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# Characteristic features of the electron spectrum of metals with dislocations

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The theoretical data on the spectrum of electron states localized near edge dislocations are presented in a systematic manner and supplemented by new results. The following types of edge dislocations are considered: an isolated rectilinear dislocation, a dislocation dipole, a prismatic loop, and a segment of a bent dislocation of finite length. A detailed study is made of the problem of concentration broadening of the dislocation energy levels and bands in the case of random and quasiregular distributions of these various types of dislocations.

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## INTRODUCTION

Distortions of the crystal lattice around dislocation lines create large-scale deviations of the crystal field from its periodic structure in a perfect crystal. In metals these distortions produce forces which act on conduction electrons and can sometimes alter significantly the nature of motion of these electrons. In the simplest cases it is found that electron excitations belonging to a continuous spectrum are scattered by dislocations exchanging energy and momentum: such processes give rise to a dislocation contribution to the electrical resistivity and to an electron contribution to the drag force exerted on dislocations. However, there can be situations in which the influence of dislocations on the electron motion is more fundamental, for example, an electron may become localized near a dislocation line. Localization is known to produce discrete levels in certain parts of the energy spectrum and such drastic changes in the structure of the electron spectrum may give rise to specific features in the thermodynamic and transport properties of a metal.

The concept of a dislocation covers a fairly wide class of different line defects of the crystal structure. The common feature of all of them is the presence of a core—representing a certain tube of radius of the order of the interatomic distance within which the deformation of the original lattice is of the order of unity—and an inhomogeneous field of elastic strains decreasing slowly away from the core. The shape of a dislocation line, microstructure of its core, and the actual law governing the decrease of the elastic field can differ considerably. This complicates greatly the formulation and solution of the quantum-mechanical problem of the interaction between electrons and dislocations. It is not possible to obtain a general solution of this problem applicable to all types of dislocation and in each case it is necessary to study much simpler specific models.

Many papers have been published on problems of this kind in the case of semiconductors and metals. Some of them deal with the conditions of formation and structure of electron states associated with dislocations[1-7]; others are concerned with the scattering of free electrons on dislocations and its influence on the electrical conductivity of a metal and on the dislocation mobility (the necessary references can be found in the monographs of Ziman[8] and Friedel[9] as well as in the review of Kaganov *et al.*[10]).

The main methodological difficulties are encountered in the analysis of changes in the electron spectrum due to dislocations. Kaner and Fel'dman[3] pointed out that an investigation of the spectrum of states localized at dislocations should include solution of problems of two types: 1) a calculation of the spectrum of an electron interacting with a single dislocation; 2) an analysis of the concentration broadening of levels or bands in such a spectrum due to the overlap of the long-range elastic fields of dislocations. In most cases, studies have been confined to the spectrum of an electron near

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an isolated rectilinear edge or screw dislocation; more complex objects—dislocation dipoles and prismatic loops—have been discussed only once.[7] The dilatation component of the elastic field of edge dislocations is found to result always in localization of electron excitations. Localized states in the energy spectrum correspond to discrete levels or bands split off from the points of minima in the dispersion law $\varepsilon(\mathbf{p})$ of electrons in a perfect metal. Some of the states corresponding to deep levels are essentially of quantum nature and they are localized in the immediate vicinity of dislocation cores. However, near edge dislocations there are always quasiclassical localized states with macroscopic radii and these have energies close to the continuous spectrum.

In the case of screw dislocations (at least in the case of the investigated models) the localization conditions are more stringent and, in particular, quasiclassical localized states are not normally observed.

The statistical weight of the quasiclassical states is considerably greater than those of the states localized in the vicinity of cores and, therefore, the former are responsible for the significant features of the physical properties of metals resulting from electron localization. Moreover, an analysis of the quasiclassical part of the spectrum is easier because its structure is governed by the interaction between an electron and the elastic field of a dislocation, and it is not very sensitive to the structure of the dislocation core about which little is known. Therefore, the interest lies mainly in the analysis of model problems of the interaction of electrons with the dilatation component of the deformation field of edge dislocations. We shall confine our attention to such models.

