{m'-m}{m} \omega(\mathbf{k}) \omega(\mathbf{k}') e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}_j}. \quad (1.10)$$

For $\mathbf{k}, \mathbf{k}' \ll 1$,

$$(U_j)_{\mathbf{k}\mathbf{k}'} = U_0 e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}_j} \quad U_0 = \frac{m'-m}{m} \omega^2(0).$$

A generalization of a delta-function perturbation is an arbitrary degenerate perturbation of rank one (i.e., a one-dimensional projection operator)*

$$\hat{U}_0\psi = U_0(\psi, f)f, \quad \hat{U}_j\psi = U_0(\psi, f_j)f_j, \quad f_j = f(\mathbf{r}-\mathbf{r}_j).$$

In \mathbf{k} -space

$$(\hat{U}_0)_{\mathbf{k}\mathbf{k}'} = U_0 f_{\mathbf{k}} f_{\mathbf{k}'}, \quad (\hat{U}_j)_{\mathbf{k}\mathbf{k}'} = U_0 e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}_j} f_{\mathbf{k}} f_{\mathbf{k}'}, \\ f(\mathbf{r}) = \int e^{i\mathbf{k}\cdot\mathbf{r}} f_{\mathbf{k}} d\mathbf{k}. \quad (1.11)$$

We see that all the examples (1.8)–(1.10) possess the form (1.11)

The very simple model describing the excitation

*The rank of the matrix U_0 is one.

spectrum in a solid solution can thus be reduced to an equation of the form

$$(E(\mathbf{k}) - E)\psi + \sum U_j \psi = 0, \quad U_j = U(\mathbf{r} - \mathbf{r}_j), \quad (1.12)$$

or

$$(E(\mathbf{k}) - E)\psi + U_0 \sum (\psi, f_j) f_j = 0, \quad f_j = f(\mathbf{r} - \mathbf{r}_j),$$

$$(\hat{H}_0 = \hat{E}(\mathbf{k}), \quad \hat{U}_0 = U_0(\cdot, f) f). \quad (1.13)$$

The local perturbation $U(\mathbf{r})$ in (1.12) or $f(\mathbf{r})$ in (1.13) is different from zero only in a small region of radius r_0 . For a delta-function perturbation, i.e., $U(\mathbf{r}) = U_0 \delta_{\mathbf{r}\mathbf{r}_0}$ or $f(\mathbf{r}) = \delta_{\mathbf{r}\mathbf{r}_0}$, both forms of (1.12) and (1.13) coincide. This case is most natural for the discrete model. When there is a continuous argument and the delta-function perturbation $U(\mathbf{r}) = U_0 \delta(\mathbf{r})$ leads to divergences, the general cases (1.12) and (1.13) must be studied together.

Subsequently we will start out in both formulations from the Hamiltonian (1.1), but in actual calculations we will work with (1.12) and (1.13).

2. FORMULATION OF THE PROBLEM. GENERAL CONSIDERATIONS

Let N be the number of cells in the crystal ($N \rightarrow \infty$), the volume of a cell will be taken as unity.

The operator \hat{H} defined by (1.1) or (1.12) is a random function, in so far as the points \mathbf{r}_j are random and only are given in a probabilistic form. If c is the impurity concentration, then the probability that an impurity atom lies at the point \mathbf{r}_1 is c ; the probability that two impurity atoms are found at the points \mathbf{r}_1 and \mathbf{r}_2 is $c^2 W_1(\mathbf{r}_2 - \mathbf{r}_1)$; for three impurity atoms it is $c^3 W_2(\mathbf{r}_2 - \mathbf{r}_1, \mathbf{r}_3 - \mathbf{r}_1)$ and so on. As $(\mathbf{r}_i - \mathbf{r}_k) \rightarrow \infty$ the correlation function $W \rightarrow 1$. $W = 0$ when $\mathbf{r}_i = \mathbf{r}_k$. Instead of a discrete function $W(\mathbf{r})$, where \mathbf{r} is the lattice site vector with integer components, it is sometimes convenient to introduce a more general continuous density distribution $w(\mathbf{r}), \dots$. For small distances $w(\mathbf{r})$ has δ -function maxima at the lattice sites, but at large distances we can neglect the structure and write $w(\mathbf{r}) = 1$.

By virtue of the spatial uniformity of the impurity-atom probability distribution as $N \rightarrow \infty$, limiting laws can be derived for the spectral density; these laws are authentic and are the object of our study. In particular, any quantity of the type $\text{Sp}[\Phi(\hat{H})/N]$ can be regarded as "self-averaging," i.e., authentic for an infinite crystal (by virtue of additivity). This includes the spectral density $\nu(E, c)$, normalized to unit volume (a single cell)

$$\nu(E, c) = \frac{dn(E, c)}{dE} = \text{Sp Im} \frac{\hat{G}}{\pi N}, \quad \hat{G} = (E - \hat{H})^{-1}, \quad E = E - i0, \quad (2.1)$$

$$\nu_0(E) = \nu(E, 0)$$

$$= \text{Sp Im} \left(\frac{G_0}{\pi N} \right) = \frac{1}{(2\pi)^3} \int_{E(\mathbf{k})=E} \frac{d\Omega_{\mathbf{k}}}{|\nabla E(\mathbf{k})|}, \quad n_0 = \frac{1}{(2\pi)^3} \int_{E(\mathbf{k}) < E} d\mathbf{k}. \quad (2.2)$$

Along with formula (2.1), it is useful to write down a formula for the change in the relative number of states $n(E, c)$

$$n(E, c) = \int_{-\infty}^E \nu dE,$$

$$\xi(E, c) = n_0(E, c) - n(E) = \overline{\text{Sp Im} \{ \ln \hat{G} - \ln G_0 \} / \pi N}$$

$$= \frac{1}{\pi N} \overline{\text{Arg Det} [(1 - \hat{G}_0 \sum_j \hat{U}_j)^{-1}]}. \quad (2.3)$$

The bar which denotes the averaging operation in (2.3) can be omitted, since the asymptotic behavior of the functions makes no difference. In calculations, however, averaging very much simplifies the problem and we will always use it. Since the excitation spectrum in our initial ideal crystal has a band character (our simple model consists of one band $E(\mathbf{k})$), the addition of disordered impurities leads on the one hand to broadening and to a change in the spectral density of the bands, and on the other to a possibility of the appearance of new impurity bands. The latter come about because of the "interactions" between the impurity levels in the case when the impurity atom in the infinite crystal gives rise to an isolated local level. We must remember that whereas in the one-dimensional problem an arbitrarily small local perturbation leads to an isolated level, in the three-dimensional case the appearance of such a level calls for some finite "critical" value of the perturbation. This circumstance significantly distinguishes the three-dimensional problem from the one-dimensional.

Near the ordinary points of the spectrum the spectral density $\nu(E, c)$ can be obtained by means of an expansion in powers of U (perturbation theory) or in powers of c (the gas approximation or the theory of localized perturbations). In the expansion in powers of the concentration, the coefficient of c^n contains at least the quantity U^n (and higher powers of U). Therefore the method of expansion in powers of the concentration, developed by the author^[7-10], appears to be more general. Any approximation derived from one of the usual forms of perturbation theory is obtained from the corresponding number of terms in the series in c by additionally expanding these terms in powers of U . In particular in order to obtain the second-order terms of perturbation theory it is sufficient to retain the terms quadratic in the concentration.

Although the method of expansion in powers of the concentration^[7-10], described briefly below (Sec. 6), makes it possible to obtain many quantitative results and also gives many qualitative features of the structure of the spectrum, it breaks down in the region near the singular points of the spectral density $\nu(E, c)$. Such points, for $c \rightarrow 0$, are end points of the band $E(\mathbf{k})$ [and other extremal points of $E(\mathbf{k})$] and also points E_0 representing isolated levels, which come from the isolated local perturbation $U_0(\mathbf{r})$. For $c = 0$, that is, for an ideal crystal, it is well known that all the singular-

ities of the function $\nu(E, 0)$ have the form $\nu(E, 0) \sim \sqrt{(E - E_g^0)}$ [E_g^0 are the extremal points of $E(\mathbf{k})$]. In the one-dimensional case, to the contrary, $\nu(E, 0) \sim (E - E_g^0)^{-1/2}$. As to the local levels which come from the isolated impurity center, as $c \rightarrow 0$ we have in their vicinity

$$\frac{\nu(E, c)}{c} \Big|_{c=0} \rightarrow \delta(E - E_0).$$

When $c \neq 0$ the singularities of $\nu(E, c)$ as functions of E are smeared out, and the problem consists in the study of the analytic character of $\nu(E, c)$ as a function of both arguments in the (E, c) plane near the points $(E_g^0, 0)$ and $(E_0, 0)$.

Besides the points $(E_g^0, 0)$ and $(E_0, 0)$ at arbitrary concentrations the new boundaries of the energy bands E_g (both ground state and impurity) become singular points of $\nu(E, c)$. It is curious that the true boundary of the band E_g does not depend on the concentration c , albeit small, there exists a finite probability

$$W = e^{\Delta\sigma}, \quad \Delta\sigma = -Vc' \ln \frac{c'}{c},$$

of a fluctuation of concentration c' in the volume V , sufficient for the realization of the given quantum state that exists at the concentration c' .*

However the expression for the probability W shows that the spectral density in this region of the spectrum is extremely small and cannot be obtained by an expansion in powers of the concentration; therefore this fact usually escapes attention in approximate methods of determination of the spectrum. The line of singularities of $\nu(E, c)$, corresponding to the true band boundaries, is thus the straight line $E = E_g$ in the (E, c) plane. Figures 1a and 1b show schematically the structure of the spectrum vs. concentration.

The possibility should be noted of the appearance of certain "true" or "natural" boundaries of the spectrum in place of the one existing for $c = 0$. This takes place in the case when the impurity band is separated from the ground state band by a gap in the spectrum (cf. Sec. 6). For this to occur in our model, it is necessary that the spectral bands of the pure crystals $c = 0$ and $c = 1$ do not overlap.

The wave functions depend essentially on the actual positions of the impurity atoms, and talk of their mean values is meaningless. In the general case only the qualitative form of these functions will be of interest to us. However there are certain cases, as we will see, when specific individualized states arise with new distinctive systematics in the aperiodic structure.

*For arbitrary (not small) c and c' the probability P of a fluctuation in the volume V is determined in the absence of correlation effects (i.e., for an ideal solution) by the formula

$$\ln P = \Delta\sigma = V \left\{ S(c') - S(c) - (c' - c) \frac{\partial S}{\partial c} \right\},$$

$$S(c) = -c \ln c - (1 - c) \ln (1 - c)$$

(σ is the entropy).

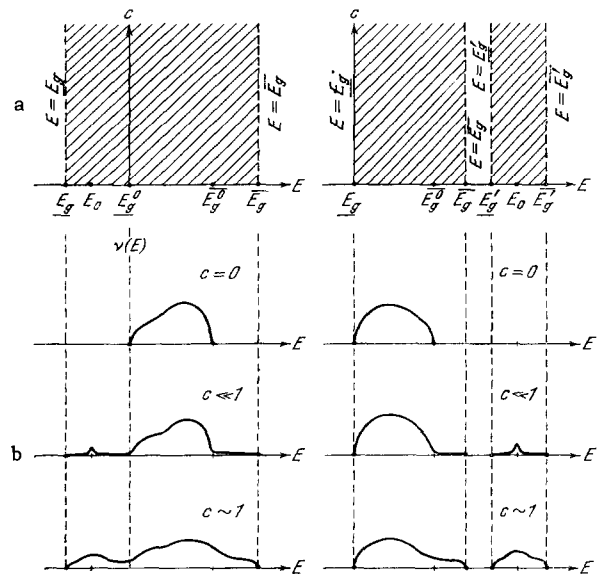


FIG. 1. Schematic distribution of the singularities of $\nu(E, c)$ in the (E, c) plane (a), and the change in $\nu(E, c)$ as c increases (b), in two cases corresponding to unsplit (left) and split (right) impurity bands.

These systematics will be manifest in the structure of a corresponding region of the energy spectrum. But of course these states must be also studied in more detail by themselves.

The study of the spectrum in the vicinity of the singular points is specially interesting because it is in this region that a complete reorganization of the quantum states and systematics occurs. Near these points the perturbation cannot be considered small in its influence either on the states or on the spectrum; but the presence of some small parameters allows the study of the new systematics and their asymptotic properties.

Therefore the study of the structure of the spectrum will begin with the study of the singularities of the function $\nu(E, c)$.

3. THE BEHAVIOR OF THE SPECTRAL DENSITY NEAR THE TRUE BOUNDARY OF THE SPECTRUM

For the study of the behavior of $\nu(E, c)$ near the true boundary of the spectrum E_g , we start with a simple model which will help us construct the character of the singularities in the general case.

We consider the discrete model of (1.12) with the point perturbation $U_0(\mathbf{r}) = U_0\delta_{\mathbf{r}\mathbf{r}_0}$. (For lattice vibrations this corresponds to each impurity atom having a changed elastic coupling with its position of equilibrium; the variation of mass of the impurity atom leads to an analogous form for the perturbation^[10]).

Evidently, each additional impurity atom can move the eigenvalues only to the left when $U_0 < 0$ and only to the right when $U_0 > 0$. This means that if we do not fix the concentration c , the boundary of the spectrum on the left coincides when $U_0 < 0$ with the left boundary of the spectrum for $c = 1$ [i.e., the spectrum of

the impurity only $E_1(\mathbf{k}) = U_0 + E(\mathbf{k})$, $E_g = U_0 + E_g^0$; the right boundary is determined by the spectrum of the initial ideal crystal for $c = 0$ [$E_0(\mathbf{k}) = E(\mathbf{k})$], that is, $E_g = E_g^0$. For $U_0 < 0$, the inverse holds

$$E_g = E_g^0, \quad \bar{E}_g = U_0 + E_g^0.$$

Consider the boundary $E_g = U_0 + E_g^0$. Its exact value can be attained only for an infinite crystal wholly made up of impurity atoms. Assume that near E_g we have

$$E(\mathbf{k}) = E_g^0 + \frac{k^2}{2\mu}.$$

It will be convenient in what follows to regard the energy E , and hence the mass μ , as dimensionless. If the characteristic energy is the band width ($k \sim 1$), then $\mu \sim 1$.

If in a solution of concentration c there is a fluctuating region of sufficiently large volume V wholly built of impurity atoms, then in this region there exist standing waves whose smallest wave number is $k \sim \pi/V^{1/3}$, which corresponds to the lowest level

$$E = E_g + \frac{\kappa}{2\mu} V^{-2/3}. \tag{3.1}$$

The value of the numerical coefficient κ depends on the shape of the region. Its minimum value κ_0 is asymptotically attained for the sphere

$$E - E_g = \frac{\kappa_0}{2\mu} V^{-2/3}; \quad \kappa_0 = \left(\frac{4}{3}\right)^{2/3} \pi^{8/3}. \tag{3.2}$$

The relative frequency or the probability of the appearance of such a spherical region (in the complete absence of correlation) is evidently c^V . Expressing the volume V in terms of the energy of the lowest level (3.2), $V = (\kappa_0/2\mu)^{3/2} (E - E_g)^{-3/2}$, and recognizing that regions of smaller volume or of non-spherical shape do not have such low levels, and that the bigger the region the smaller the probability, we get for the probability of the level E in the vicinity of E_g , or alternatively for the spectral density $\nu(E, c)$, the estimate

$$\nu \sim \exp\{\lambda (E - E_g)^{-3/2} \ln c\}, \quad \lambda = \frac{\sqrt{2}}{3\mu^{3/2}} \pi^4. \tag{3.3}$$

We have left out the coefficient of the exponential, the exact value of which is difficult to estimate.

Near the right boundary, considering regions constructed wholly out of the host atoms and taking

$$E(\mathbf{k}) = \bar{E}_g - \frac{k'^2}{2\mu'}, \quad \mathbf{k}' = \mathbf{k} - \mathbf{k}_0,$$

we obtain

$$\nu(E, c) \sim \exp\{\lambda' (\bar{E}_g - E)^{-3/2} \ln(1-c)\}; \quad \lambda' = \frac{\sqrt{2}}{3\mu'^{3/2}} \pi^4. \tag{3.4}$$

If $c \ll 1$ it is possible to estimate the coefficient of the exponential by going to the limit*

*Formula (3.5) joins the dependence $\nu = a(\bar{E}_g - E)^{1/2}$, correct for $(\bar{E}_g - E) \gg c$, to the exponential dependence (3.4) for $(\bar{E}_g - E) \ll c$ (cf. Sec. 5.4).

$$c \rightarrow 0, \quad \nu(E, 0) = a \sqrt{\bar{E}_g - E}, \quad a = (2\pi)^{-2} (2\mu)^{3/2},$$

$$\nu(E, c) = a \sqrt{\bar{E}_g - E} \exp\{-\lambda' (\bar{E}_g - E)^{-3/2} c\}. \tag{3.5}$$

It follows that formulae (3.3)–(3.5) remain correct in all cases where the boundaries of the intervals of the continuous spectrum of the random operator $\hat{H} = \hat{H}_0 + \Sigma \hat{U}_i$ are reached in the limiting cases $c = 0$ or $c = 1$ (i.e., for a lattice of pure A or pure B). This takes place in particular in the case $\hat{H}_0 = -\nabla^2/2\mu$ if the local perturbation $U_0(\mathbf{r})$ has always the same sign (cf. Fig. 2).

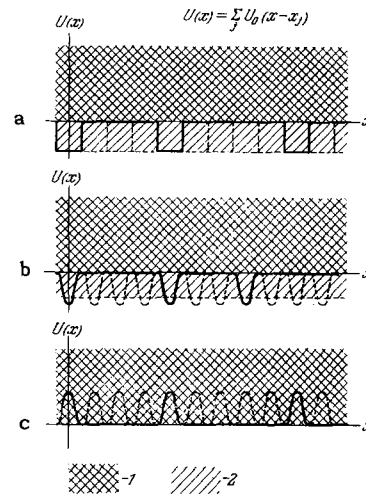


FIG. 2. Distribution of allowed levels in a disordered system: 1 – for $c = 0$, 2 – for $c \neq 0$ (the lower boundary corresponds to a fluctuation cluster with $c = 1$).