In the first section we shall present systematically all the known results and new data on the spectrum of electrons localized near edge dislocations of different types. The second section deals with the concentration broadening of the spectrum of localized states. This problem was considered earlier by Kaner and Fel'dman[3] but they studied only the simplest case of a randomly distributed rectilinear dislocation. It should be pointed out immediately that the existence of a long-range interaction between dislocations prevents the establishment of a completely random distribution in real cases and it is more realistic to expect partly ordered structures. In the second section we shall analyze the concentration broadening of dislocation levels and bands for all types of dislocations discussed in the first section and we shall do this for random and quasiregular distributions.

## 1. SPECTRUM OF ELECTRONS LOCALIZED AT SINGLE DISLOCATION ENTITIES

An analysis of the electron motion near a dislocation in a metal simplifies greatly because one can use the deformation potential approximation to describe the interaction. In this approximation the interaction energy is given by the phenomenological relationship

$$U(\mathbf{r}-\mathbf{r}_0)=\lambda_{ik}(\mathbf{p})u_{ik}(\mathbf{r}-\mathbf{r}_0),$$

where $\mathbf{r}_0$ is a vector describing the position of a dislocation line; $u_{ik}$ is the elastic strain tensor; $\lambda_{ik}(\mathbf{p})$ is the deformation potential tensor depending generally on the electron quasimomentum $\mathbf{p}$. It follows from general considerations that the absolute values of the component of the tensor $\lambda_{ik}$ are of the order of the width of the electron band ($\lambda \sim \mu$, where $\mu$ is the Fermi level).

A self-consistent allowance for the screening of the unrenormalized deformation potential by electrons in a metal, which is based on the electrical neutrality condition, does not alter the coordinate dependence of the potential (1) at large distances from a dislocation ($|\mathbf{r}-\mathbf{r}_0| \gg a$, where $a$ is the lattice parameter) and it reduces simply to renormalization of the parameter $\lambda$ (Ref. 11). The electrical neutrality condition breaks down near a dislocation line in a region of dimensions of the order of the Debye screening radius, which is of the order $a$ in the case of metals. In this region the structure of the potential $U$ differs from Eq. (1); in particular, Eq. (1) has formally a divergence at $|\mathbf{r}-\mathbf{r}_0| \to 0$ and this now disappears. A qualitative analysis shows that $\max|U| \sim \lambda \sim \mu$. It is usual to assume that $\max|U|$ does not exceed the width of the conduction band, which makes it possible to study the interaction of electrons with a dislocation in the one-band approximation. It may be that in some cases this approximation is incorrect, but failure to use this approximation would have complicated the problem greatly.

In the case of semiconductors an allowance for the screening of the deformation potential by electrons alters very greatly the form of this potential.[1,2] This is probably the main difference in the formulation of the problem of the interaction of electrons with dislocations in metals from the corresponding problem in the case of semiconductors.

Qualitative ideas on the nature of the singularities resulting from the interaction of an electron with a dislocation can be obtained simply by assuming that a metal is elastically isotropic, allowing only for the dilatation part of the strains $\mathrm{Tr}\, u_{ik} \equiv u_{kk}$, and neglecting the dependence of $\lambda_{ik}$ on the quasimomentum $\mathbf{p}$. In this approximation the deformation potential is

$$U(\mathbf{r}-\mathbf{r}_0)=\lambda_0 u_{kk}(\mathbf{r}-\mathbf{r}_0). \tag{1}$$

The quasiclassical motion of an electron near a dislocation is described by the Hamiltonian[1,2,4]

$$\hat{H}=\varepsilon(\hat{\mathbf{p}})+U(\mathbf{r}-\mathbf{r}_0), \tag{2}$$

where $\varepsilon(\mathbf{p})$ is the dispersion law of an electron in the conduction band in the absence of a dislocation; $\hat{\mathbf{p}} = -i\hbar\nabla_{\mathbf{r}}$ is the momentum operator. It has been pointed out above that dislocations alter radically the nature of motion of those electrons which have momenta belonging in the vicinity of minima $\mathbf{p}_k$ of the function $\varepsilon(\mathbf{p})$. Near these minima the Schrödinger equation for the electron wave function $\psi(\mathbf{r})$ becomes