It will be shown below that the spectrum of the operator \hat{H} consists of either one or several intervals and all the foregoing applies to the boundaries of any interval. Finally, in the case of anisotropic dependence of $E(\mathbf{k})$ near the extremum

$$E(\mathbf{k}) = E_g^0 + \sum \frac{k_i^2}{2\mu_i}$$

the optimal shape of the fluctuating region ensuring an approximation to the bottom of the band is no longer spherical. This changes the values of the parameters λ and λ' in (3.3)–(3.5) slightly, but does not change the essence of the results.

Going to the general case it follows that if the lowest (highest) level in an interval of continuous spectrum of the operator \hat{H} is attained for a crystal which is neither pure A nor pure B ($c = 0$, $c = 1$), then it necessarily corresponds to some case of ideal ordering of the atoms (e.g., the structure ABAB). Let

$$E_I(\mathbf{k}) = E_g^I + \frac{k^2}{2\mu_I}$$

be the dispersion relation for this type of ordering near the lower boundary of the spectrum.

Then, as before, a level E sufficiently close to $E_g = E_g^I$ is attained via a fluctuating, completely or-

dered alignment of a spherical region of minimal volume

$$V = \lambda_I (E - \underline{E}_g)^{-3/2}, \quad \lambda_I = \frac{V\sqrt{2}}{3\mu_I^{3/2}} \pi^4.$$

The probability of such fluctuations is now no longer c^V even when there is no correlation (short-range order) but depends on the actual type of ordering. In the general case this probability is of the form $\exp\{-V\varphi(c)\}$, $\varphi(c) > 0$, where the form of $\varphi(c)$ is determined both by the type of ordering and by the character of the correlation in any given case. Thus, for example, for the ordering ABAB and in the absence of correlation

$$\varphi(c) = -\frac{1}{2} \ln c (1-c).$$

Finally, in the general case the singularity on the boundary of the spectrum of the random operator \hat{H} is of the form

$$\nu(E, c) \sim \exp\{-\lambda\varphi(c)(E - \underline{E}_g)^{-3/2}\}. \quad (3.6)$$

If the boundary of the spectrum does not correspond to the case $c = 0$ then $\varphi(c) \sim \ln c$ for small c .

For systems with partial ordering $\varphi = \varphi(c, \eta)$ (η is the ordering coefficient). If the boundary of the spectrum corresponds to complete ordering then, just as for (3.4) and (3.5), we can obtain when $(1 - \eta) \ll 1$ (i.e., for almost complete order)

$$\nu(E, c) = a \sqrt{E - \underline{E}_g} \exp\{-\lambda'(1 - \eta)(E - \underline{E}_g)^{-3/2}\}.$$

A special case is that of the lower bound of the acoustic branch $E(\mathbf{k}) = \omega^2(\mathbf{k}) = s^2k^2$; $E(0) = 0$.

As has already been shown, this bound does not move when impurities are added, and plane waves with $\omega^2 \sim k^2$ exist near it for arbitrarily disordered structures (the medium can be considered as continuous for acoustic vibrations), and it follows that $\nu(E, c) \sim \sqrt{E}$ as $E \rightarrow 0$.

To conclude this section we will show how the analogous formulae look in the one-dimensional case (a linear chain). For an ideal one-dimensional periodic structure it is well known that $\nu(E, 0) \sim (E - \underline{E}_g^0)^{-1/2}$ on the boundary of the spectral interval. Besides this, if L is the length of the fluctuating region, then the minimum level will be

$$E - \underline{E}_g^0 = \frac{\pi^2}{2\mu L^2}, \quad L = \pi(2\mu)^{-1/2}(E - \underline{E}_g^0)^{-1/2}.$$

Therefore formulae (3.3) and (3.5) can be written in the form

$$\nu(E, c) \sim \exp\{\pi(2\mu)^{-1/2}(E - \underline{E}_g)^{-1/2} \ln c\}, \quad (3.7)$$

$$\nu(E, c) \sim a(\bar{E}_g - E)^{-1/2} \exp\{-\pi(2\mu')^{-1/2}(\bar{E}_g - E)^{-1/2}c\}, \quad (3.8)$$

and in the general case

$$\nu(E, c) \sim \exp\{-\varphi(c)(E - \underline{E}_g)^{-1/2}\}. \quad (3.9)$$

4. THE BEHAVIOR OF THE SPECTRAL DENSITY NEAR IMPURITY LEVELS. THEORY OF THE BROADENING OF LEVELS WITH CONCENTRATION

1. Local Impurity Levels

Before going over to the study of the singularities of $\nu(E, c)$ near the impurity levels, we consider the whole situation in more detail. To this end we again start out with the simplest example of a delta-function perturbation $U(\mathbf{r}) = U_0\delta_{\mathbf{r}\mathbf{r}_0}$ in the discrete model (1.12)

$$(\hat{H}_0 - E)\psi + U_0 \sum_j f_j \psi = 0, \quad f_j = \delta_{\mathbf{r}\mathbf{r}_j}, \quad \hat{H}_0 = E(\mathbf{k}). \quad (4.1)$$

Hence

$$\psi = U_0 \hat{G}_0 \sum_j \tau_j f_j = U_0 \sum_j \tau_j F(E, \mathbf{r} - \mathbf{r}_j), \quad \tau_j = \psi(\mathbf{r}_j),$$

$$G_0 = (E - \hat{H}_0)^{-1}, \quad F(E, \mathbf{r}) = \hat{G}_0 f_0 = \frac{1}{8\pi^3} \int \frac{e^{i\mathbf{k}\mathbf{r}} d\mathbf{k}}{E - E(\mathbf{k})}. \quad (4.2)$$

Taking $\mathbf{r} = \mathbf{r}_i$ in (4.2), we get for τ_i the system

$$\tau_i - U_0 \sum_j F_{ij} \tau_j = 0, \quad F_{ij} = F(E, \mathbf{r}_{ij}), \quad \mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j. \quad (4.3)$$

The impurity levels of interest to us are determined in accordance with (4.3) from the condition

$$\text{Det}(\delta_{ij} - U_0 F(E, \mathbf{r}_{ij})) = 0. \quad (4.4)$$

We consider the case of one impurity atom at the origin.

In this case, as is evident from (4.3) and (4.4), the impurity level E_0 , if it exists, is the root of the equation

$$1 - U_0 F_0(E_0) = 0,$$

$$F_0(E) \equiv F(E, 0) = \frac{1}{(2\pi)^3} \int \frac{d\mathbf{k}}{E - E(\mathbf{k})} = \int_{\underline{E}_g^0}^{\bar{E}_g^0} \frac{\nu_0(E') dE'}{E - E'}, \quad (4.5)$$

and corresponding to it is the wave function

$$\psi_0(\mathbf{r}) = \tau F(E_0, \mathbf{r}). \quad (4.6)$$

Inasmuch as $|F_0(E)|$ increases monotonically on approaching the boundaries of the region $(\underline{E}_g^0, \bar{E}_g^0)$ from outside, a unique root of (4.5) (lying outside the region) exists for $E < \underline{E}_g^0$, if

$$|F_0(\underline{E}_g^0)| = \int_{\underline{E}_g^0}^{\bar{E}_g^0} \frac{\nu_0(E') dE'}{E_g^0 - E'} > \left| \frac{1}{U_0} \right|, \quad U_0 < 0$$

and correspondingly, on the right of \bar{E}_g^0 , if $U_0 > 0$,

$$|F_0(\bar{E}_g^0)| > \frac{1}{U_0}.$$

The critical value of the perturbation U_0 is therefore

$$|U_0|_{cr} = \begin{cases} 1/F_0(\underline{E}_g^0) & U_0 < 0, \\ 1/F_0(\bar{E}_g^0) & U_0 > 0. \end{cases} \quad (4.7)$$

The convergence of the integral (4.5) when $E = \underline{E}_g^0$

[i.e., the finiteness of $F(E_g^0)$ and $F(\bar{E}_g^0)$] follows from the fact that $\nu_0(E) \sim \sqrt{(E - E_g^0)}$ near the boundary. (In the one-dimensional case, when $\nu_0(E) \sim (E - E_g^0)^{-1/2}$, the integrals $F_0(E_g^0)$ diverge and therefore levels $E - E_g^0 \sim -U_0$ exist for arbitrarily small U_0 ; in the two-dimensional case $\nu_0(E_g^0)$ is constant and therefore $E_g^0 - E \sim \exp(-\text{const}/U_0)$.)

In the general case of an arbitrary local perturbation, E_0 is determined by the analogous equation

$$1 = I(E_0) = \int \frac{c(\mathbf{k}) d\mathbf{k}}{E_0 - E(\mathbf{k})}, \tag{4.8}$$

where the actual form of $c(\mathbf{k})$ is connected with the form of the potential $U_0(\mathbf{r})$. The quantity $c(\mathbf{k})$ may be of alternating sign; $I(E)$ is then no longer a monotonic function on both sides of the interval (E_g^0, \bar{E}_g^0) and (4.8) can have several roots.

For continuous \mathbf{r} , for example, if

$$\hat{H}_0 = -\Delta/2m, \quad E(\mathbf{k}) = k^2/2\mu, \quad \bar{E}_g^0 = \infty,$$

any local (not point) perturbation leads to a $c(\mathbf{k})$ that decreases rapidly when $k \gg 1/r_0$ (r_0 is the radius of the perturbation). This ensures convergence of the integral $I(E)$ as $k \rightarrow \infty$.

In the presence of two impurity centers at a distance \mathbf{r} apart the equation for the local levels is in accordance with (4.4) of the form

$$\begin{vmatrix} 1 - U_0 F_0(E) & -U_0 F(E, \mathbf{r}) \\ -U_0 F(E, \mathbf{r}) & 1 - U_0 F_0(E) \end{vmatrix}. \tag{4.9}$$

For large \mathbf{r} , $F(E, \mathbf{r})$ decreases rapidly; if $E(\mathbf{k}) = E_g^0 + k^2/2\mu$ near E_g^0 , then

$$F(E, \mathbf{r}) = \frac{-1}{(2\pi)^3} \int \frac{e^{i\mathbf{k}\mathbf{r}} d\mathbf{k}}{\frac{E_g^0 - E}{2\mu} + \frac{k^2}{2\mu}} = -A \frac{e^{-\alpha r}}{r},$$

$$\alpha^2 = 2\mu(E_g^0 - E), \quad A = \frac{\mu}{2\pi}. \tag{4.10}$$

The roots of (4.9) thus tend to E_0 as $r \rightarrow \infty$. Taking $E = E_0 - \epsilon$ and using (4.5) we have

$$1 - U_0 F_0(E_0 - \epsilon) \approx U_0 B \epsilon, \quad B = \frac{1}{(2\pi)^3} \int \frac{d\mathbf{k}}{(E(\mathbf{k}) - E_0)^2}.$$

Hence

$$\begin{vmatrix} \epsilon & \lambda \frac{e^{-\alpha r}}{r} \\ \lambda \frac{e^{-\alpha r}}{r} & \epsilon \end{vmatrix} = 0, \quad \lambda = \frac{A}{B}, \tag{4.11}$$

that is,

$$\epsilon_{1,2}(\mathbf{r}) = \pm \lambda \frac{e^{-\alpha r}}{r}$$

Both states ψ_1 and ψ_2 corresponding to these levels are ‘‘resonances’’ and ‘‘belong’’ in equal amount to both impurity centers \mathbf{r}_1 and \mathbf{r}_2

$$\Psi_{1,2} = \frac{1}{\sqrt{2}} (\Psi_{10} \pm \Psi_{20}), \quad \Psi_{j0} = \psi_0(\mathbf{r} - \mathbf{r}_j). \tag{4.12}$$

For an arbitrary number n of impurity centers located large distances $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ apart the levels $E = E_0 - \epsilon$ are found from

$$\text{Det} \left(\epsilon \delta_{ij} + \lambda \frac{e^{-\alpha r_{ij}}}{r_{ij}} (1 - \delta_{ij}) \right) = 0. \tag{4.13}$$

We shall consider the systematics of the levels and states defined by the roots of (4.13) in the next section. We mention here only that the unique nature of the systematics, as in the case of two centers, is connected with the identity of the impurity atoms (of the perturbations U_j). If, for example, the impurity atom at \mathbf{r} is different from the others (in our model the amplitude $U_1 \neq U_0$) then there corresponds to this impurity center a level $E_1(\mathbf{r}_{12}, \mathbf{r}_{13}, \dots) = E_1 - \epsilon(\mathbf{r}_{12}, \dots)$ with the end-point value E_1

$$1 = U_1 F_0(E_1) \tag{4.14}$$

and with a wave function localized around \mathbf{r}_1 . The shift $\epsilon_1(\mathbf{r}_{12}, \dots)$ of this level caused by the other impurities is obtained for large r_{ik} from the equations

$$\begin{vmatrix} U_1 B \epsilon_1(\mathbf{r}_{12}, \dots) & -U_0 A \frac{e^{-\alpha r_{12}}}{r_{12}} & \dots \\ -A U_1 \frac{e^{-\alpha r_{12}}}{r_{12}} & 1 - U_0 F_0(E_1) & \dots \\ \dots & \dots & \dots \end{vmatrix} = 0$$

and it follows that

$$\epsilon_1 = \epsilon_1(r_{12}) = \lambda_1 \frac{e^{-2\alpha r_{12}}}{r_{12}^2}, \quad \lambda_1 = \frac{A^2 U_0}{B(F_0(E_0) - F_0(E_1))}, \tag{4.15}$$

where r_{12} is the distance to the nearest impurity center.

As we shall soon see, the whole situation is completely different for identical impurities ($U_1 = U_0$). Since the analysis of this situation is based on the asymptotic formula for the elements of the determinant in (4.13), we must point out that this formula remains valid not only for the point perturbations $\hat{U}_0 = U_0 \delta_{\mathbf{r}0}$ used by us, but for arbitrary local perturbations of extremely general form. For this result to be valid it is necessary in fact that the perturbation $U_0(\mathbf{r})$ be local in the sense of having a sufficiently rapid decrease at large distances (if $U_0(\mathbf{r})$ does not vanish identically outside a finite radius r_0). If on the other hand $U_0(\mathbf{r})$ decreases more slowly than $e^{-\alpha r}$, $\alpha = 2\mu(E_g^0 - E)$, then the whole effect of displacement of the levels is determined for small ϵ purely by the classical reduction of the sum of potentials at a given point \mathbf{r}_i ($\epsilon = \sum_{\mathbf{k} \neq i} U_0(r_{ik})$). The quantum or ‘‘wave’’ part connected with overlapping of the wave functions gives here only a small contribution (cf. Sec. 4.4).

2. The Systematics of Levels and States in the Impurity Band at Low Concentrations

The mean distance between impurity atoms is the large quantity $\bar{r} \sim c^{-1/3}$ ($c \ll 1$). Therefore random meetings of impurity atoms (pairs, triads, and so on) have the small probabilities c^2, c^3, \dots ; thus the neighbors of each impurity atom are with overwhelmingly large probability at distances $r \sim \bar{r} \sim c^{-1/3}$. When the impurities are situated far from each other the ground

level E_0 is shifted slightly; relatively large displacements ϵ from this level correspond to small distances r_{ik} . The overwhelmingly probable configurations of impurity centers, which we are going to consider in this section, are thus characterized by distances $r_{ik} \sim \bar{r} \sim c^{-1/3}$. At such large distances we can evidently neglect correlations in the distribution of impurities. Since the volume per impurity atom is c^{-1} , we can assume, introducing the coordinate $\mathbf{x} = \mathbf{rc}^{1/3}$, that the impurity atoms are distributed with uniform probability density $\rho(\mathbf{x}) = 1$ per unit volume in \mathbf{x} -space. Finally, introducing the large parameter of the theory $\alpha c^{-1/3} = t \gg 1$, we have

$$\text{Det} \left(\eta \delta_{ik} + (1 - \delta_{ik}) \frac{e^{-tx_{ik}}}{x_{ik}} \right) = 0, \quad (4.16)$$

$$x_{ik} = |\mathbf{x}_i - \mathbf{x}_k|, \quad \eta = \frac{\epsilon c^{-1/3}}{\lambda}$$

or

$$\text{Det} \left(\delta_{ik} + (1 - \delta_{ik}) z \frac{e^{-tx_{ik}}}{x_{ik}} \right) = 0, \quad z = \frac{1}{\eta}. \quad (4.17)$$

Let us consider (4.17) for any finite number n of impurity centers. In the study of the asymptotic ($t \rightarrow \infty$) systematics of levels and states we can consider $x_{ik} \gtrsim 1$, and since we have excluded the situations of small probability for which $x_{ik} \sim 1/t \rightarrow 0$, we can also exclude other random coincidences of the type $|x_{ik} - x_{il}| \sim 1/t \rightarrow 0$ ($k \neq l$), which have zero probability in the limit. Coincidences of such a form lead to the special "resonance" situations characteristic of periodic structures. For example, a chain consisting of a large number n of equidistant centers leads to an almost uniform distribution of levels in the strip $\Delta\eta \sim e^{-tx}/x$ (x is the distance between the centers), and the corresponding states are fully collectivized (plane waves). Such situations, which have infinitesimally small probability, are completely excluded.

We expand the determinant (4.17) in powers of z

$$1 + \sum_{m=2}^n \Lambda_m z^m = 0. \quad (4.18)$$

Each of the coefficients can be represented as the sum of all possible terms proportional to $e^{-t\mathcal{L}_m}$, where

$$\mathcal{L}_m = \sum_{\Gamma} l(\Gamma^{(j)}), \quad \sum_j j = m.$$

Here $l(\Gamma^{(j)})$ is the perimeter of a polygon Γ of j vertices, constructed on the points \mathbf{x}_k without any vertex occurring twice (the polygons do not have common vertices).

If $L_m = \min \mathcal{L}_m$, then in the limit

$$t^{-1} \ln \Lambda_m = -L_m.$$

Taking

$$|\eta| = e^{-st}, \quad |z| = e^{st}, \quad s = -\frac{\ln |\eta|}{t}, \quad (4.19)$$

we have for each term in (4.18) the estimate

$$t^{-1} \ln |\Lambda_m z^m| = ms - L_m. \quad (4.20)$$

For arbitrary s every term has a different order of smallness (in the sense of e^{-st}) and the whole determinant is determined by the one term $t^{-1} \ln D(s) = \max (s_m - L_m)$. Therefore (4.18) can only have a solution when the exponential indices of any two terms coincide as s is varied (the coincidence of a large number of terms simultaneously has a vanishingly small probability). Let us consider the sequence of exponents in (4.18) and (4.20)

$$0, 2s - L_2, 3s - L_3, \dots$$

If we put $L_{m+1} - L_m = a_m$, $L_{m+2} - L_m = 2b_m$, then the geometrical meaning of the quantity L_m leads to the inequalities

$$a_m + a_{m+1} = 2b_m > 0, \quad b_{m+1} > b_m. \quad (4.21)$$

The distribution of the roots s is clearly demonstrated graphically in Fig. 3. As s increases from 0, the first root appears for $2s = L_2 = 2x_{12}$ ($x_{12} = \min x_{ik}$); this root satisfies the two equations

$$\eta_{1,2} = \pm \eta, \quad s = -\frac{\ln |\eta|}{t} = x_{12}.$$

With further increase in s , by virtue of inequalities (4.21), roots appear in succession at the points determined either by the equation

$$ms - L_m = (m+2)s - L_{m+2}, \quad 2s = 2b_m. \quad (I)$$

or by the equation*

$$ms - L_m = (m+1)s - L_{m+1}, \quad s = a_m. \quad (II)$$

The first case occurs when $b_m < a_m$ and corresponds to the appearance of two levels $\eta = \pm |\eta|$ with equal

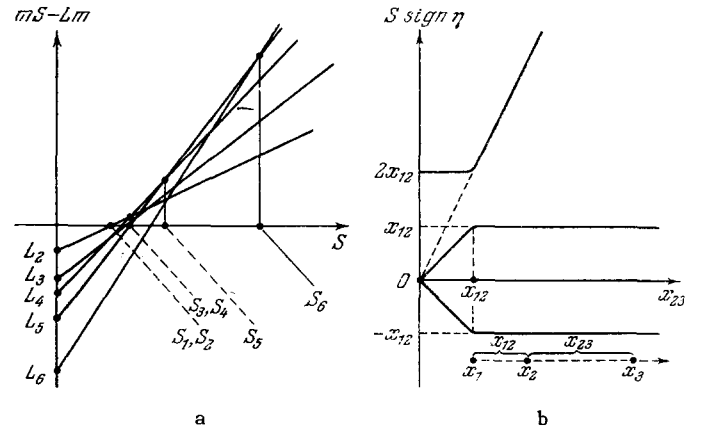


FIG. 3. a) Graphical solution of equations I and II [$s_m = \min (a_m, b_m)$]; b) position of levels s as a function of x_{23} with fixed x_{12} .

*This last result follows from very simple considerations: the equation $ms - L_m = (m+k)s - L_{m+k}$ corresponds to the equation

$$\eta^k = \exp \{-t(L_{m+k} - L_m)\}$$

for the characteristic values η . Since η is real (\hat{H} is the Hermitian), only the cases $k = 1, k = 2$ are possible.

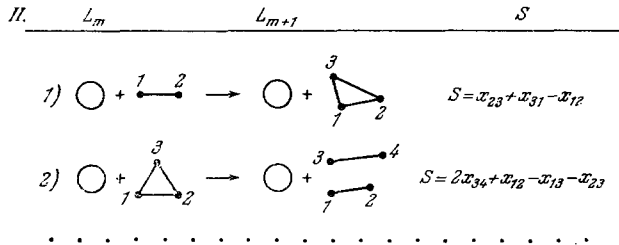
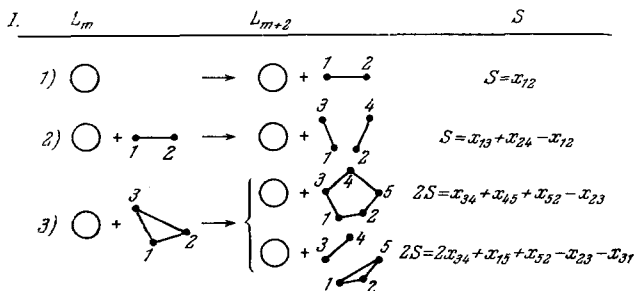
$s = b_m$. To them correspond two states, collectivized (in the zeroth approximation in e^{-t}) between the additional impurity centers which are in the contour L_{m+2} but are not in L_m .

In the second case, $a_m < b_m$, the root $s = a_m$ corresponds to a local state of one of the impurity centers and to an energy of definite sign. (Of course, this local state is slightly contaminated by exponentially small admixtures of other states). Equations (I) and (II) lead to a geometrical construction for the system of roots s . In the study of these it is important to note that the minimal contour $L_m = \min L_m$ for an arbitrary number of vertices m can with very high probability be broken up into separate contours containing a very small number of vertices: most often of all with two vertices ($2x_{ik}$), and less often with three, five, and so on (contours with an even number of vertices $2k, k > 1$, always break up into smaller parts; in particular such a contour can be decomposed into a sum of "two-cornered" polygons—sides without a common vertex—which has a smaller perimeter). Therefore the most frequent case of equations of type (I) is when the contours in L_{m+2} and L_m differ from each other by one "two-cornered" segment; i.e., $b_m = L_{m+2} - L_m = 2x_{ik}$, where x_{ik} is the smallest segment compared with all neighbors (i.e., $x_{ik} < x_{il}, x_{kl}$ for all $l \neq i, k$). In this case the energy level depends therefore only on one of the distances x_{ik} and is not affected by the others. In the general case it follows from (I) and (II) that the quantities s , that is to say the energy levels on a logarithmic scale, are of the form

$$s = \sum a_{jk} x_{jk}, \quad \sum a_{jk} = 1, \quad \begin{cases} a_{jk} = 0, \pm \frac{1}{2}, \pm 1, & \text{(I)} \\ a_{jk} = 0, \pm 1, \pm 2. & \text{(II)} \end{cases} \quad (4.22)$$

The actual values a_{jk} depend on the inequalities satisfied by x_{jk} for the impurity centers surrounding the given center.

From these considerations of the structures L_m , we can produce a classification of the roots s with the help of the diagrams below. The sum of polygons common to the contours L_m and L_{m+2} (I) or to L_m and L_{m+1} (II) is depicted by a circle; the contours which are changed on adding supplementary vertices and which determine the quantity s are shown on each graph separately and form the basis of the classification. We define the "order" of a diagram as the number of "reconstructed" vertices on the right hand side of the diagram.



$L_2 = 2 \min(x_{1k}, x_{2k}), L_3 = \min(x_{1k} + x_{k2} + x_{1i}),$ $L_4 = 2 \min(x_{ik} + x_{1m}), i \neq k \neq m$		
$a_2 = L_3 - L_2$ $b_2 = (L_4 - L_2)/2$ $L_2 = 2x_{12}$	$a_2 > b_2$	$a_2 < b_2$
$L_4 = 2(x_{12} + x_{34})$ $S_{1,2} = b_2 = x_{12}$	(a)	(b)
$L_4 = 2(x_{13} + x_{24})$ $S_{1,2} = b_2 = x_{12}$	(c)	(d)
	--- L_3	— L_4

FIG. 4. Scheme for obtaining levels s_1, s_2, s_3, s_4 in a system with four impurity centers.

As an example we show in Fig. 4 the conditions (inequalities) for the realization of each of the possible cases for the roots s of a group of four impurity centers.

We should emphasize some peculiarities of the states (wave functions) corresponding to the diagrams I.2, I.3, etc. For example, in I.2 the wave function, apart from exponentially small additional terms, is

$$\psi = \frac{1}{\sqrt{2}} (\psi_3^0 \pm \psi_4^0),$$

that is, the states are collectivized near the comparatively distant centers 3 and 4 while the intermediate centers 1 and 2 do not make a contribution to ψ . At the same time the energy levels are determined from the lengths x_{12}, x_{13}, x_{24} and are not connected at all with the tunnel effect for large x_{34} (i.e., with the overlapping of the wave functions ψ_3^0 and ψ_4^0). The situation here is rather reminiscent of what happens in a periodic structure in the strong-coupling approximation: the overlapping of the wave functions for neighboring centers ($\sim e^{-\alpha r_{12}}$) leads to collective states (with a wave function of finite amplitude) at large distances, where no direct tunnelling is possible at all.

The "pairing" of distant centers by means of a longer chain of intermediate centers is obtained from diagrams of type I with a large number of "reconstructed" vertices (i.e., diagrams of higher order). Since the inequalities in x_{jk} , which generate such diagrams, define a finite region of variation of x_{jk} in

\mathbf{x} -space, the states formed are stable against relatively small but finite displacements of the points \mathbf{x}_i . However, it is easy to see that the probability of such states decreases rapidly as the order of the graphs increases. Finally we notice that the systematics obtained here do not depend on the number of impurity centers n and hence are correct in the limit $n \rightarrow \infty$.

3. Determination of the Spectral Density near an Impurity Level

The foregoing systematics of the levels and the expressions for s in terms of the lengths x_{ijk} reduce the problem of the determination of $\nu(E, c)$ near E_0 to the calculation of the probability density $\mathcal{P}(s) ds$. It is evident from the physical meaning of ν that

$$\frac{\nu(E-\epsilon, c)}{c} = p(\epsilon) = \mathcal{P}(s) \frac{ds}{d\epsilon}, \quad s = c^{1/3} \alpha^{-1} \ln \left| \frac{c^{1/3}}{\epsilon} \right|. \quad (4.23)$$

In the expression for s in (4.23) the coefficients a_{ijk} are determined by the numerical inequalities for x_{ijk} , and the points \mathbf{x}_i are distributed with uniform probability density $\rho(\mathbf{x}) = 1$ in \mathbf{x} -space. Therefore the spectral density $\mathcal{P}(s) ds$ does not depend either on the concentration or on the other characteristics of the problem and hence is some universal function, determined below.

To make the subsequent calculations clearer, we start with the simple subsidiary problem of the broadening of the level $E_1 \neq E_0$ by a foreign perturbation $U_1 \neq U_0$ in a solution of impurity atoms, each of which produces a perturbation $U_0(\mathbf{r} - \mathbf{r}_j)$ [cf. (4.14) and (4.15)].

If we choose the origin of coordinates at the location of the perturbation U_1 , then it follows from (4.15) that the shift of this level is expressed in terms of the distance $r_1 = x_1 c^{-1/3}$ to the nearest impurity center (using $\hat{U}_j = U_0 \delta_{rr_j}$) by

$$s = -t^{-1} \ln \frac{|e_1| c^{-2/3}}{\lambda_1} = 2x_1, \quad \epsilon_1 = E - E_1, \quad t = \alpha c^{-1/3}. \quad (4.24)$$

The probability that there are no impurity atoms in a sphere of radius x centered at the origin is $e^{-\Omega(x)}$, where $\Omega(x) = \frac{4}{3} \pi x^3$ is the volume of the sphere. Therefore the probability that the nearest impurity atom is at a distance x is $e^{-\Omega(x)} d\Omega(x)/dx$ and the corresponding probability density, taking (4.24) into account, is

$$\mathcal{P}^*(s) = \frac{d}{ds} e^{-\Omega(\frac{s}{2})} = \frac{1}{2} e^{-\Omega(\frac{s}{2})} \Omega' \left(\frac{s}{2} \right), \quad (4.25)$$

i.e., in terms of ϵ_1

$$p(\epsilon_1) d\epsilon_1 = e^{-\frac{1}{3} \Omega(\frac{s}{2})} \frac{d\Omega}{d\epsilon_1} d\epsilon_1, \quad \Omega(s) = \frac{4\pi}{3} s^3 = \frac{4}{3} \pi \alpha^{-3} \ln^3 |e_1|^{-1} c^{2/3}. \quad (4.26)$$

The probability $\mathcal{P}(s) ds$ is calculated with the help of a similar argument, except that the very simple formula $s = 2x_1$ is now replaced by the formulas for each

diagram of type I or type II. Inequalities that express the conditions for the realization of the possible diagrams determine the contribution of each diagram to the total probability. Thus

$$\left. \begin{aligned} \mathcal{P}(s) &= \mathcal{P}^I(s) + \mathcal{P}^{II}(s), & \int \mathcal{P}(s) ds &= 1, \\ \mathcal{P}^I(s) &= \sum \mathcal{P}_h^I(s), & \mathcal{P}^{II}(s) &= \sum \mathcal{P}_h^{II}(s), \\ & & \mathcal{P}_h^I \mathcal{P}_h^{II} &> 0. \end{aligned} \right\} \quad (4.27)$$

The term $\mathcal{P}^I(s)$ corresponds to contributions from diagrams of type I and corresponds to collectivized states with energies $\epsilon = \pm |\epsilon|$. These terms give a symmetric contribution (relative to $\epsilon = 0$) to the density $\rho(\epsilon)$.

The second part of the probability, $\mathcal{P}^{II}(s)$, is due to terms corresponding to diagrams of type II, i.e., to states localized near one of the impurity centers. These terms correspond to energies of definite sign and give an asymmetric contribution to the spectral density, $\rho(\epsilon)$. So the spectral density for $\epsilon > 0$ is given by the expression

$$\mathcal{P}_+(s) = \frac{\mathcal{P}_+^I(s)}{2} + \mathcal{P}_+^{II}(s),$$

and for $\epsilon < 0$

$$\mathcal{P}_-(s) = \frac{\mathcal{P}_-^I(s)}{2} + \mathcal{P}_-^{II}(s).$$

We write down as an example the conditions for the realization of some simple (i.e., most probable) cases and calculate their probabilities*

$$\left. \begin{aligned} \text{(I.1)} \quad s &= x_{12} & \text{for } x_{1l}, x_{2l} > x_{12} \quad (l > 2), \\ \text{(II.4)} \quad s &= x_{23} + x_{31} - x_{12} & \text{for } x_{12} < x_{23}, x_{31}; \\ & & x_{1l} > x_{13}, x_{2l} > x_{23}; x_{3l} > x_{23} + x_{31} - x_{12} = s. \end{aligned} \right\} \quad (4.28)$$

The inequalities in (4.28) determine the volumes $\omega_1(x_{12}), \omega_2(x_{12}, x_{13}, x_{23}), \dots$, which do not contain other impurity centers besides those on which the values of s depend. The probability of such an event is $e^{-\omega}$. Therefore for the probabilities $\mathcal{P}_1^{II}(s), \mathcal{P}_1^I(s), \dots$ we get

$$\left. \begin{aligned} \mathcal{P}_1^I(s) &= \frac{d}{ds} \int_{x < s} e^{-\omega_1(x)} d\mathbf{x} \quad (x_{12} = x), \\ \mathcal{P}_1^{II}(s) &= \frac{1}{2} \frac{d}{ds} \int_{\substack{x_{12} < x_{23}, x_{31}, \\ x_{23} + x_{31} - x_{12} < s}} e^{-\omega_2(x_{12}, x_{23}, x_{31})} d\mathbf{x} d\mathbf{x}' \\ & \quad (x_{13} = x, x_{23} = x', x_{12} = |\mathbf{x} - \mathbf{x}'|). \end{aligned} \right\} \quad (4.29)$$

$\mathcal{P}_1^I(s)$ corresponds to the case, as is seen from (4.28), when there are no other impurity centers in spheres of radius $x_{12} = s$ drawn about each of the

*It is well to notice that the inequalities written down for the case $s = x_{12}$ do not include all cases of type I, 1 but only those for which the wave functions of the nearest neighbors are "paired." An analogous restriction takes place for the inequalities II, 2. We can understand this, and also write out inequalities for other cases, by examining the scheme for four impurity centers on Fig. 4.

points $\mathbf{x}_1, \mathbf{x}_2$. The volume $\omega_1(\mathbf{x}_{12})$ occupied by these intersecting spheres is

$$\omega_1(x_{12}) = \frac{9}{4} \pi x_{12}^3 \quad (x_{12} = s).$$

Therefore $\mathcal{P}_1^I(s)$ is [according to (4.28)]

$$\mathcal{P}_1^I(s) = e^{-\frac{9}{4} \pi s^3} 4 \pi s^2. \quad (4.30)$$

Or in more convenient notation $\Omega = \frac{4}{3} \pi s^3$

$$\rho_1^I(\Omega) = e^{-\frac{27}{16} \Omega},$$

$$q(\Omega) d\Omega = \mathcal{P}(s) ds, \quad q(\Omega) = \sum_k (q_k^I(\Omega) + q_k^{II}(\Omega)). \quad (4.31)$$

We notice from (4.31) that the first term [or alternately $\rho_1^I(\Omega)$] gives almost $\frac{2}{3}$ of the integrated density

($\int_0^\infty \rho_1^I d\Omega = \frac{16}{27}$). On the other hand, inasmuch as the full probability $\rho(\Omega) d\Omega$ as $\Omega \rightarrow 0$ is simply equal to the volume $d\Omega$, i.e., $\rho(0) = 1 = \rho_1^I(0)$, all the remaining terms tend to zero as $\Omega \rightarrow 0$. Finally, for large Ω ($s \gg 1$), the configurations in which the nearest neighbor is situated at a distance $x = s/2$ give the main contribution, and the remaining neighbors are at arbitrary distances from one another outside the sphere of radius $s/2$. This gives $\rho(\Omega)|_{\Omega \rightarrow \infty} \sim e^{-\Omega/8}$. Finally we get for $\nu(E, c)$ near $\epsilon = 0$ (the \pm correspond to positive and negative ϵ)

$$\left. \begin{aligned} \frac{\nu(\epsilon, c)}{c} = q(\epsilon) = q_\pm(\Omega) \frac{d\Omega}{d\epsilon} = c \frac{4\pi}{\alpha^3} \frac{\ln^2 |\epsilon|}{|\epsilon|} q_\pm(\Omega), \\ \Omega = \frac{4}{3} \pi s^3 = \frac{4\pi}{3} \frac{c}{\alpha^3} \ln^3 \left| \frac{\lambda c^{1/3}}{\epsilon} \right|, \\ q_\pm(\Omega) \sim e^{-\Omega/8} \quad (\Omega \gg 1), \quad q_\pm(\Omega) \approx \frac{1}{2} e^{-\frac{27}{16} \Omega} \quad (\Omega \ll 1). \end{aligned} \right\} \quad (4.32)$$

For $\epsilon = 0$, i.e., $\Omega \rightarrow \infty$, $\rho_\pm(\Omega)$ tends to zero. That is to say, there is a dip in $\rho(\epsilon)$ at $\epsilon = 0$ ($c \rightarrow 0$) and the maximum of $\rho(\epsilon)$ in the region of $\epsilon = 0$ is split. But for $s \ll 1$, i.e., for not too small ϵ ($\ln |c^{1/3}/\epsilon| \ll \alpha c^{-1/3}$),

$$\nu(\epsilon, c) = \frac{2\pi}{\alpha^3} c^2 \frac{\ln^2 |\epsilon|}{|\epsilon|}. \quad (4.33)$$

The entire level systematics and the method of calculation of probabilities remain the same in the one-dimensional case,^[11] where the computations are significantly simpler. However, the final form of the spectral density near E_0 and the character of the singularity of $\nu(E, c)$ are entirely different.