$$[(\hat{\mathbf{p}}-\mathbf{p}_k)^2/2m_k+U(\mathbf{r}-\mathbf{r}_0)]\psi(\mathbf{r})=(\varepsilon-\varepsilon_k)\psi(\mathbf{r}), \quad \varepsilon_k=\varepsilon(\mathbf{p}_k), \tag{3}$$

where $m_k=m(\mathbf{p}_k)$ is the effective mass of an electron at a point $\mathbf{p}_k$; for simplicity, we shall assume that the dispersion law in the vicinity of the minima is isotropic.

Clearly, the solution of Eq. (3) can be represented in the form

$$\psi(\mathbf{r})=\chi(\mathbf{r})\exp(i\mathbf{p}_k\mathbf{r}/\hbar),$$

and the functions $\chi(\mathbf{r})$ are given by the equation

$$[-\hbar^2\Delta_{\mathbf{r}}/2m_k+U(\mathbf{r}-\mathbf{r}_0)]\chi(\mathbf{r})=(\varepsilon-\varepsilon_k)\chi(\mathbf{r}). \tag{4}$$

Further analysis requires the knowledge of the actual form of the potential $U(\mathbf{r}-\mathbf{r}_0)$.

## Isolated rectilinear dislocations

For completeness, we shall begin by recounting the results of an analysis of the interaction between an electron and a rectilinear edge dislocation.[4] In terms of cylindrical coordinates $\rho$, $\varphi$, and $z$ with the $z$ axis directed along a dislocation line and the polar axis along the Burgers vector **b**, and with the coordinate origin located on the dislocation line (Fig. 1), the potential $U$ is

$$U=U_1(\rho,\varphi)=-\frac{\lambda b}{\rho}\sin\varphi,\qquad \lambda=\frac{|\lambda_0|}{2\pi}\frac{1-2\nu}{1-\nu}\sim|\lambda_0|, \tag{5}$$

where $\nu$ is the Poisson ratio. In view of the homogeneity of the potential along the $z$ axis, the motion of an electron can be divided into longitudinal and transverse:

$$\chi(\mathbf{r})=\chi_\perp(\rho,\varphi)\exp(ipz/\hbar),$$

$$\left(-\frac{\hbar^2}{2m_k}\Delta_{\rho\varphi}-\frac{\lambda b}{\rho}\sin\varphi\right)\chi_\perp=\left(\varepsilon-\varepsilon_k-\frac{p^2}{2m_k}\right)\chi_\perp. \tag{6}$$

The symbol $p$ denotes the conserved electron momentum along the dislocation.

It is not possible to find the explicit form of the transverse part of the wave function $\chi_\perp$ but the known rules for quasiclassical quantization[12] allow us to determine qualitatively the structure of the spectrum of transverse motion. Clearly, in the case of electrons whose transverse energy is $\varepsilon_\perp=\varepsilon-p^2/2m_k<\varepsilon_k$ the classically accessible part of space is of limited dimensions: it is governed by the condition $(\lambda b/\rho)\sin\varphi \geqslant \varepsilon_k-\varepsilon_\perp$ and represents a circle of diameter

$$D_1(\varepsilon_\perp)=\lambda b/(\varepsilon_k-\varepsilon_\perp), \tag{7}$$

lying in a sector defined by $0<\varphi<\pi$ (see Fig. 1). For an electron with the coordinate $\rho$ and a transverse energy less than $\varepsilon_\perp$, the size of the classically accessible part of the momentum space is governed by the maximum value of the momentum

$$\max|\mathbf{p}-\mathbf{p}_k|_\perp=\{2m_k[\varepsilon_\perp-\varepsilon_k-U_1(\rho,\varphi)]\}^{1/2}.$$

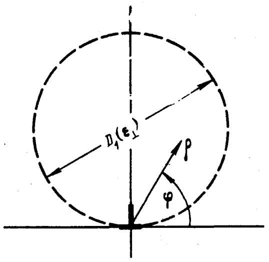

FIG. 1. Region of electron localization near an isolated rectilinear dislocation.