4. "Classical" Broadening of Impurity Levels with Concentration

As has already been seen, the level systematics studied above related to the case of a perturbation $U_0(\mathbf{r})$ localized in a finite (small) region of space or decreasing faster than $e^{-\alpha r}$ at $r \sim \bar{r}$. In this case the overlapping of the wave functions of local states is the main effect causing the shifts and splitting of the levels. If $U_0(\mathbf{r})$ decreases slower than $e^{-\alpha r}$, then the

main contribution to the shift of the level E_0 for large r_{jk} is made by the net random decrease in the potential at the point \mathbf{r}_j where the given impurity atom is situated, caused by all other atoms,

$$u_i = - \sum_{k \neq i} U_0(\mathbf{r}_i - \mathbf{r}_k).$$

We henceforth assume $U_0(\mathbf{r}) < 0$. The quantity u_i is a random displacement of the bottom of the potential well about the point \mathbf{r}_i . Therefore the corresponding local level will be $E_i = E_0 - U_i$, i.e., $\epsilon = U_i$. This means that the spectral density $\rho(\epsilon) = \nu(\epsilon, c)/c$ is the density of the distribution of the random variable u_i . Choosing the origin at the point \mathbf{r}_i we have

$$u = - \sum_{r_j \neq 0} U_j, \quad U_j = U(\mathbf{r}_j). \quad (4.34)$$

As before, in the region of large r_j we can neglect correlations and write $\rho(r) = c$. We present some results relevant to this case.

The probability $\rho(u)$ can be calculated by well-known methods. For the generating function

$$F(z) = \overline{e^{-z u}} = \int_0^\infty e^{-z \epsilon} p(\epsilon) d\epsilon \quad (4.35)$$

we have, regarding U_i as independent in (4.34),

$$F(z) = e^{-c \varphi(z)},$$

$$\varphi(z) = \int (1 - e^{z U_0(r)}) dr = z \int_0^\infty e^{-z u} V(u) du. \quad (4.36)$$

Here $V(u)$ is the volume in which $-U_0(r) > U_0$.

From (4.36) we get by the inversion formula

$$p(\epsilon) = \frac{1}{2\pi i} \int_{-i\infty+0}^{i\infty+0} e^{\epsilon z - c \varphi(z)} dz. \quad (4.37)$$

Thus, for example if $U_0(r) \sim r^{-k}$ ($V(u) = (u/U_1)^{-3/k}$) at large distances, it is possible to obtain from (4.37) in the energy region $\epsilon \ll U$

$$\left. \begin{aligned} p(\epsilon) d\epsilon = q(y) dy, \quad y = c y \epsilon^{-3/k}, \\ \gamma = U_1^{3/k} \Gamma\left(1 - \frac{3}{k}\right), \\ q(y) = \frac{k}{3} \frac{i}{2\pi y} \int_{-i\infty+0}^{i\infty+0} \exp\{\zeta - y \zeta^{3/k}\} d\zeta, \end{aligned} \right\} \quad (4.38)$$

or

$$p(\epsilon) = c \frac{3}{k} \gamma q(y) \epsilon^{-3/k-1}. \quad (4.39)$$

In particular, in the important case $U_0(r) \sim r^{-6}$ characteristic of Van der Waals forces, $3/k = 1/2$ in (4.38). This gives $\rho(y) = (1/2\sqrt{\pi}) e^{-y^2/4}$, hence

$$p(\epsilon) = \frac{c \sqrt{U_1}}{4} \frac{\exp\left\{-\frac{c^2 \pi U_1}{4\epsilon}\right\}}{\epsilon^{3/2}}, \quad (4.40)$$

i.e., the level broadening in this case is $\Delta\epsilon \sim c^2 U_1 \pi/4$. It is necessary to make one remark concerning this "classical" broadening. This broadening is connected

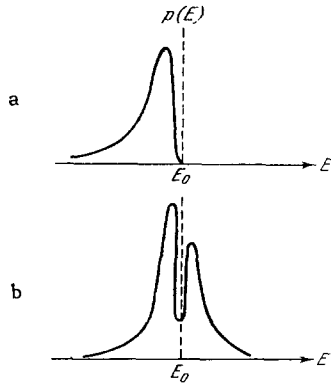


FIG. 5. Concentration smearing of the level E_0 .

with neither true damping nor with collectivization of states. Therefore the states remain local and the resultant smearing is not connected with the transition probability; in particular, it makes no contribution to the mobility of the corresponding quasiparticles.

5. STRUCTURE OF THE SPECTRUM NEAR THE UNPERTURBED BOUNDARY E_g^0

1. "Shift" and Smearing of the Boundary E_g^0

Inside a spectral band of an ideal crystal, a small impurity addition $c \ll 1$ has only an insignificant influence on the solution of (1.2) and (4.1) in any finite (not too large) region of space. This means that a solution exists and differs only slightly in this region from a plane wave. Physically such a solution corresponds to a wave (or quasiparticle) partially scattered by individual, sparsely distributed impurity atoms, which is well known to lead to some "effective" damping. Since there exist other causes of finite lifetime for an excitation, it is physically justifiable to raise the question of solutions similar to those of (1.2), in spite of the fact that no eigenfunction of (1.2) anywhere in space has, even approximately, the form of a plane (standing or traveling) wave. Strictly speaking, the actual form of the exact wave functions "as a whole" depends essentially on the boundary conditions (zero and periodic boundary conditions, of course, lead to very different situations, even though neither solution has the form of standing or traveling waves). On the other hand it is physically evident that the spectral density cannot be sensitive to the choice of boundary conditions (as the dimensions tend to infinity), and therefore the study of the exact eigenfunctions, having a perfectly random character, is in many ways a useless exercise. It is possible, however, to speak in not too large a region of space of certain averaged characteristics of the solution, and these can serve as the basis for studying the energy spectrum.

We have already mentioned that special interest is attached to the study of the spectrum near singular points (as $c \rightarrow 0$), where the perturbation brings about a full realignment of the systematics of the states and, from this point of view, cannot be regarded as small. Such points are the boundaries of the initial spectral

band of an ideal crystal, which we now proceed to study.

Without loss of generality we can reckon E from the unperturbed boundary E_g^0 ; for definiteness we will speak of the left boundary, i.e., we put $E(\mathbf{k}) = k^2/2\mu$ (for $k \ll 1$).

We consider again the simple case of a perturbation $\hat{U}_0\psi = U_0(\psi, f)f$ (in particular a delta-function perturbation $f(\mathbf{r}) = \delta_{\mathbf{r}0}$). The function $f(\mathbf{r})$ is normalized by the condition $\int f(\mathbf{r}) d\mathbf{r} = 1$; $(\Sigma f(\mathbf{r}) = 1)$. Hence, in \mathbf{k} -space $|f_{\mathbf{k}}| = (2\pi)^{-3}$ (for $k \ll 1$).

To analyze the situation near $E = 0$ it is most convenient to start out from Eq. (4.3) for the wave functions in the representation $f_j = f(\mathbf{r} - \mathbf{r}_j)$. After separating the diagonal elements, we write this equation as

$$[1 - U_0 F_0(E)]\tau_j = U_0 \sum_{l \neq j} F(E, \mathbf{r}_{jl})\tau_l, \quad \tau_j = (\psi, f_j). \quad (5.1)$$

The coefficients $F(E, \mathbf{r}_{jl})$ are the integrals introduced earlier

$$F(E, \mathbf{r}) = \int \frac{e^{i\mathbf{k}\mathbf{r}} |f_{\mathbf{k}}|^2 d\mathbf{k}}{E - E(\mathbf{k})}, \quad E = E - i0, \\ F_0(E) = F(E, 0) = \int \frac{I(E') dE'}{E - E'}, \quad I(E) = \int_{E(\mathbf{k})=E} \frac{|f_{\mathbf{k}}|^2 d\Omega_{\mathbf{k}}}{|\nabla E(\mathbf{k})|}. \quad (5.2)$$

For small E we have

$$F_0(E) = \int \frac{I(E') dE'}{E - E'} + i\pi I(E) = \\ -\frac{1}{U_{cr}} (1 + a_1 E + \dots) + i\gamma \sqrt{E} + \dots (E > 0), \\ F_0(E) = -\frac{1}{U_{cr}} + \gamma \sqrt{-E} + \dots (E < 0), \quad \gamma = \frac{\mu^{3/2}}{\pi \sqrt{2}}.$$

Here $U_{cr} = -1/F_0(0)$ is, according to (4.7), the critical value of the perturbations, at which the split-off local impurity level arises.

We shall explain first for which values of E (near $E = 0$) and with what accuracy the initial systematics (i.e., plane waves) are conserved. For $E = -\alpha^2/2\mu < 0$, $F(E, \mathbf{r})$ decreases like $e^{-\alpha r}/r$, so that for $\alpha r \ll 1$ ($r - \bar{r} \sim c^{-1/3}$) the right hand side of (5.1) is determined by the sum (and consequently in the first approximation, by the average) of a large number of terms ($n \sim c|E|^{-3/2}$). In accord with the spatial homogeneity of these averages, we will look for states which represent plane waves "in the mean" i.e., we set

$$\tau_j = \tau e^{i\mathbf{k}\mathbf{r}_j} (1 + \xi_j), \quad \bar{\xi}_j = 0 \quad (5.3)$$

(the averaging is over a space region with dimensions $L \gg \bar{r}$). Substitution of (5.3) in (5.1) gives

$$1 + \xi_j = \beta(E) \sum_{l \neq j} F(E, \mathbf{r}_{jl}) e^{i\mathbf{k}\mathbf{r}_{jl}} + \beta(E) \sum_{l \neq j} F(E, \mathbf{r}_{jl}) e^{i\mathbf{k}\mathbf{r}_{jl}} \xi_l, \\ \beta(E) = [1 - U_0 F_0(E)]^{-1} U_0, \quad \beta_0 = \beta(0) = U_{cr}/\Delta, \quad \Delta = \frac{U_{cr} + U_0}{U_0}. \quad (5.4)$$

The mean value of the sum $\Sigma F_{jl} e^{-ik \cdot r_{jl}}$ is*

$$\sum_{l \neq j} F(E, r_{jl}) e^{ik \cdot r_{jl}} = c \int w(r) F(E, r) e^{ik \cdot r} dr = \frac{c}{E - E(\mathbf{k})} + cA,$$

$$A = \int F(E, r) e^{ik \cdot r} (w(r) - 1) dr$$

$$\cong \int F(E, r) (w(r) - 1) dr \sim |F(0, 0)| = \frac{1}{U_{cr}}. \quad (5.5)$$

Therefore, averaging (5.4) and imposing the condition $\xi = 0$, we obtain the condition linking E and \mathbf{k} in first approximation in $c\beta_0$:

$$1 = \frac{c\beta(E)}{E - (k^2/2\mu)}, \quad c\beta \ll 1. \quad (5.6)$$

In the first approximation in c we obtain

$$E = \frac{k^2}{2\mu} + c\beta \left(\frac{k^2}{2\mu} \right). \quad (5.7)$$

According to (5.2) and (5.4), for k not too large,

$$\beta \left(\frac{k^2}{2\mu} \right) = \beta_0 + i\beta_0^2 \gamma_1 k, \quad \gamma_1 = \frac{\mu}{2\pi}, \quad (5.8)$$

from which it follows that

$$E = \frac{k^2}{2\mu} + c\beta_0 + ic\beta_0^2 \gamma_1 k. \quad (5.9)$$

It is well to recall that in this procedure a complex value of E signifies attenuation of the plane wave with distance, due to scattering.† The new dispersion law is therefore

$$E(\mathbf{k}) = E_c^* + \frac{k^2}{2\mu}, \quad E_c^* = c\beta_0 = \frac{cU_0 U_{cr}}{U_0 + U_{cr}}, \quad (5.10)$$

and the damping $ic\beta_0^2 \gamma_1 k$ is zero on the boundary E_c^* . This means that the first approximation in $c\beta_0$ displaces the boundary only by $E_c^* = c\beta_0$.

It is clear from (5.10) that for $U_0 > 0$ this boundary is moved to the right. For $U_0 < 0$ the boundary moves to the left if $|U_0| < U_{cr}$ (i.e., if impurity levels are absent) and to the right if $|U_0| > U_{cr}$ (i.e., when impurity levels are present).

For the case $U_0 > 0$ the point $E = 0$ is the true boundary of the spectral band (cf. Sec. 3). For $U_0 < 0$

*In the averaged expression (5.5) we put $W(r)|_{r \rightarrow \infty} = 1$. The replacement of a discrete density [$w(r) = \Sigma \delta(r - n)$; n is the integer-valued lattice vector] with a continuous one [$w(r) = 1$] does not influence the result of averaging. This is because the Fourier components of both expressions

$$w(r) = \sum_n \delta(r - n) \div \frac{1}{8\pi^3} \sum_k \delta(k - 2\pi n^*),$$

$$w(r) = 1 \div \frac{1}{8\pi^3} \delta(k),$$

coincide inside the range of variation of k (inside a reciprocal lattice cell $2\pi n^*$). No periodic continuation of $w(k)$ is involved anywhere.

†In this formalism a real energy E corresponds to a complex k ; the imaginary part of k determines the spatial damping of the plane wave. The wave functions can therefore take on the form (5.3) only over sections that are not too large.

Equation (5.6) is again derived below (5.12)–(5.14) and the shift of the renormalized boundary of E_c^* (5.10) and (5.11) is obtained independently from other considerations in Sec. 6 [(6.20)].

the true boundary of the spectrum lies at a finite distance E_g , which is independent of the concentration. Finally for $|U_0| > U_{cr}$ the true boundary of the band can again be situated at the point $E = 0$ only if the impurity band does not overlap with the ground band (cf. Sec. 5.2).

When the true boundary coincides with the point $E = 0$ then, as we have seen in Sec. 3, near this point

$$\nu(E, c) \sim \exp\{-c\lambda' E^{-3/2}\},$$

and for $E \approx c\beta_0$ this dependence is a continuation of the shifted spectral density

$$\nu(E, c) = \frac{\gamma}{\pi} \sqrt{E - c\beta_0} \quad \left(\gamma = \frac{\mu^{3/2}}{\pi \sqrt{2}} \right). \quad (5.11)$$

In the opposite case the true boundary E_g and the "renormalized" boundary $E_c^* = c\beta_0$ are a finite distance apart, and $\nu(E, c)$ is sensitive in this region to the actual forms of the local perturbation, correlation functions, and the dispersion of $E(\mathbf{k})$.

If $-U_0$ comes sufficiently close to U_{cr} , then the condition $c\beta_0 \ll 1$ breaks down ($\beta_0 \rightarrow \infty$) and formula (5.10) is inapplicable. This case will be investigated later.

Figures 6a–6d show schematically the spectral density $\nu(E, c)$ near $E = 0$ for all the cases considered.

We have already seen that the appearance of an imaginary contribution to expression (5.9) for E signifies the damping of the plane waves, that is to say, at sufficiently large distances the real states (corresponding to real E) differ even "in the mean" from plane waves. The renormalized "boundary" $E_c^* = c\beta_0$ found in the first approximation is the energy boundary of such states (of the plane wave type). It is clear that essentially such a boundary does not represent an exact concept and it is meaningless to define it more precisely (in the sense of including terms of higher order in $c\beta_0$). To explain the behavior of the spectral density near the renormalized boundary E_c and on the

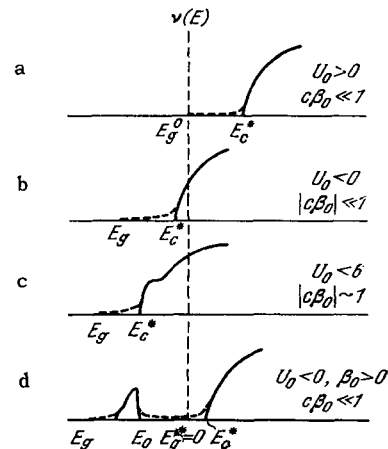


FIG. 6. (a-d) Behavior of $\nu(E, c)$ near the unperturbed boundary $E_g^0 = 0$ for fixed c and varying U_0 .

left of it, it is necessary to understand the nature of the states responsible for this spectral region.

We shall now show that the levels adjacent to this boundary and causing its smearing arise out of fluctuations and do not correspond to plane-wave states. Let us turn our attention first to the fact that formula (5.10) for the displacement of the boundary ceases to be correct when the perturbation $-U_0$ is sufficiently close to U_{cr} ($c\beta_0 \gtrsim 1$), i.e., when a local level appears or "almost" appears at the boundary. At first sight such cases seem very exceptional. However even when a separate impurity center does not cause the formation of a local impurity level, such levels must occur upon fluctuational clustering of several impurity centers lying side by side or at small distances from each other. By changing the distribution of the impurity centers in the fluctuation region (including its surroundings) it is possible to shift these levels, in particular towards the boundary E_C^* or towards the true boundary E_g . It is precisely clusters of this kind, of sufficiently large size, that cause the exponential dependence of (3.3) and (3.6) near the true boundary of the spectrum. For small concentrations, the intervening region between E^* and E_g contains mainly contributions from comparatively small clusters and therefore is highly individualized.

The spectral density at the "boundary" E_C^* is determined by the total probability of those fluctuations that lead to a local level at this boundary (in practice —to the most probable fluctuation). It has already been shown that in general this expression does not have a simple form, although for $|\beta_0| \sim 1$ the probability is proportional to some not very high power of c . We will calculate these probabilities in the two limiting cases $|\beta_0| \ll 1$ and $|\beta_0| \gg 1$.

2. Smearing of Impurity Levels near the Boundary of the Continuous Spectrum

We shall explain first how an impurity level E_0 , corresponding to an isolated impurity center, is smeared when the level is close to an unperturbed spectral band. To this end we turn again to (5.1). If $\alpha_0 \bar{r} \ll 1$ ($\alpha_0^2/2\mu = -E_0$, $\bar{r} \sim c^{-1/3}$), the sum on the right side of the equation depends weakly on the distribution of the impurity atoms situated at distances $r_{jl} \sim \bar{r}$; therefore the smearing of the level E_0 ($1 - U_0 F_0(E_0) = 0$) is determined not by the random arrangement of several nearest neighbors (as when $\alpha_0 \bar{r} \gg 1$), but by the averaged distribution of all the remaining centers. This means that in the first approximation (5.1) can be replaced by

$$(1 - U_0 F_0(E)) \tau(r) = cU_0 \sum_{\mathbf{r}'} F(E, \mathbf{r}' - \mathbf{r}) W(\mathbf{r}' - \mathbf{r}) \tau(\mathbf{r}')$$

(\mathbf{r} and \mathbf{r}' are the discrete lattice vectors and $\tau(\mathbf{r})$ a sufficiently smooth function of \mathbf{r}) or, in the same approximation, by its continuous analog, the integral equation

$$[1 - U_0 F_0(E)] \tau(\mathbf{r}) = cU_0 \int F(E, \mathbf{r}' - \mathbf{r}) w(\mathbf{r}' - \mathbf{r}) \tau(\mathbf{r}') d\mathbf{r}' \tag{5.12}$$

In \mathbf{k} -space this equation has the form

$$\{1 - U_0 F_0(E) - cU_0 \Phi(E, \mathbf{k})\} T(\mathbf{k}) = 0, \\ T(\mathbf{k}) \div \tau(\mathbf{r}), \quad \Phi(E, \mathbf{k}) \div w(\mathbf{r}) F(E, \mathbf{r}) \tag{5.13}$$

and consequently satisfies the dispersion relation

$$F_0(E_0) - F_0(E) = c\Phi(E, \mathbf{k}), \quad 1 - U_0 F_0(E_0) = 0. \tag{5.14}$$

This equation is essentially the same as (5.6), but it applies to another region, near the local level $E_0 < 0$ ($-U_0 > U_{cr}$). For small \mathbf{k} we have $\Phi(E, \mathbf{k}) = [E - E(\mathbf{k})]^{-1}$; in addition, for small negative E we have

$$F_0(E) = -\frac{1}{U_{cr}} + \gamma \sqrt{|E|} \quad (E < 0), \tag{5.15}$$

hence

$$\sqrt{|E|} = \sqrt{|E_0|} + \frac{c\gamma^{-1}}{|E| + E(\mathbf{k})}, \quad |E_0| = \frac{2\pi^2}{\mu^3 \beta_0^3}, \quad \beta_0 \gg 1. \tag{5.16}$$

If $2\mu|E_0| \gg c^{2/3}$, then

$$\varepsilon = E_0 - E = \frac{2\gamma^{-1} \sqrt{|E_0|}}{(E_0) + k^2/2\mu} = \frac{4\pi c \alpha_0}{\mu(\alpha_0^2 + k^2)} > 0, \quad \alpha_0 = \frac{2\pi}{\mu\beta_0}, \\ k^2 = \alpha_0^2 \left(\frac{2c\beta_0}{\varepsilon} - 1 \right). \tag{5.17}$$

This means that the spectral density in the vicinity of E_0 is

$$p(\varepsilon, c) = \frac{\nu(E, c)}{c} = \frac{k^2}{2\pi^2} \left| \frac{dk}{d\varepsilon} \right| = \frac{4\pi c}{\mu^3 \beta_0^3} e^{-\varepsilon/2} (2c\beta_0 - \varepsilon)^{1/2}. \tag{5.18}$$

It follows from (5.17) that the expression (5.18) for $p(\varepsilon, c)$ is correct for $\alpha_0^2 \ll \varepsilon/2c\beta_0 < 1$ ($\alpha_0 \ll 1$), and is cut-off at $\varepsilon/2c\beta_0 \sim \alpha_0^2$ ($k \sim 1$).

If $2\mu|E_0| = \alpha_0^2 \gg c^{2/3}$ the width of the smearing is $\delta\varepsilon \sim c/\alpha$, i.e., $\delta E/|E_0| \sim c/\alpha^3 \ll 1$, and it is possible to speak of a "smeared level." On the other hand, for $\alpha^2 \lesssim c^{2/3}$ we have $\varepsilon \delta\varepsilon \sim c^{2/3}$ and $\delta E/|E_0| \lesssim 1$ (in particular, when $E = 0$ we have $\varepsilon_{\max} = -E|_{\mathbf{k}=0} = (c/\gamma)^{2/3}$). Finally for $-U_0 < U_{cr}$ the strip $\varepsilon(\mathbf{k})$ unites with the ground band and gradually goes over into a unified dispersion relation for $E^*(\mathbf{k})$. Thus, as the impurity level approaches the edge of the unperturbed spectrum, the shift (together with smearing) of the "boundary" of plane-wave states amounts to $\sim c^{2/3}$.

3. The Spectral Density to the Left of E_C^* for $U_0 < 0$

We now turn to the fluctuational impurity levels at the boundary of the spectrum under the condition $-U_0 < U_{cr}$, i.e., $|F_0(0)| < 1/|U_0|$. In the presence of a secondary impurity center at a distance \mathbf{r} from the first, the level E_1 is found, according to (4.9), from the condition

$$[1 - U_0 F_0(E_1)]^2 = F(E_1, \mathbf{r})^2 U_0^2,$$

i.e.,

$$U_{cr} F_0(0) + U_0 F_0(E_1) = -U_0 F(E_1, \mathbf{r}). \tag{5.19}$$

For small $\Delta = U_{cr} + U_0 \ll 1$ the roots occur when $\bar{r} \gg r \gg 1$; here

$$F(E_1, r) = \frac{Ae^{-ar}}{r} \cong \frac{A}{r}, \quad A = \frac{\mu}{2\pi} \quad (a\bar{r} \ll 1).$$

Equation (5.19) gives

$$\frac{1}{\beta_0} + \gamma \sqrt{|E_1|} = \frac{A}{r} \quad \left(\frac{1}{\beta_0} = \frac{U_0 + U_{cr}}{U_0 U_{cr}} \ll 1 \right). \quad (5.20)$$

The level at the boundary occurs for $r = r_{cr} = A\beta_0$; for $r < r_{cr}$ we have

$$-E_1 = \frac{1}{2\mu} \left(\frac{1}{r} - \frac{1}{r_{cr}} \right)^2. \quad (5.21)$$

The probability that the nearest impurity center is at a distance r from the given center is $c \cdot 4\pi r^2 dr \times e^{-4\pi r^3 c/3}$. Therefore the probability of a fluctuation of a local level E_1 at a given impurity center is

$$\rho(E_1) dE_1 = c\chi'(E_1) e^{-c\chi(E_1)} dE_1 \cong c\chi'(E_1) dE_1, \\ \chi(E) = \frac{4\pi A^3}{3} \left(\frac{1}{\beta_0} + \gamma |E|^{1/2} \right)^{-3}. \quad (5.22)$$

This probability determines essentially the spectral density to the left of the renormalized "boundary" for $|\Delta| \ll 1$ ($\beta_0 \gg 1$)

$$\nu(E, c) = c\rho(E) = c^2 \cdot 2\pi\gamma A^3 |E|^{-1/2} \left(\frac{1}{\beta_0} + \gamma |E|^{1/2} \right)^{-4}. \quad (5.23)$$

For $|E|^{1/2} \ll \Delta$ we have

$$\nu(E, c) = Bc^2 |E|^{-1/2}, \quad B = \beta_0^4 \mu^{3/2} \sqrt{2}. \quad (5.24)$$

As we saw earlier, an account of the "mean" distribution of impurity atoms leads in first approximation to a renormalized dispersion relation, that is to say, $E - k^2/2\mu$ is replaced by

$$E - \frac{k^2}{2\mu} - c\beta \left(\frac{k^2}{2\mu} \right).$$

This gives grounds for assuming that the influence of the "impurity background" on the position of isolated fluctuation levels, similar to those already considered, is equivalent to a change of the reference level of the energy E , i.e., to a substitution of $E - E_c^*$ for E :

$$\nu(E, c) = Bc^2 (E_c^* - E)^{-1/2}, \quad E_c^* = c\beta_0.$$

Since concentration x of the "two-particle" fluctuations of interest to us is of the order of c^2 , and since it is possible to speak of "level broadening" (as was previously shown) only for distances $E_1 \sim x^{2/3} \sim c^{4/3}$, formula (5.24) is valid starting with distances $E_c^* - E \gg c^{4/3}$ ($E_c^* = c\beta$); on the other hand, when $E - E_c \gg c^{4/3}$, we should already have to the right of this boundary

$$\nu(E, c) = \frac{\gamma}{\pi} \sqrt{E - E_c^*}.$$

Thus the joining of these two functions takes place in the region $|E - E_c^*| \approx c^{4/3}$, and $\nu(E, c)$ falls in this section from the value $\sim c^{2/3}$ (on the right) to $\sim c^{4/3}$ (on the left). A detailed analysis of the region of joining calls for the use of other methods.

At smaller values of $|U_0|$ the two-particle fluctuation is insufficient to give rise to an impurity level, and the corresponding probabilities are determined by higher powers of c .

We now consider the opposite case $|U_0| \ll U_{cr}$. This can be studied on the basis of considerations, analogous to those in Sec. 3. For $|U_0| < 1$ the distance between the "true" boundary E_g and the unperturbed boundary $E_g^0 = 0$ is $E_g - E_g^0 \approx |U_0|$. Therefore any state $E = E_c^* - \epsilon |U_0|$ lying to the left of $E_c^* = cU_0$ must be connected with a significant fluctuation of the concentration c' on a sufficiently large portion of the volume $V_{c'}$; since the renormalized boundary at concentration c' is $E_c^* = c'U_0$, the concentration fluctuation must exceed the value $c' - c = \epsilon$. As we now show, if $U_0 < 0$ the most probable fluctuation causing the appearance of the level $E = E_c^* - \epsilon |U_0|$ (for sufficiently small $|U_0|$) is the formation of a spherical region made up of impurity atoms, of volume

$$V = \lambda (1 - c - \epsilon)^{-3/2} |U_0|^{-3/2}, \quad \lambda = \kappa_0^{3/2} = \frac{\pi^4 \sqrt{2}}{3\mu^{3/2}}. \quad (5.25)$$

Let us consider this spherical region of volume V and concentration c' . The lowest non-fluctuation level E in such a region is

$$E = E_c^* + \kappa_0 V^{-2/3}, \quad \epsilon = c' - c - \kappa_0 |U_0|^{-1} V^{-2/3}.$$

(In particular for $c' = 1$ and $c \ll 1$ we have $\epsilon = 1 - \kappa_0 |U_0|^{-1} V^{-2/3}$.)

The minimal volume $V_{c'}$ ensuring the appearance of the level $\epsilon = (E_c^* - E)/|U_0|$ is thus equal to

$$V_{c'} = V_1 (c' - c - \epsilon)^{-3/2}, \\ V_1 = \lambda |U_0|^{-3/2}, \quad c' - c > \epsilon. \quad (5.26)$$

For small c the probability of the fluctuation c' in the volume $V_{c'}$ is

$$P_{c'} \sim \exp\{-V_{c'} \varphi(c', c)\} = \exp\{-V_1 \varphi(c', c) (c' - c - \epsilon)^{-3/2}\}, \\ \varphi(c', c) = c' \ln \frac{c'}{c} - (c' - c) = \begin{cases} (c' - c)^2/2c, & c' - c \ll c, \\ -c' \ln c, & c' \gg c \end{cases} \quad (5.27)$$

(cf. the footnote on page 553; for arbitrary c' formula (5.27) is correct in the absence of correlation between the distribution of the atoms in the different sites).

The argument of the exponential in the expression for the probability $P_{c'}$ is of the form

$$\frac{\varphi(c', c)}{(c' - c - \epsilon)^{3/2}} = \begin{cases} \frac{(\epsilon + x)^2}{2cx^{3/2}}, & \epsilon + x = c' - c \ll c, \\ -\frac{(\epsilon + x) \ln c}{x^{3/2}}, & \epsilon + x = c' - c \gg c. \end{cases}$$

It is easy to verify that for $\epsilon \gg c^2 \ln^2 c$ the greatest probability corresponds to the value $c' = 1$ ($x = 1 - c - \epsilon$), that is, to a fluctuational cluster consisting only of impurities, in a volume $V_1 (1 - c - \epsilon)^{-3/2}$. Therefore the spectral density $\nu(E, c)$ to the left of the boundary E_c^* is determined fundamentally by the con-

tribution of such fluctuations, and its order of magnitude is

$$\nu(E, c) \sim \exp\{V_1(1-c-\epsilon)^{-3/2} \ln c\} = \exp\{\lambda |E_g - E|^{-3/2} \ln c\},$$

$$\epsilon = \frac{E_c^* - E}{E_g}, \quad E_g = U_0. \quad (5.28)$$

This expression is correct for $\epsilon \gg c^2 \ln^2 c$, that is, practically right up to the renormalized boundary.

4. The Spectral Density Inside the Interval $0 < E < E_C^*$ for $U_0 > 0$

Formulae (5.25) and (5.28) pertain to an attractive potential $U_0 < 0$. In the case of purely repulsive forces $U_0 > 0$, the situation becomes somewhat different. As before, on the left of the renormalized boundary $E_C^* = cU_0$ there are "fluctuation-like" states; however, they are constructed from fluctuations of concentration $c' < c$ (right up to $c' = 0$) and are therefore always "smeared out" over large regions (even for large U_0). In addition, we will now show that the most probable fluctuations, which determine the spectral density on the left of E_C^* , do not correspond to clusters of pure A (i.e., $c' = 0$), but only to small deviations from the mean concentration c .

Actually, for $U_0 > 0$ and $E = E_C^* - \xi cU_0 = cU_0(1 - \xi)$ the minimal concentration fluctuation $c = c' > \xi c$ must take place in the volume

$$V_{c'} = V_1(c - c' - c\xi)^{-3/2}, \quad 0 < c' < c(1 - \xi).$$

The probability $p_{c'}$ of such a fluctuation, as in (5.27), is given by

$$-\frac{c^{1/2}}{V_1} \ln p_{c'} = h(y, \xi) = \frac{(1-y) \ln(1-y) + y}{(y-\xi)^{3/2}},$$

$$y = \frac{c-c'}{c}, \quad \xi = \frac{E_c^* - E}{E_c^*},$$

$$h(y, \xi) = \begin{cases} \frac{y^2}{2(y-\xi)^{3/2}}, & y \ll 1, \\ (1-\xi)^{-3/2} \left\{ 1 + x \ln x + \frac{3x}{2(1-\xi)} - x \right\}, \end{cases}$$

$$x = 1 - y \ll 1.$$

The major term in the expression for $\ln \nu(E, c)$ is determined by the most probable fluctuation, i.e.,

$$\left. \begin{aligned} -\frac{c^{1/2}}{V_1} \ln \nu(E, c) &= g(\xi), \quad \xi = \frac{E_c^* - E}{E_c^*} = 1 - \frac{E}{cU_0}, \\ g(\xi) &= \min h(y, \xi) |_{\xi < y < 1}; \quad \left(y = \frac{c-c'}{c} \right). \end{aligned} \right\} \quad (5.29)$$

An elementary calculation gives for $g(\xi)$

$$g(\xi) = \begin{cases} \frac{8}{3\sqrt{3}} \xi^{1/2}, & \xi \ll 1, \\ (1-\xi)^{-3/2}, & 1-\xi \ll 1 \quad (E \ll E_c^*). \end{cases} \quad (5.30)$$

Correspondingly, the most probable values of the concentration fluctuation will be in these cases

$$\frac{c'}{c} = 1 - y_m = \begin{cases} 1 - 4\xi; & \xi \ll 1, \\ \exp\left\{-\frac{3}{2(1-\xi)}\right\}, & (1-\xi) \ll 1. \end{cases} \quad (5.31)$$

We thus obtain an expression for $\nu(E, c)$

$$\nu(E, c) \sim \exp\{-V_1 c^{-1/2} g(\xi)\}, \quad (5.32)$$

$$\nu(E, c) \sim \begin{cases} \exp\left\{-\frac{8}{3\sqrt{3}} \lambda \frac{(E_c^* - E)^{1/2}}{c}\right\}, & E_c^* - E \ll E_c^*, \\ \exp\{\lambda E^{-3/2} c\}, & E \ll E_c^*, \quad \lambda = \frac{\pi^4 \sqrt{2}}{3\mu^{3/2}}. \end{cases} \quad (5.33)$$

As $\xi \rightarrow 0$ the concentration fluctuation $(c - c')/c = 4\xi \rightarrow 0$ and this whole fluctuation approach no longer makes sense. Formula (5.32) is applicable so long as $E_C^* - E \gg c^2/\lambda^2$.