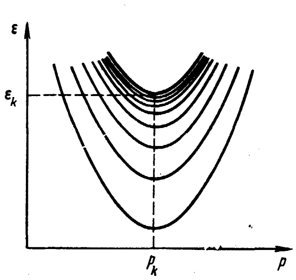

FIG. 2. Dislocation bands in the electron energy spectrum.

Consequently, the total number of states with energies below $\varepsilon_\perp$ is

$$N_\perp(\varepsilon_\perp)=\frac{2\pi m_k}{(2\pi\hbar)^2}\int d\rho[\varepsilon_\perp-\varepsilon_k-U_1(\rho,\varphi)],\qquad U_1(\rho,\varphi)<\varepsilon_\perp-\varepsilon_k. \tag{8}$$

The density of states of transverse motion is

$$\nu_\perp(\varepsilon_\perp)=\frac{dN_\perp(\varepsilon_\perp)}{d\varepsilon_\perp}=\frac{2\pi m_k}{(2\pi\hbar)^2}\int d\rho=\frac{m_kD_1^2(\varepsilon_\perp)}{8\hbar^2},\qquad U_1(\rho,\varphi)<\varepsilon_\perp-\varepsilon_k. \tag{9}$$

Equations (7) and (9) yield the spectrum of localized states which have split off from the bottom of the valley of the function $\varepsilon(\mathbf{p})$:

$$\varepsilon_{np}=\varepsilon_k-\varepsilon_0/n+p^2/2m_k,\qquad \varepsilon_0=m_kb^2\lambda^2/8\hbar^2,\quad n\gg1, \tag{10}$$

where $n$ is an integer.

Thus, if $\varepsilon<\varepsilon_k$, the electron spectrum consists of a set of parabolic energy bands, whose minima are denser on approach to the point $\varepsilon_k$ (Fig. 2). The electrons belonging to these bands are in free infinite motion along the dislocation line and in finite motion in a transverse plane in a region of size $D_1(\varepsilon_\perp)\approx b\lambda n/\varepsilon_0$. Naturally, the dislocation bands retain their individuality in those parts of the momentum space where they do not intersect branches of the function $\varepsilon(\mathrm{p})$ or bands split off from other valleys.

The total density of states localized at a dislocation is

$$\nu_1(\varepsilon)=2\sum_{p,n}\delta\left(\varepsilon-\varepsilon_k+\frac{\varepsilon_0}{n}-\frac{p^2}{2m_k}\right)$$

$$\approx\frac{Lm_k^{1/2}\varepsilon_0}{2^{1/2}\hbar(\varepsilon_k-\varepsilon)^{1/2}}\left[1+\frac{2}{\pi}\left(\frac{\varepsilon_k-\varepsilon}{\varepsilon_0\Delta_1}\right)^{1/2}\right],\qquad \varepsilon_k-\varepsilon\ll\mu, \tag{11}$$

where $L$ is the dislocation length; $\Delta_1=\{\varepsilon_0/(\varepsilon_k-\varepsilon)\}$ is the fractional part of the expression in the braces.

## Dislocation dipoles

Bound states similar to those described above appear also near a dipole composed of two rectilinear edge dislocations of opposite signs (Fig. 3). The deformation potential of a dipole is given by a sum of expressions of the Eq. (5) type. If in mechanical equilibrium the length $2^{1/2}d$ of a dipole is oriented at an angle $\pi/4$ to dislocation glide planes, the polar axis being directed along the Burgers vector and the origin being located on the symmetry axis of the dipole (Fig. 3), we then find that $U$ is described by the expression

$$U_2(\rho,\varphi)=-2\lambda bd\frac{2d^2-\rho^2(\cos2\varphi+\sin2\varphi)}{\rho^4+4d^4-4d^2\rho^2\sin2\varphi}. \tag{12}$$

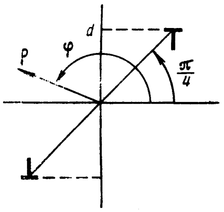

FIG. 3. Dislocation dipole composed of rectilinear edge dislocations of opposite sign.