It is easy to see that formulae of the type (5.25) and (5.32) cannot be obtained either by an expansion in powers of U_0 (perturbation theory) or by an expansion in powers of the concentration.

In the standard technique the calculation of the spectral density reduces to the calculation of $\text{Sp Im}(G/\pi N)$. In place of Green's functions, we can calculate an equivalent quantity $\overline{G^*}$ [cf. (5.1)]

$$\overline{G^*} = \overline{(1 - \beta \hat{F})^{-1}} = \sum \beta^n \overline{\hat{F}^n}, \quad \hat{F} = F_{ik} = F(E, r_{ik}), \quad \hat{G} = \hat{G}^* \beta \hat{C}_0.$$

It is evident from the results of this section and of the preceding ones that near the singularities it is necessary to sum accurately all the graphs which are responsible for the new systematics of the states appearing in the vicinity of the singularities. Yet the structure of these states is such, that it is highly inconvenient to construct them out of plane waves by the standard technique. This explains why a comparatively simple study of the region of singularities is possible only after preliminary elucidation of the character and of the systematics of the new states.

5. Influence of Ordering

We saw that in the first approximation in $c\beta$ the change of the spectral density inside the initial (unperturbed) region of the spectrum is determined by the averaged effect of all the impurity centers and is described by Eq. (5.12). This change is shown to be appreciable and qualitatively important for small $c\beta$ only near the boundaries E_g^0 of the region. It is easy to see that this is connected with the fact that the averaged impurity distribution density possesses the symmetry of the original lattice. Therefore the situation is changed in the presence of ordering, where $\rho(\mathbf{r}) = cw(\mathbf{r})$ possesses a lower translational symmetry. For example, the disordered mean density $w_0(\mathbf{r}) = \sum \delta(\mathbf{r} - \mathbf{n})$ goes over upon ordering along two equivalent translational superlattices \mathbf{n}^I and \mathbf{n}^{II} into the partially ordered density

$$w^*(\mathbf{r}) = (1 + \eta) \sum \delta(\mathbf{r} - \mathbf{n}^I) + (1 - \eta) \sum \delta(\mathbf{r} - \mathbf{n}^{II}),$$

$$\{\mathbf{n}\} = \{\mathbf{n}^I\} + \{\mathbf{n}^{II}\}. \quad (5.34)$$

If the lattice \mathbf{n}^I is constructed from the basis vectors $\mathbf{e}_i = \mathbf{e}_k + \mathbf{e}_l$, where \mathbf{e}_k are the unit vectors of the initial lattice, $i \neq k \neq l$ (ordering in staggered rows, as in NaCl), then the reciprocal lattice is body-centered,

that is, the Fourier transform inside the region of variation of \mathbf{k} is of the form*

$$(w^*)_{\mathbf{k}} = \delta(\mathbf{k}) + 2\eta\delta(\mathbf{k} - 2\pi\mathbf{u}), \quad \eta > 0, \\ \mathbf{u} = \frac{e_1^* + e_2^* + e_3^*}{2}. \quad (5.34')$$

This signifies that (5.13) becomes

$$1 - U_0 F_0(E) = U_0 c \left\{ \frac{1}{E - E(\mathbf{k})} + \frac{2\eta}{E - E(\mathbf{k} + 2\pi\mathbf{u})} \right\}, \\ [E - E(\mathbf{k})][E - E(\mathbf{k} + 2\pi\mathbf{u})] \\ = c\beta(E) \{ (1 + 2\eta)E - E(\mathbf{k} + 2\pi\mathbf{u}) - 2\eta E(\mathbf{k}) \}. \quad (5.35)$$

The solution of this equation leads to the well known splitting of the band $E = E(\mathbf{k})$ into two bands, owing to the new and lower symmetry of the averaged density

$$E_{1,2}(\mathbf{k}) = \frac{E(\mathbf{k}) + E(\mathbf{k} + 2\pi\mathbf{u}) + \gamma_1 \pm \sqrt{(E(\mathbf{k}) - E(\mathbf{k} + 2\pi\mathbf{u}) + \gamma_2)^2 + \delta^2}}{2}, \\ \gamma_1 = c\beta(E)(1 + 2\eta), \quad \gamma_2 = c\beta(E)(1 - 2\eta), \quad \delta^2 = (\beta c)^2 8\eta \quad (\eta > 0). \quad (5.36)$$

The strong-perturbation region is only the vicinity of the band separation points, i.e., the points

$$E(\mathbf{k}) - E(\mathbf{k} + 2\pi\mathbf{u}) + \gamma_2 = 0. \quad (5.37)$$

The size of the gap δ is of first order in $c\beta_0$. In the remaining region we have $E_1(\mathbf{k}) \simeq E(\mathbf{k})$ and $E_2(\mathbf{k}) \simeq E(\mathbf{k} + 2\pi\mathbf{u})$, i.e., the initial dispersion relation is retained, apart from a transformation.

For sufficiently small $c\beta$, the bands necessarily overlap as a consequence of the angular dependence of $E(\mathbf{k})$, and no gap appears in the spectral density

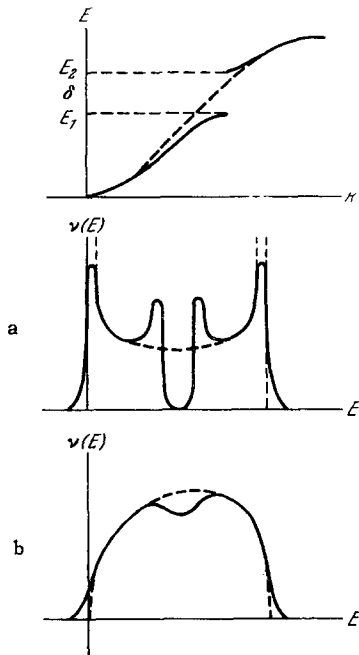


FIG. 7. Change of the spectrum following partial ordering.

$\nu(E, c)$. A different situation exists in the one-dimensional case, where the splitting of the dispersion relation for arbitrarily small $c\beta$ signifies a gap in the spectral density (cf. Fig. 7). Such a gap can arise in the three-dimensional case only for sufficiently large U_0 and $c \sim 1$. But even in this case the gap exists only in the approximation of (5.12); actually the gap is filled with "fluctuation" levels and no singularities in $\nu(E, c)$ appear. It is possible, as always, to make qualitative calculations and estimates of the region of the possible "dip" in the spectral density only when there are some small parameters. Such a small parameter can be in this case a small deviation from full order. It is easy to see that having chosen a fully ordered crystal as our initial ideal structure, we can regard in this case the boundaries of the split zones as the unperturbed boundaries E_g^0 ; then the whole preceding theory is fully applicable to this case. In particular, inasmuch as the true boundaries of the regions of the continuous spectrum in the disordered solution cannot depend either on concentration or on the degree of ordering, and for full disorder there is no dip in $\nu(E, c)$ between the bands, there is likewise no dip for small deviations from full ordering.

In the one-dimensional case, where the "splitting" of $\nu(E, c)$ [in the averaged equation (5.12)] arises for arbitrarily small U_0 and the distance between the renormalized boundaries is $\sim U_0$, we obtain from considerations similar to those already developed above an expression for $\nu(E, c)$ in the "dip":

$$\nu(E, c) \sim \exp\{\varphi(c, \eta) U_0^{-1/2}\}.$$

6. THE STRUCTURE OF THE ENTIRE SPECTRUM

1. Method of Expansion in Powers of the Concentration. General Considerations and Formulae

The study of the spectral density far from the singular points of $\nu(E, c)$ is best made by using an expansion in powers of the concentration c . This method is especially effective for the quantitative construction of various statistical (thermodynamic) mean values of the type

$$\varphi(c) = \text{Sp} \frac{\Phi(\hat{H})}{N} = \int \Phi(E) \nu(E, c) dE, \\ \varphi(c) - \varphi(0) = \int \Phi'(E) \xi(E, c) dE, \\ -\xi(E, c) = n(E, c) - n(E, 0). \quad (6.1)$$

However, the method affords also many possibilities for a qualitative study of the structure of the spectrum as a whole.

Since we use for the zeroth approximation the Hamiltonian of an ideal lattice and correspondingly an unperturbed spectral density $\nu_0(E)$, both the mathematical procedure of expansion in powers of c and the physical meaning of the resultant approximations are utterly different in two cases:

*cf. footnote on p. 562.

$$(w^*)_{\mathbf{k}} = \sum \delta(\mathbf{k} - 2\pi\mathbf{n}^*) + 2\eta \sum \delta(\mathbf{k} - 2\pi\mathbf{n}^* - 2\pi\mathbf{u}).$$

- a) when E lies inside the initial spectrum $\nu_0(E)$;
- b) when E lies outside this band.

In the first case the initial states are plane waves with quasi-momentum \mathbf{k} and with the symmetry of the initial crystal. The perturbed states, in any finite order in c , are superpositions of the initial waves and of waves scattered by the impurity centers. For small c such a picture corresponds to the true physical situation. For arbitrary concentrations, but small perturbations of \hat{U}_0 , any finite n -th-order approximation in U_0 contains, as already mentioned in Sec. 2, the concentration c raised to a power not higher than n and also corresponds to waves, partially scattered by the concentration fluctuations.

In the second case the first approximation in c corresponds to local impurity levels, and subsequent approximations correspond to splitting and shifts of these levels on account of the interaction. Therefore the initial approximation corresponds here to a "gas" model and gives the probability of tracing the formation of the energy spectrum of the disordered (amorphous) structure as the mean distance between atoms decreases. From this point of view the structure of the impurity band and its evolution with increasing concentration are of special interest.

Of course, it is evident beforehand that near the singular points of $\nu(E, c)$, in particular near the boundaries E_g^0 of the unperturbed spectral band, the expansion in powers of c ceases to be valid. Nevertheless the character of the formal expansion in the vicinity of E_g^0 allows us to draw certain qualitative conclusions.

We introduce the subsidiary quantities

$$\begin{aligned} \varphi_1 &= \text{Sp} \{ \Phi(\hat{H}_1) - \Phi(\hat{H}_0) \}, \quad \hat{H}_1 = \hat{H}_0 + \hat{U}_0, \\ \varphi_2 &= \text{Sp} \{ \Phi(\hat{H}_2^0) - \Phi(\hat{H}_0) \}, \quad \hat{H}_2^0 = \hat{H}_0 + \hat{U}_0 + U_r, \end{aligned} \quad (6.2)$$

which represent the variation of $\text{Sp} \varphi(H)$ upon successive addition of one, two, or more impurity centers.

With their help it is possible to construct a power expansion of the functional $\varphi(c)$ in powers of concentration

$$\varphi(c) = \varphi(0) + \sum a_n c^n, \quad a_n = a_n \{ \Phi \}, \quad (6.3)$$

$$\left. \begin{aligned} a_1 &= \varphi_1, \quad a_2 = \frac{1}{2} \int w(\mathbf{r}) [\varphi_2(\mathbf{r}) - 2\varphi_1] d\mathbf{r}, \\ a_3 &= \frac{1}{3!} \int \int w_3(\mathbf{r}_1, \mathbf{r}_2) \{ \varphi_3(\mathbf{r}_1, \mathbf{r}_2) - \varphi_2(\mathbf{r}_1) - \\ &\quad - \varphi_2(\mathbf{r}_2) - \varphi_2(\mathbf{r}_1 - \mathbf{r}_2) + 3\varphi_1 \} d\mathbf{r}_1 d\mathbf{r}_2. \end{aligned} \right\} \quad (6.4)$$

The form of the functionals a_1, a_2, \dots , has a simple physical meaning and is obtained by taking the limit

$$\begin{aligned} a_1 &= \left. \frac{\partial \varphi}{\partial c} \right|_{c=0} = \lim_{N \rightarrow \infty} \frac{\text{Sp} \{ \Phi(H_1) - \Phi(H_0) \} / H}{1/N} = \varphi_1, \\ a_2 &= \left. \frac{\partial^2 \varphi}{\partial c^2} \right|_{c=0} = \lim_{N \rightarrow \infty} \frac{\{ \varphi_2(\mathbf{r}) - 2\varphi_1 \} / N}{1/N^2} = \frac{1}{2} \int w(\mathbf{r}) \{ \varphi_2(\mathbf{r}) - 2\varphi_1 \} d\mathbf{r}. \end{aligned}$$

For $\Phi(x) = (1/\pi) \text{Im} \ln(E - x)$ we get

$$-\xi(E, c) = \sum_1^{\infty} \mu_n(E) c^n, \quad (6.5)$$

$$\left. \begin{aligned} -\mu_1 &= \xi_1(E), \quad -\mu_2(E) = \frac{1}{2} \int w(\mathbf{r}) \{ \xi_2(E, \mathbf{r}) - 2\xi_1(E) \} d\mathbf{r}, \\ -\mu_3 &= \frac{1}{3!} \int \int w_3(\mathbf{r}_1, \mathbf{r}_2) \{ \xi_3(E, \mathbf{r}_1, \mathbf{r}_2) - \xi_2(E, \mathbf{r}_2) - \\ &\quad - \xi_2(E, \mathbf{r}_1) - \xi_2(E, \mathbf{r}_1 - \mathbf{r}_2) + 3\xi_1(E) \} d\mathbf{r}_1 d\mathbf{r}_2, \\ \xi_1(E) &= \frac{1}{\pi} \text{Arg Det} \{ 1 - \hat{G}_0(E) \hat{U}_0 \}^{-1}, \\ \xi_2(E) &= \frac{1}{\pi} \text{Arg Det} \{ 1 - \hat{G}_0(\hat{U}_0 + \hat{U}_r) \}^{-1}. \end{aligned} \right\} \quad (6.6)$$

Evidently, as the distance \mathbf{r} between impurity centers increases we get $\xi_2(E, \mathbf{r}) \rightarrow 2\xi_1(E)$ ($\varphi_2(\mathbf{r}) \rightarrow 2\varphi_1$), and so on. This ensures the convergence of the integrals in (6.4) and (6.5).

It is clear from (6.2), (6.6), φ_1, \dots and ξ_1, \dots are connected by the trace formulae

$$\begin{aligned} \varphi_1 &= \int \Phi'(E) \xi_1(E) dE, \\ \varphi_2(\mathbf{r}) &= \int \Phi'(E) \xi_2(E, \mathbf{r}) dE. \end{aligned} \quad (6.7)$$

The quantities $\xi_1(E), \xi_2(E, \mathbf{r}), \dots$ have an extremely simple form in the case when \hat{U}_0 is a one-dimensional projection operator $\hat{U}_0 = U_0(\cdot; f)f$; and in particular in the case of a point perturbation $f(\mathbf{r}) = \delta_{\mathbf{r}0}$. Considering that $\hat{G}_0 \hat{U}_0$ is a matrix of rank one and that the elements of \hat{G}_0 in \mathbf{r} -space are

$$(\hat{G}_0)_{\mathbf{r}\mathbf{r}'} = \int \frac{e^{i\mathbf{k}(\mathbf{r}-\mathbf{r}')}}{E-E(\mathbf{k})} d\mathbf{k},$$

we obtain*

$$\left. \begin{aligned} -\xi_n(E, \mathbf{r}_1 \dots \mathbf{r}_n) &= \frac{1}{\pi} \text{Arg } D_n(E, \mathbf{r}_1 \dots \mathbf{r}_n), \\ E &= E - i0, \quad D_n = \text{Det} | \delta_{ik} - U_0 F(E, \mathbf{r}_{ik}) | \quad (1 \leq i, k \leq n), \\ F(E, \mathbf{r}) &= \int \frac{|f_{\mathbf{k}}|^2 e^{i\mathbf{k}\mathbf{r}} d\mathbf{k}}{E-E(\mathbf{k})} = \int \frac{I(E', \mathbf{r}) dE'}{E-E'}, \\ I(E, \mathbf{r}) &= \int_{E(\mathbf{k})=E} \frac{|f_{\mathbf{k}}|^2 e^{i\mathbf{k}\mathbf{r}} d\Omega_{\mathbf{k}}}{|\nabla E(\mathbf{k})|}. \end{aligned} \right\} \quad (6.8)$$

(the integral $I(E)$ is taken over the surface $E(\mathbf{k}) = E$). In particular,

$$\begin{aligned} -\xi_1 &= \frac{1}{\pi} \text{Arg} (1 - U_0 F_0), \\ -\xi_2 &= \frac{1}{\pi} \text{Arg} \begin{vmatrix} 1 - U_0 F_0 & -U_0 F_r \\ -U_0 F_{-r} & 1 - U_0 F_0 \end{vmatrix}, \quad F_r = F(E, \mathbf{r}). \end{aligned} \quad (6.9)$$

The coefficients of the series $\mu_n(E)$ are therefore

$$\begin{aligned} \mu_1(E) &= -\frac{1}{\pi} \text{Im} \ln [1 - U_0 F_0(E)], \\ \mu_2(E) &= \frac{1}{2\pi} \int w(\mathbf{r}) \text{Im} \ln \left\{ 1 - \frac{U_0^2 F_r F_{-r}}{(1 - U_0 F_0)^2} \right\} d\mathbf{r}. \end{aligned} \quad (6.10)$$

In the expression for the spectral density

$$\nu(E, c) = \nu_0(E) + \sum_1^{\infty} \nu_n(E) c^n \quad (6.11)$$

the coefficients $\nu_n(E)$ are equal to the derivatives

$$\nu_n(E) = \frac{d}{dE} \mu_n(E) \quad (6.12)$$

*It is easily seen that the form of the determinants in (6.8) coincides with (4.4) and could have been obtained directly from the system (4.3).

as is clear from the determinant $\xi(\mathbf{E}, c)$.

The form of the expressions for $\mu_n(\mathbf{E})$ shows that $\nu_n(\mathbf{E})$ is non-zero inside the region (I) of the spectrum of \hat{H}_0 (i.e., for the values $\mathbf{E}(\mathbf{k})$), and also at all points (II) outside this region for which the argument of the logarithm in (6.10) vanishes for some \mathbf{r} . These points are the roots of (4.3), that is, they are impurity levels in the presence of one, two, or more impurity centers. We will carry out the analysis separately for these cases. Correspondingly, in the calculation of the statistical mean values $\varphi(c)$ it will be convenient to break up the coefficients of the series (6.3) [i.e., the functionals $\alpha_n(\Phi)$] into two parts

$$\alpha_n\{\Phi\} = \alpha_n^I\{\Phi\} + \alpha_n^{II}\{\Phi\},$$

arising from the values \mathbf{E} in regions I and II.

2. The Spectral Density $\nu(\mathbf{E}, c)$ Inside the Zone of the Spectrum of the Unperturbed Operator

For \mathbf{E} lying inside the region of the spectrum of \hat{H}_0 [i.e., for values $\mathbf{E}(\mathbf{k})$] evidently

$$F_0(E) = \int \frac{I(E') dE'}{E - E'} = K(E) + i\pi I(E),$$

$$K(E) = \oint \frac{I(E') dE'}{E - E'}, \quad I(E) = \int_{E(\mathbf{k})=E} \frac{|f_{\mathbf{k}}|^2 d\Omega_{\mathbf{k}}}{|\nabla E(\mathbf{k})|} \quad (6.13)$$

(the symbol \oint signifies the principal value of the integral). This gives, for example, according to (6.10)

$$\mu_1 = -\frac{1}{\pi} \operatorname{arctg} \frac{\pi U_0 I(E)}{1 - U_0 K(E)}. \quad (6.14)^*$$

In the following we will be interested in the behavior of the spectral density in the vicinity of the boundary of the unperturbed spectrum E_g^0 . Without restricting the generality of the discussion we can agree to measure \mathbf{E} from this boundary (for definiteness we shall speak of the left boundary), i.e., we put $E_g^0 = 0$. We normalize the local perturbation function $f(\mathbf{r})$ by

$$\int f(\mathbf{r}) d\mathbf{r} = 1, \quad \left(\sum f(\mathbf{r}) = 1 \right)$$

(in \mathbf{k} -space $|f_{\mathbf{k}}|^2|_{\mathbf{k} \rightarrow 0} \rightarrow (2\pi)^{-3}$).

It follows from (6.13) that near $\mathbf{E} = 0$

$$I(E) = \nu_0(E) = a\sqrt{E}, \quad K(E) = -\frac{1}{U_{cr}}(1 + a_1 E). \quad (6.15)$$

Here U_{cr} is, according to (4.7), the critical value of the perturbation, beginning with which the splitting of the local impurity level begins. The substitution of (6.15) in (6.14) gives near $\mathbf{E} = 0$

$$\mu_1(E) = -\beta_0 \nu_0(E), \quad \beta_0 = \frac{U_0 U_{cr}}{U_{cr} + U_0}. \quad (6.16)$$

Considering now the terms $\mu_2(\mathbf{E}), \mu_3(\mathbf{E}), \dots$, it is first necessary to isolate in (6.8) and (6.10) the contribution from the terms with large \mathbf{r} , which determine

the singularity near $\mathbf{E} = 0$. For large \mathbf{r} evidently

$$w(\mathbf{r}) = 1, \quad \ln \left[1 - \frac{U_0^2 F_{\mathbf{r}} F_{-\mathbf{r}}}{(1 - U_0 F_0)^2} \right] \approx -\frac{U_0^2 F_{\mathbf{r}} F_{-\mathbf{r}}}{(1 - U_0 F_0)^2};$$

on the other hand, for small \mathbf{E} ,

$$\int F(\mathbf{r}) F(-\mathbf{r}) d\mathbf{r} = \int \int \frac{\int e^{-i(\mathbf{k}-\mathbf{k}')\mathbf{r}} d\mathbf{r} |f_{\mathbf{k}}|^2 |f_{\mathbf{k}'}|^2 d\mathbf{k} d\mathbf{k}'}{(E - E(\mathbf{k}))(E - E(\mathbf{k}'))}$$

$$= 8\pi^3 \int \frac{|f_{\mathbf{k}}|^4 d\mathbf{k}}{[E - E(\mathbf{k})]^2} = -\frac{d}{dE} \int \frac{g(E') dE'}{E - E'} = L_1 + i\pi \nu_0'(E),$$

$$g(E) = (2\pi)^3 \int \frac{|f_{\mathbf{k}}|^4 d\Omega_{\mathbf{k}}}{|\nabla E|}, \quad \oint \frac{g(E') dE'}{E - E'} = -\frac{1}{U_{cr}} + L_1 E + \dots$$

Therefore, taking (6.10) and (6.12) into account, we have near the boundary

$$\begin{aligned} \nu_1(E) &= -\beta_0 \nu_0'(E) = -a\beta_0 (\sqrt{E})', \\ \nu_2(E) &= \frac{\beta_0^2}{2} \nu_0''(E) = a \frac{\beta_0^2}{2} (\sqrt{E})''. \end{aligned} \quad (6.17)$$

In exactly the same way, for $\nu_3(\mathbf{E}) (\mu_3(\mathbf{E}))$ the principal terms in \mathbf{E} are obtained by summing in the region of large \mathbf{r}_1 and \mathbf{r}_2 . This gives

$$\xi_3(\mathbf{r}_1, \mathbf{r}_2) - \xi_2(\mathbf{r}_1) - \xi_2(\mathbf{r}_2) - \xi_2(\mathbf{r}_1 - \mathbf{r}_2) + 3\xi_1$$

$$\approx \operatorname{Im} \frac{F_{\mathbf{r}_1} F_{\mathbf{r}_2 - \mathbf{r}_1} F_{-\mathbf{r}_2} + F_{\mathbf{r}_2} F_{\mathbf{r}_1 - \mathbf{r}_2} F_{-\mathbf{r}_1}}{\pi(1 - U_0 F_0)^3} U_0^3,$$

$$\sum_{\mathbf{r}_1 \mathbf{r}_2} F_{\mathbf{r}_1} F_{\mathbf{r}_2 - \mathbf{r}_1} F_{-\mathbf{r}_2} = \int \frac{d\mathbf{k}}{[E - E(\mathbf{k})]^3} = \frac{d^2}{dE^2} \{K(E) + i\pi \nu_0(E)\},$$

from which we have near $\mathbf{E} = 0$

$$\nu_3(E) = -\frac{\beta_0^3}{3!} \nu_0'''(E).$$

It is easy to see that for arbitrary n

$$\nu_n(E) c^n = E^{1/2} \left(\frac{c}{E} \right)^n \{A_{n0} + A_{n1} E + \dots\}, \quad (6.18)$$

and, accurate to the principal terms in \mathbf{E} ,

$$\nu_n(E) c^n = (-1)^n \frac{\beta_0^n c^n}{n!} \nu_0^{(n)}(E) = a (-1)^n \frac{\beta_0^n c^n}{n!} \frac{d^n}{dE^n} \sqrt{E}. \quad (6.19)$$

The divergence of the coefficients of the series for $\nu_n(\mathbf{E})$ near the points $\mathbf{E} = E_g^0 = 0$ is connected with the displacement and smearing of the singularity in $\nu_0(\mathbf{E})$ when $c \neq 0$. In the first approximation in c the displacement of the singularity can be obtained by summing the principal terms in \mathbf{E} in (6.18):

$$\nu(E, c) = \sum (-1)^n \frac{\beta_0^n c^n}{n!} \nu_0^{(n)}(E) = \nu_0(E - \beta_0 c),$$

i.e., near \mathbf{E} we have in accord with Sec. 5

$$\nu(E, c) = a\sqrt{E - \beta_0 c}, \quad \beta_0 = \frac{U_0 U_{cr}}{U_0 + U_{cr}}, \quad \beta_0 c \ll 1. \quad (6.20)$$

The previously investigated "smearing" of the renormalized singularity arises, as follows from the result obtained here, only in a higher order in c , and requires the summation of all the divergent terms in the expansion (6.11).

We turn now to the calculation of the statistical mean values and the construction of the functionals $\alpha_n\{\Phi\}$. Simple substitution of (6.18) for $\nu_n(\mathbf{E})$ into the formal equality

* $\operatorname{arctg} = \tan^{-1}$.

$$\alpha_n^I \{\Phi\} = \int v_n(E) \Phi(E) dE$$

is inapplicable, because of the divergence of the integral $\int E^{1/2-n} \Phi(E) dE$. Therefore, prior to taking the limit $E = E - i0$, it is necessary, starting from (6.5) and (6.7), to carry out integration by parts in expressions of the type

$$\lim \int \Phi(E) \frac{d^n}{dE^n} \left\{ \int \frac{v_0(E') dE'}{E-E'-i\gamma} \right\} dE = (-1)^n \int \{K(E) + i\pi v_0(E)\} \Phi^n(E) dE. \tag{6.21}$$

We thus get

$$\left. \begin{aligned} \varphi^I(c) &= \varphi(0) + \sum_{n=1}^{\infty} c^n \int v_0(E) \sum_{k=1}^n a_{nk}(E) \Phi^{(k)}(E) dE \\ &= \int v_0(E) \{ \Phi(E) + c(a_{11} + ca_{21} + \dots) \Phi'(E) \\ &\quad + c^2(a_{22} + \dots) \Phi''(E) + \dots \} dE, \\ a_{11} &= -\frac{1}{\pi v_0(E)} \operatorname{arctg} \frac{\pi I(E) U_0}{1 - U_0 K(E)}, \\ a_{22} &= \frac{U_0^2 g(E)}{2\pi v_0(E)} \operatorname{Re} \frac{1}{[1 - U_0 F_0(E)]^2}. \end{aligned} \right\} \tag{6.22}$$

All the coefficients $a_{jk}(E)$ in the expansion (6.22) remain finite near $E = 0$

$$a_n(0) = -\beta_0, \quad a_{22}(0) = -\frac{\beta_0^2}{2}.$$

These formulae can be simplified much further if we consider U_0 as a small quantity. Up to terms of order U_0^2 we have for arbitrary concentrations

$$\begin{aligned} \varphi(c) &= \varphi(0) - U_0 c \int I(E) \Phi'(E) dE \\ &\quad + U_0^2 \int \left\{ c(1-c) I(E) K(E) \Phi'(E) - \frac{c^2}{2} g(E) \Phi''(E) \right\} dE \dots \end{aligned} \tag{6.23}$$

For a point perturbation

$$\left. \begin{aligned} I(E) &= g(E) = v_0(E), \quad K(E) = \int \frac{v_0(E') dE'}{E-E'}, \\ \varphi(c) &= \int v_0(E) \left\{ \Phi(E) - c U_0 \Phi'(E) \right. \\ &\quad \left. + U_0^2 \left[c(1-c) K(E) \Phi'(E) - \frac{c^2}{2} \Phi''(E) \right] + \dots \right\} dE. \end{aligned} \right\} \tag{6.24}$$

For U_0 small enough we have already seen that the impurity levels appear only if the number of impurity centers is $n \sim U_0^{-3/2}$; therefore $\varphi^I(c)$ coincides with $\varphi(c)$ for any finite number n of terms in the expansion in U_0 provided $U_0 \ll n^{-2/3}$.

3. The Spectral Density Outside the Region of the Unperturbed Spectrum. The Structure of the Impurity Band

Outside the interval (E_g^0, \bar{E}_g^0) it is also possible to use formula (6.4) and (6.12) in an expansion in powers of the concentration, but a direct application of the expression (6.10) is not very convenient. These formulas take on a much simpler form if we take it into account that each group of n impurity atoms at distances r_{jk} from one another brings about the appear-

ance of separate discrete levels $E_i(r_{12}, \dots)$, (in our case there are no more than n such levels). The contribution of such a group to the spectral density is therefore

$$\sum_i \delta(E - E_i(r_{12}, \dots)).$$

For the quantities $\varphi_n(r_{12}, \dots)$ introduced earlier in (6.2) this yields (outside the region E_g^0, \bar{E}_g^0)

$$\varphi_n(r_{12}, \dots) = \sum_i \Phi(E_i(r_{12}, \dots)). \tag{6.25}$$

Thus, for example, if an isolated impurity atom leads to the level E_0 , then the coefficient $\alpha^{\text{II}} \{\Phi\}$ in the expansion (6.3) for $\varphi^{\text{II}}(c)$ will be

$$\alpha_1^{\text{II}} \{\Phi\} = \varphi_1^{\text{II}} = \Phi(E_0).$$

For two impurity centers situated at a distance r from each other there will be levels $E_{1,2} = E_0 + \epsilon_{1,2}(r)$. Therefore

$$\varphi_2^{\text{II}}(r) = \Phi(E_0 - \epsilon_1(r)) + \Phi(E_0 - \epsilon_2(r)) \tag{6.26}$$

and

$$\begin{aligned} \varphi^{\text{II}}(c) &= c\Phi(E_0) + \frac{c^2}{2} \int w(r) \{ \Phi(E_0 - \epsilon_1) \\ &\quad + \Phi(E_0 - \epsilon_2) - 2\Phi_0(E_0) \} dr + \dots \end{aligned}$$

Because of the rapid decrease of $\epsilon(r)$ ($\epsilon(r) \sim e^{-\alpha r}/r$), the integrals in (6.26) converge, and this expansion is quite effective for any function $\Phi(z)$ that is smooth enough. Corresponding to this expansion we have a formal decomposition of the spectral density in region II:

$$\begin{aligned} v(E, c) &= c\delta(E - E_0) + \frac{c^2}{2} \int w(r) \{ \delta(E - E_0 - \epsilon_1) \\ &\quad + \delta(E - E_0 - \epsilon_2) - 2\delta(E - E_0) \} dr + \dots \end{aligned} \tag{6.27}$$

Such an expansion is meaningless in the immediate neighborhood of E_0 ; however, at small distances $\epsilon = E_0 - E$ from this point we have

$$\begin{aligned} v(E_0 - \epsilon, c) &= \frac{c^2}{2} \Psi(\epsilon) + \dots, \\ \Psi(\epsilon) &= \frac{d}{d\epsilon} (\Omega_1 + \Omega_2), \quad \Omega_i(E) = \int_{\epsilon_i(r) > \epsilon} w(r) dr. \end{aligned} \tag{6.28}$$

For small ϵ , that is at large distances r , $w(r) = 1$. If the interaction is spherically symmetrical [i.e., $\epsilon_i = \epsilon_i(r)$], then

$$\Psi(\epsilon) = -\frac{4\pi}{3} \frac{d}{d\epsilon} (r_1^3 + r_2^3), \quad \epsilon_i(r_i) = \epsilon. \tag{6.29}$$

For short-range perturbations (in particular, delta-functions) $\epsilon_i(r) \sim e^{-\alpha r}/r$, i.e., $r_i \sim -\alpha^{-1} \ln |\epsilon|$, and consequently for small ϵ

$$v(E_0 - \epsilon, c) = \frac{2\pi}{3} c^2 \frac{\ln^2 |\epsilon|}{\alpha^3 |\epsilon|}, \tag{6.30}$$

i.e., the result obtained earlier in (4.33). Formula (6.30) holds only for sufficiently small ϵ , corresponding to large distances $\alpha r \gg 1$. On the other hand, if ϵ becomes of the order $\epsilon_j (c^{-1/3})$ that is, of the order of the level shift, due to the neighboring center, by an

average distance $\bar{r} \sim c^{-1/3}$, then all distances between impurities turn out to be of the same order of magnitude and thus "pair collisions" no longer provide the principal contribution to the spectral density. Therefore in the region $|\epsilon| \lesssim \epsilon(c^{-1/3})$ the expansion (6.27) is meaningless, and the spectral density in the region of the concentration smearing of the level E_0 is described by the formulae of Sec. 4. This means that not only the level E_0 but each discrete level, even one due to "pair" collisions of two centers $\epsilon_1(\mathbf{r})$, has a concentration width Δ ($\ln(1/\Delta) \sim \alpha c^{-1/3}$).

In view of the discrete nature of \mathbf{r} , we arrive thus at the following structure for the impurity band arising from the splitting of the level E_0 ($\epsilon = 0$). For $c \rightarrow 0$ the point $\epsilon = 0$ corresponds to levels of isolated impurity centers and possesses a "strength" c . The points $\epsilon_{1,2}(\mathbf{r})$ are discrete levels with "strength" c^2 [i.e., they give a contribution $c^2 \delta(\epsilon - \epsilon(\mathbf{r}))$ to $\nu(E, c)$]; these levels possess a limiting condensation point $\epsilon = 0$. Each level $\epsilon_{1,2}(\mathbf{r})$ is a limit point for the levels $\epsilon(\mathbf{r}_1, \mathbf{r}_2)$, which correspond to "triple collisions" of the impurities and have "strength" c^3 , and so on (cf. Fig. 8a). However we have seen that the interaction with distant impurities [the calculation of which is already outside the degree of approximation of (6.27)] leads to concentration broadening of each discrete level and smears out this "fine structure" of the band. It is evident that the fine structure of the split levels is retained only in the energy region where the distances between neighboring discrete "pair" levels are $\delta\epsilon \gg \Delta$ (Δ is the concentration width of the level).