We can easily see that for transverse motion energies satisfying the condition $\varepsilon_k - \varepsilon_\perp \ll z_d = \lambda b/d$, the classically accessible part of space has the characteristic size

$$D_2(\varepsilon_\perp) \approx 2(bd)^{1/2}[\lambda/(\varepsilon_k - \varepsilon_\perp)]^{1/2}. \tag{13}$$

The density of transverse motion states and the spectrum of an electron localized at a dipole are given by the expressions[7]

$$\frac{dN_\perp(\varepsilon_\perp)}{d\varepsilon_\perp} = \frac{N_0}{\varepsilon_k - \varepsilon_\perp}, \quad \varepsilon_{np} = \varepsilon_k - z_d e^{-n/N_0} + \frac{p^2}{2m_k},$$
$$n \gg N_0 = \frac{m_k \lambda b d}{2\hbar^2}. \tag{14}$$

If the dipole length is microscopic $(d \sim b)$, the formulas in Eq. (14) describe the spectrum practically throughout the energy range $|\varepsilon_k - \varepsilon_\perp| \ll \mu$ where the quasiclassical description is valid. In the case of dipoles of longer length $(d \gg b)$ the spectrum of localized states has two regions. One of them corresponds to the localization of electrons near isolated dislocations in regions of size small compared with $d$. The spectrum of these states is described by Eq. (10) subject to the additional restriction $n \ll d/b$.

The second region of the spectrum corresponds to states with localization radii of larger (compared with $d$) dimensions and the spectrum is described by the formulas in Eq. (14). The total density of states in these regions of the spectrum is

$$\nu_2(\varepsilon) = \begin{cases} \dfrac{L(2m_k)^{1/2} N_0}{\hbar(\varepsilon_k - \varepsilon)^{1/2}} \left(1 + \dfrac{1}{\pi (N_0 \Delta_2)^{1/2}}\right), & \varepsilon_k - \varepsilon \ll z_d \\ 2\nu_1(\varepsilon), & z_d \ll \varepsilon_k - \varepsilon \ll \mu \end{cases}. \tag{15}$$

Here,

$$\Delta_2 = \left\{ N_0 \ln \frac{z_d}{\varepsilon_k - \varepsilon} \right\}$$

is the fractional part of the quantity in the braces.

### Circular prismatic dislocations and finite segments of bent dislocations

The systematics of electron states localized at bent dislocations has a number of special features compared with the above cases of rectilinear dislocations: these features are essentially due to the three-dimensional nature of the deformation potential $U$. The simplest illustration of this fact is provided by considering the localization of electrons on a circular prismatic loop. The explicit form of the coordinate dependence of the dilatation field around such a loop is not known everywhere in space,[13] so that we shall analyze only the motion of electrons near a dislocation loop and far from it (i.e., at distances small and large compared with the loop radius $R$). If the coordinate origin is selected at the loop center, then at large distances $r \gg R$ the potential $U(\mathbf{r})$ is

$$U_3(\mathbf{r}) = -\frac{\pi}{2} \lambda b R^2 \frac{1 - 3\cos^2\theta}{r^3}. \tag{16}$$

The energy range $\varepsilon_k - \varepsilon \ll \lambda b/R$ corresponds to the part of space which is classically accessible to an electron and whose characteristic size is $D_3(\varepsilon) \gg R$:

$$D_3(\varepsilon) \approx (4\pi \lambda b R^2/(\varepsilon_k - \varepsilon))^{1/3}. \tag{17}$$

If we use the three-dimensional analog of Eq. (9), we find that the density of localized states $\nu_3(\varepsilon)$ and the energy levels $\varepsilon_n$ are described by

$$\nu_3(\varepsilon) = \frac{dN(\varepsilon)}{d\varepsilon} = \frac{2\pi}{9\sqrt{6}} \frac{m_k^{3/2} \lambda b R^2}{\hbar^3 (\varepsilon_k - \varepsilon)^{1/2}}, \quad \varepsilon_k - \varepsilon \ll \lambda \frac{b}{R}, \tag{18}$$

$$\varepsilon_n = \varepsilon_k - z_l \left(1 - \frac{n}{N_0}\right)^2, \; N_0 - n \ll N_0 \approx \frac{R^3}{3\hbar^3} (m_k z_l)^{3/2}, \tag{19}$$

where $z_1 \approx \lambda b/R$. Consequently, formation of a dislocation loop in a metal results in splitting off of a finite number of discrete levels described by Eq. (19) from the bottom of a valley of the dispersion law $\varepsilon(\mathbf{p})$ and these levels correspond to localized electron states around a loop in a region of dimensions given by Eq. (17).

In those cases when the loop has macroscopic dimensions $R \gg b$, there is a finite energy range $z_l \ll \varepsilon_k - \varepsilon \ll \mu$, which corresponds to quasiclassical electron motion along a dislocation line in a toroidal region of length which is of the same order as the loop length and of diameter small compared with $R$. At short distances from the loop the deformation potential can be expressed conveniently in terms of coordinates with the $z$ axis perpendicular to the loop plane and passing through its center and with the radius vector $\boldsymbol{\xi}$ in the plane of the loop:

$$U_3(\xi, z) \approx \lambda b (R - \xi)/[z^2 + (R - \xi)^2], \quad [z^2 + (R - \xi)^2]^{1/2} \ll R. \tag{20}$$

The solutions of the Schrödinger equation (4) with the potential (20) exhibiting cylindrical symmetry are states with the conserved projection of the momentum on the $z$ axis:

$$\chi(\mathbf{r}) = e^{im\alpha} \xi^{-1/2} \Phi_m(\xi, z), \quad m = 0, \pm 1, \pm 2, \ldots, \tag{21}$$

where $\alpha$ is the polar angle of the vector $\boldsymbol{\xi}$. The function $\Phi_m(\xi, z)$ satisfies the equation

$$\frac{\hbar^2}{2m_k}\left(\frac{\partial^2}{\partial \xi^2} + \frac{\partial^2}{\partial z^2}\right)\Phi_m - \left[U_3(\xi, z) + \frac{\hbar^2}{2m_k}\frac{m^2 - 1/4}{\xi^2}\right]\Phi_m = (\varepsilon - \varepsilon_k)\Phi_m. \tag{22}$$

Retaining in the above equation the zeroth approximation with respect to the parameter $R^{-1}$ and using the coordinates

$$\rho = [(\xi - R)^2 + z^2]^{1/2}, \quad \varphi = \operatorname{arctg}[(R - \xi)/z],$$

we can reduce it to the form

$$\left(-\frac{\hbar^2}{2m_k}\Delta_{\rho\varphi} - \frac{\lambda b}{\rho}\sin\varphi\right)\Phi_m(\rho, \varphi) = \left(\varepsilon - \varepsilon_k - \frac{\hbar^2}{2m_k}\frac{m^2 - 1/4}{R^2}\right)\Phi_m(\rho, \varphi). \tag{23}$$

where $\rho \ll R$. This equation is identical with Eq. (6) if the orbital energy

$$\frac{\hbar^2}{2m_k}\frac{m^2-{}^1/_4}{R^2}$$

is identified with the kinetic energy of motion along a dislocation $p^2/2m_k$. Consequently, the quasiclassical part of the spectrum of the operator on the left-hand side of Eq. (23) is described, as in the case of a rectilinear dislocation, by the expression $\varepsilon_0/n$.

We thus find that in the energy range $z_l \ll \varepsilon_k - \varepsilon \ll \mu$ we can identify an interval in which the total energy $\varepsilon$ represents the sum of energies of motion along the dislocation line and in a plane perpendicular to this line:

$$\varepsilon_{nm}=\varepsilon_k-\frac{\varepsilon_0}{n}+\frac{\hbar^2}{2m_k}\frac{m^2-{}^1/_4}{R^2}, \qquad \lambda\left(\frac{b}{R}\right)^{1/2} \ll \varepsilon_k-\varepsilon_{nm}\ll\mu. \tag{24}$$

The lower limit of the energy range is related to allowance for the curvature of a dislocation line. Clearly, the change from Eq. (22) to Eq. (23) is possible if the next approximation with respect to the parameter $R^{-1}$ gives a small correction to the potential energy. We can easily show that this is true if $nm \ll (R/b)^{3/2}$, i.e., when $\varepsilon_k - \varepsilon_{nm} \gg \lambda(b/R)^{1/2}$. At energies $\varepsilon_k - \varepsilon \lesssim \lambda(b/R)^{1/2}$, the minimum distances between levels with the same values of $m$ and the maximum distances between the levels with the same values of $n$ are of the same order of magnitude. This means that the spectrum of ground states should be characterized by a single quantum number.