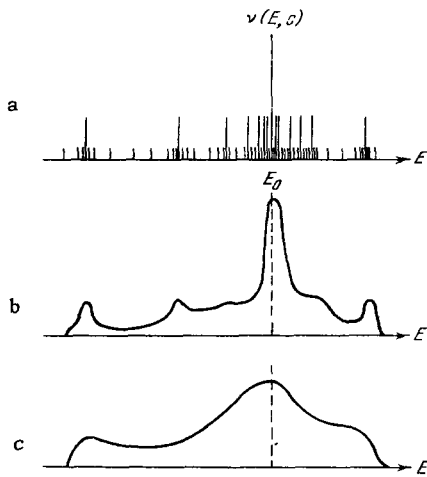


FIG. 8. Schematic variation in structure of the impurity band with concentration.

The distance between neighboring levels is found from the condition

$$4\pi r^2 \frac{dr}{d\epsilon} \delta\epsilon \sim 1.$$

Therefore fine structure of the band exists when

$$\Delta 4\pi r^2 \frac{dr}{d\epsilon} \ll 1.$$

For $\epsilon \sim e^{-\alpha r}$ we get the condition for the resolvability of the maxima:

$$\epsilon \gg E_0 e^{-x}, \quad x = \alpha c^{-1/3} \gg 1. \quad (6.31)$$

For a gradual decrease in the energy of the local perturbation $U(\mathbf{r})$, we have $\epsilon(r) \approx U(r) \sim U_1 r^{-k}$ and $r(\epsilon) \sim (U_1/\epsilon)^{1/k}$, and the condition for the resolvability of the maxima is $\epsilon > U_1 c^{2/3(k-3)}$.

As the concentration increases the maxima "fill out" and the fine structure of the band disappears (cf. Figs. 8b,c).

All the preceding quantitative estimates and formulae relate to the case of comparatively distant "collisions" of the impurity centers, $r \gg 1$. We now discuss in somewhat greater detail the situation at small distances $r \sim 1$. The distinguishing feature of small distances is that the strong influence of a close neighborhood of the impurity centers can lead to the disappearance of part of the levels due to the splitting of E_0 , or on the contrary to the appearance of discrete levels in those cases when an isolated atom does not give rise to a local state. The latter has already been discussed in Sec. 5 in connection with questions of "fluctuation-type" levels. We consider again equation (4.9) for levels in the presence of two centers at a distance r (as before, for definiteness we put $U_0 < 0$ and consider levels on the left of $\underline{E}_g^0 = 0$)

$$1 - U_0 F_0(E) = \pm U_0 F(E, r). \quad (6.32)$$

For $|U_0| > U_{cr}$ and $r \gg 1$ this equation has two real roots. One of these roots tends with decreasing r to the boundary $\underline{E}_g^0 = 0$ and vanishes for $r < r_k$

$$|F(0, r_k)| = \frac{1}{U_{cr}} - \left| \frac{1}{U_0} \right|. \quad (6.33)$$

The equation written down for r_k always has a solution if $|F(0, 0)| = 1/U_{cr}$ and $|F(0, \infty)| = 0$. However, because the possible values r are discrete, we obtain a meaningful solution for the equation only if $r_k > 1$.

For $|U_0| < U_{cr}$, on the contrary, the first real root of (6.32) appears when $r < r'_k$, where

$$|F(0, r'_k)| = \left| \frac{1}{U_0} \right| - \frac{1}{U_{cr}} \quad (U_0 < 0). \quad (6.34)$$

This equation (6.34) has a solution if $U_{cr}/2 < |U_0| < U_{cr}$; for $U_0 < |U_{cr}/2|$ a discrete level appears only for a cluster of three or more impurity centers.

These simple remarks lead to several qualitative corollaries concerning the structure of the spectrum. If (6.33) and the analogous equations for a large number of centers have no solution $r_k > 1$, then all the levels arising from the splitting and shift of E_0 remain outside region I, and consequently the impurity band is separated from the ground state zone. Since the influence of subsequent additional centers on the level shift decreases rapidly with the increase in their number, the existence of a split-off impurity band is deduced in practice, generally speaking, by an analysis of lev-

els with two or three impurity centers. For $r_k > 1$ the impurity levels can approach the boundary of region (I) and there is no gap between bands in this case.

For $|U_0| < U_{CR}$ as already mentioned, impurity levels are produced only by a whole group of two or more impurity centers. Qualitatively, all the considerations concerning splitting and smearing used earlier for the level E_0 are applicable to each such level E_1 . The difference is that the remote isolated impurity centers, which cause the shifts and splitting of the "collective" level E_1 , are "extraneous" impurities with respect to this level, and therefore the splitting and smearing of the level is determined by the much simpler formulae (4.26) (of course the smearing width is of the same order). Such levels evidently can also lead to a split-off impurity band; this is, however, significantly less probable since the minimal cluster of impurity centers, which brings about the impurity level, is determined by a level situated near the boundary (this level does not reach the boundary itself only because \mathbf{r} is discrete). Therefore it is most probable that the influence of the farther neighbors will bring about an overlapping of these bands. If the band brought about by such a collective level turns out to be split-off just the same, then its integrated spectral density is of a higher power in the concentration, (for a "two-particle" level, $\sim c^2$). Finally, it follows from the foregoing that both for $|U_0| < U_{CR}$ and for $|U_0| > U_{CR}$ it is possible, in principle to have cases where some discrete "two-particle" levels form their own non-overlapping bands of integral "strength" c^2 , along with a principal band containing the level E_0 and having a "strength" $\sim c$.

7. SOME OTHER MODELS OF DISORDERED STRUCTURES

In conclusion we discuss the question of some other approximations and models of disordered and amorphous structures, which are also possible within the framework of a random chaotic potential of an external field (or random parameters in a system with coupled oscillator).

We begin with an analysis of the physical meaning and role of the approximations used in the model we assumed for the solid solution. Without dwelling on qualitatively inessential details [for example the assumed absence of a mutual "polarization" of the impurity centers, i.e., the assumption $U_j = U_0(\mathbf{r} - \mathbf{r}_j)$], we shall discuss only the fact that the possibility of representing the Hamiltonian \hat{H} in the form (1) $\hat{H} = \hat{H}_0 + \sum \hat{U}_j$ appears at first glance to be tantamount to the assumption that the replacement of some of the atoms by the disordered impurity centers does not change the geometric distribution of the lattice sites. Actually, however, the situation is not that bad: in a three-dimensional crystal where displacement fluctuations are bounded, \hat{H}_0 can be taken to correspond to

a new averaged parameter of the solution unit cells, and we should speak only of local fluctuation distortions of the lattice near the impurity centers. Evidently, these distortions can be included in the definition of the potential U_0 ; for example, a convenient method is simply a redefinition of the coordinate system corresponding to the distorted crystal planes. It is clear that such a refinement does not lead to qualitative changes in the model; in particular, this can be seen from the fact that the smearing of the discrete density $w(\mathbf{r}) = \sum \delta(\mathbf{r} - \mathbf{n})$ at large distances (i.e., the replacement of $w(\mathbf{r})|_{\mathbf{r} \rightarrow \infty}$ by the continuous distribution $w(\mathbf{r}) = 1$) does not change the results in the more sensitive region, near the singular points.

It follows that the "bare" crystal structure only determines the spectral structure and the distribution of the singularities for $c \rightarrow 0$, but does not appear at all for $c \sim 1$. This can be seen even from the fact that when the initial Hamiltonian is isotropic (e.g., $\hat{H}_0 = -\Delta/2\mu = k^2/2\mu$) the character of the structure and of the singularities of the spectrum is the same. However, since this investigation is carried out sufficiently thoroughly only for small concentrations, or small perturbations U_0 , it is interesting to find other models of disordered or amorphous structure which allow a simple analysis.

In some respects a contrasting model of an aperiodic (amorphous) structure is a system which is almost crystalline in each small region, but whose parameters (size and direction of the lattice vectors, potential distribution, etc.) vary slowly from point to point. Such a model allows essentially different interpretations:

(a) There exists "topologically" a single crystal lattice which we can take as the fundamental (integer-valued) coordinate grid; this grid however, is curvilinear and not isometric, and changes appreciably at large distances (cf. Fig. 9a). Point defects (vacancies, extra atoms, etc.) which do not violate the topology, can exist in such a system. A system of this type is essentially a deformed crystal and is not of special interest as a model for an amorphous solid.

(b)–(c) The point-to-point variation of the crystal structure is due to violation of the "topology" of the crystal (coordinate) grid. Such violations can be produced by one-dimensional defects like dislocation loops (b) or by two-dimensional defects like discontinuity surfaces between regions differing somewhat in orien-

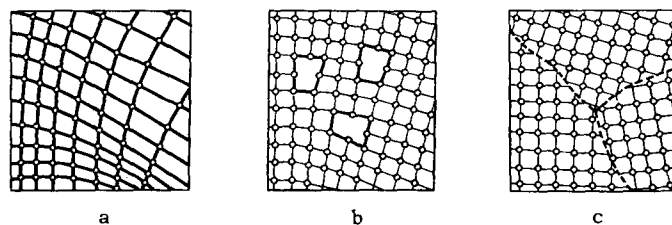


FIG. 9. Models of 'slow' variation of a crystal structure.

tation and parameters (c) (cf. Figs. 9b,c). The first of these two types is qualitatively closer to an imitation of an amorphous structure; a gradual transition to the general case of an amorphous structure is obtained by increasing the density and decreasing the diameter of the dislocation loops. The second type of violation is characteristic of a finely-dispersed polycrystal with small disorientation of the neighboring crystallites. As the size of these "crystallites" is reduced, the distinction between the two cases, of course, disappears. It is precisely cases (b) and (c) which are of interest as models of an "amorphized" structure.

The small parameter in this model is the quantity $1/\mathcal{L}$ where \mathcal{L} is the characteristic length over which an appreciable variation in structure occurs. Therefore in the zeroth approximation in this parameter the Hamiltonian of an elementary excitation for all three cases (a)–(c), can be written in the form

$$H = \epsilon(\mathbf{p}, \mathbf{r}), \quad \mathbf{p} = \mathbf{k} \quad (\hbar = 1), \quad (7.1)$$

where $\epsilon(\mathbf{p}, \mathbf{r})$ is a dispersion law periodic in \mathbf{p} for a quasi-particle in the crystalline lattice existing in the vicinity of the point \mathbf{r} . The dependence on the coordinate \mathbf{r} enters through the lattice-period vectors and the other parameters characterizing the crystal structure near \mathbf{r} . We shall not analyze the many interesting properties of such particles, but we shall formulate certain simple results which we need and which are evident practically without any calculation.

For $p \gg 1/\mathcal{L}$, \mathbf{p} and \mathbf{r} can be regarded in the zeroth approximation as c-numbers. Therefore the possible energy levels of such a system are determined by the range of values of the function $\epsilon(\mathbf{p}, \mathbf{r})$ (cf. Fig. 10), and the states are determined by the classical mechanics of a particle with the Hamiltonian (7.1)

$$\mathbf{v} = \dot{\mathbf{r}} = \frac{\partial \epsilon}{\partial \mathbf{p}}, \quad \mathbf{p} = -\frac{\partial \epsilon}{\partial \mathbf{r}}. \quad (7.2)$$

In the first (quasi-classical) approximation the wave functions are also defined by the classical form of $\epsilon(\mathbf{p}, \mathbf{r})$ and the order of writing the non-commuting operators \mathbf{p} and \mathbf{r} in the complicated function $\epsilon(\mathbf{p}, \mathbf{r})$ does not matter. Thus, for example in the one-dimensional case, it is easy to integrate the classical equations (7.2) and we obtain

$$\begin{aligned} \epsilon(p, x) = E = \text{const}, \\ \frac{dx}{v(p, x)} = dt, \quad p = p(x, E), \end{aligned} \quad (7.3)$$

the wave function in the first approximation is evidently

$$\begin{aligned} \psi = c(x) e^{iS}, \\ c(x) = v^{-1/2}(p(x, E), x), \quad S = \int p(x, E) dx \end{aligned} \quad (7.4)$$

(S is the action). This equation is the result of the fact that probability $|\psi|^2$ in the classically allowed region is

$$|\psi|^2 dx \sim dt,$$

from which (7.4) follows. For example, if

$$\epsilon(p, x) = A + B \cos ap; \quad A, B, a = A(x), B(x), a(x), \quad (7.5)$$

then

$$v(p, x) = a \sqrt{B^2 - (E - A)^2},$$

whence

$$\begin{aligned} \psi \sim a^{-1/2}(x) \{B^2(x) - (E - A(x))^2\}^{-1/4} e^{iS(x)}, \\ S = \int \arccos\left(\frac{E - A}{B}\right) \frac{dx}{a}. \end{aligned} \quad (7.6)$$

The level density, is determined, in accordance with the quasi-classical character of motion, by the volume of phase space for a given energy interval (cf. Fig. 10). Therefore, if for a given crystal structure (α) the density is $\nu_\alpha(E)$, then in the averaged spectral density

$$\nu(E) = \overline{\nu_\alpha(E)} = \int \nu_\alpha(E) \varrho(\alpha) d\alpha = \lim_{V \rightarrow \infty} \frac{1}{V} \int \nu(E, \mathbf{r}) d\mathbf{r}$$

$\nu_\alpha(E)$ has a weight $\rho(\alpha)$, equal to the relative volume of the regions occupied by this structure. Upon averaging over the volume (i.e., over α), the initially split bands may remain split, or may overlap.

It is clear from the equation $\epsilon(\mathbf{p}, \mathbf{r}) = E$ that both finite and infinite classical motion can exist (cf. Fig. 10). For finite motion the rules of quantization in the first (quasi-classical) approximation also do not require precise specification of the non-commuting operators in $\epsilon(\mathbf{p}, \mathbf{r})$ (generally this follows from the fact that the energy levels are real, but \hbar enters in the commutation conditions in pure imaginary combinations). This quantization turns out to be important in practice only near states corresponding to extrema of the energy in the bands. In the mean, the contribution from these levels is vanishingly small everywhere except around the true boundary of the spectrum. The behavior of the spectral density at this boundary is linked with the finite motion at the bottom of the band in the section where this band lies deepest. For the determination of $\nu(E)$ at this boundary we need to make definite assumptions about the distribution of the regions with a given crystal ordering. Thus, if E_g is the boundary (i.e., the bottom of the lowest band), and $V \sim L^3$ is the size of the region with a structure corresponding to such a band, then the corresponding level is, as indicated before,

$$E - E_g \sim \frac{1}{L^2}.$$

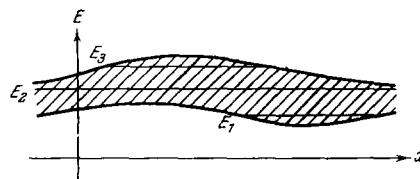


FIG. 10. Band of allowed energy values as a function of one of the coordinates (for 'slow' variation in crystal structure) E_1 and E_2 correspond to finite motion.

Therefore if $p(V)$ is the probability that the region of the required structure has a volume V , then near E_g we have as before, in order of magnitude,

$$\nu(E) \sim p(\kappa(E_g - E)^{-3/2}),$$

and for $p(V) \sim e^{-\gamma V}$

$$\nu(E) \sim \exp\{-\lambda(E_g - E)^{-3/2}\}, \quad \lambda = \kappa\gamma.$$

Thus the whole program formulated above for the study of classical motions and quasi-classical states and for the determination of the averaged spectral density can be carried out in the zeroth approximation and partially in the first approximation in $1/\mathcal{L}$, provided that there is a concrete definition of the structures (α) and definite assumptions are made concerning the distribution of these structures [i.e., concerning the probabilities $\rho(\alpha)$].

So far we have dealt only with consequences resulting only from a "classical" specification of the Hamiltonian $\epsilon(\mathbf{p}, \mathbf{r})$, connected with a local structure, without requiring an explanation of either the microscopic variation of this structure [variants (a), (b), and (c)] or the genesis of this local dispersion law. Both are necessary to define more precisely the operator $\epsilon(\mathbf{p}, \mathbf{r})$ and the corrections to it in the non-quasi-classical approximation. Such a refinement is needed for the determination of the scattering and damping of waves corresponding to quasi-classical motion, and is quite important when one is interested not only in thermodynamic but also in kinetic problems. Of course, variants (a), (b), and (c) differ radically with respect to scattering and damping: variant (a), which describes a deformed crystal, corresponds to an "adiabatic" variation (with respect to the small parameter $1/\mathcal{L}$) of the periodic field and leads to exponentially small damping. The damping in the more interesting models (b) and (c) has a power-law order and needs a separate investigation.

A unique case, apparently one of the most interesting, occurs when the crystal structure in the zeroth approximation differs at different points only in orientation, and rotations result from the one-dimensional and two-dimensional defects already considered. Inasmuch as the spectral density cannot depend on the crystal orientation, $\nu(E, \mathbf{r})$ does not depend in the zeroth approximation on \mathbf{r} and coincides with the spectral density $\nu_0(E)$ of an ideal crystal. Therefore in this case the difference between $\nu(E)$ and $\nu_0(E)$ is wholly determined precisely by the difference between the Hamiltonian \hat{H} and the quasi-classical Hamiltonian $\epsilon(\mathbf{p}, \mathbf{r})$.

The entire content of this section is extremely schematic and is aimed principally at clarifying the situation connected with the application of such a model of an amorphous body, and not at all at constructing a detailed theory of the model. We therefore restrict ourselves in this paper to what has already been said and we abstain from any further analysis of either this or any other possible model.

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