Since in the case of electrons with energies $\lambda b/R \ll \varepsilon_k - \varepsilon \ll \mu$ the classically accessible (for motion) region in a cross section perpendicular to the plane of a loop is small compared with $R$, it follows that in calculating the total number of states with an energy less than $\varepsilon$ we can use the approximate expression (20) for $U(\xi, z)$ and thus obtain

$$N(\varepsilon)\approx\frac{\pi}{2^{5/2}\hbar^3}\frac{m_k^{3/2}\lambda^2 b^2 R}{(\varepsilon_k-\varepsilon)^{1/2}}. \tag{25}$$

Hence, we find that the energy levels $\varepsilon_n$ are described by

$$\begin{gathered}\varepsilon_n=\varepsilon_k-\lambda N_1^2/n^2, \qquad (R/b)^{5/4}\ll n\ll(R/b)^{3/2},\\ N_1=2^{-5/2}\pi m_k^{3/2}\lambda^{3/2}b^2R/\hbar^3.\end{gathered} \tag{26}$$

This range of values of $n$ corresponds to the energies

$$\lambda b/R\ll\varepsilon_k-\varepsilon_n\ll\lambda(b/R)^{1/2}.$$

The energy-level systematics described by Eqs. (24) and (26) corresponds to the following spectral densities:

$$\nu_3(\varepsilon) = \begin{cases} \dfrac{\pi R\varepsilon_0(2m_k)^{1/2}}{\hbar(\varepsilon_k-\varepsilon)^{3/2}}\left(1+\dfrac{2}{\pi}\left(\dfrac{\varepsilon_k-\varepsilon}{\varepsilon_0\Delta_1}\right)^{1/2}\right), & \lambda\left(\dfrac{b}{R}\right)^{1/2}\ll\varepsilon_k-\varepsilon\ll\mu \\ \dfrac{\pi R\varepsilon_0(2m_k)^{1/2}}{\hbar(\varepsilon_k-\varepsilon)^{3/2}}, & \lambda\dfrac{b}{R}\ll\varepsilon_k-\varepsilon\ll\lambda\left(\dfrac{b}{R}\right)^{1/2}. \end{cases} \tag{27}$$

A part of the electron spectrum analogous to Eq. (24) can also be identified for a segment of a bent dislocation line of finite length $L < R$, where $R$ is the radius of curvature of this line. Let us assume that the two ends of this dislocation emerge on the surface of a crystal; then, the requirement that the wave function should vanish on the surface leads to the substitution $m \to mR\pi/L$ in Eqs. (22)–(24). As we go over to a rectilinear dislocation segment (a segment of a loop with an infinite radius of curvature), levels with identical values $n$ and neighboring values of $m$ approach one another forming electron energy bands in the field of a rectilinear dislocation, as mentioned at the beginning of the present section.

## 2. CONCENTRATION BROADENING OF THE SPECTRUM

The presence of many dislocations in a metal has the effect that the deformation potential at each point is a sum of contributions of all the dislocations. Near an isolated dislocation with a radius vector $\mathbf{r}_0$ the total potential $V(\mathbf{r})$ can be conveniently divided into the singular and regular parts:

$$V(\mathbf{r})=U(\mathbf{r}-\mathbf{r}_0)+\sigma(\mathbf{r}), \quad \sigma(\mathbf{r})=\sum_{\alpha=1}^{N}U(\mathbf{r}-\mathbf{r}_\alpha), \tag{28}$$

where $U(\mathbf{r})$ is the potential of an isolated dislocation given by Eq. (1); $\mathbf{r}_\alpha$ is the radius vector of elements of the $\alpha$-th dislocation line; $N$ is the total number of dislocations in the investigated metal. Clearly, the spectrum of an electron localized at a dislocation considered on its own depends on the environment, i.e., on the spatial distribution of its neighbors in a dislocation ensemble. Since the distribution of dislocation lines in a real sample is more or less random, the correction $\sigma(\mathbf{r})$ should be a random quantity. In general, the presence of corrections $\sigma$ modifies the spectrum of individual dislocations and complicates greatly the systematics of the electron states of a sample as a whole.

There are no basic difficulties in describing the concentration effects in those parts of the spectrum for which the localization radius is considerably less than the average distance between dislocations. In such cases the correction $\sigma$ can, in the first approximation, be regarded as constant within the localization region and its role reduces to a shift of the energy origin in the Schrödinger equation (3) and in the expressions for the spectra of the type given by Eqs. (10), (14), (19), and (26). The spectrum of a sample with a large number of dislocations represents a set of levels described by the above formulas and shifted relative to one another by random amounts $\sigma$; this effect is known as the concentration broadening of the spectrum. Such broadening disappears for a regular distribution of dislocations and the degree of degeneracy of each level is then $N$.

The concentration broadening in the case of a system of randomly distributed monotypic rectilinear dislocations was analyzed by Kaner and Fel'dman.[3] It should be pointed out that an analysis of the concentration broadening of the spectrum of electrons localized at dislocations is in many respects equivalent to an analysis of the dislocation broadening of the x-ray spectra of crystals[14]: both problems reduce to statistical averaging of random fields created by dislocation ensembles. We shall use methods developed in Refs. 3 and 14 to describe the broadening of the spectra obtained in the preceding section.

Calculation of the density of the distribution $P(\sigma)$ of random shifts $\sigma$ reduces to derivation of a characteristic function $F(x)$ related to $P(\sigma)$ by the Fourier transformation:

$$F(x)=\int_{-\infty}^{\infty} d\sigma P(\sigma)\,e^{i\sigma x}\equiv\langle e^{i\sigma x}\rangle. \tag{29}$$

It should be noted that the averaging over $\sigma$ is equivalent to averaging over an ensemble of dislocation configurations specified by the density of probabilities in the spatial distribution of dislocations.

In the case of a completely random distribution of a large number $N$ of rectilinear dislocations or dislocation dipoles in a sample of cross section $S$, we find that—in the limit when $N\to\infty$ and $S\to\infty$ but the densities $c_{1,2}=N/S$ are finite (the symbol 1 refers to single dislocations and the symbol 2 refers to dipoles)—the characteristic function $F_{1,2}(x)$ can be represented in the form[3]

$$\begin{gathered}F_{1,2}(x)=\left\langle\exp\left[ix\sum_{\alpha=1}^{N}U_{1,2}(\rho_\alpha)\right]\right\rangle\\ =\left\{\frac{1}{S}\int d\rho\exp[ixU_{1,2}(\rho)]\right\}^N\approx\exp[-c_{1,2}f_{1,2}(x)],\\ f_{1,2}(x)=\int d\rho\{1-\exp[ixU_{1,2}(\rho)]\}.\end{gathered} \tag{30}$$

For a completely random distribution of dislocation loops in a sample of volume $\Omega$ we can easily obtain similar expressions:

$$\begin{gathered}F_3(x)=\left\{\frac{1}{\Omega}\int d\mathbf{r}\exp[ixU_3(\mathbf{r})]\right\}^N\approx\exp[-c_3f_3(x)],\\ f_3(x)=\int d\mathbf{r}\{1-\exp[ixU_3(\mathbf{r})]\};\end{gathered} \tag{31}$$

here, $c_3=N/\Omega$ is the number of loops per unit volume. In all cases the function $f(x)$ is dominated by the contributions from those parts of space where $|xU|\ll 1$; consequently, an approximate value of $f(x)$ can be obtained by expanding the integrands as a series in terms of this parameter.

We have mentioned earlier that the hypothesis of uniformly random distributions of dislocations is clearly only a very rough approximation to real situations. In this connection, it is interesting to study also the concentration broadening of dislocation levels in the case of partly ordered quasiregular dislocation structures. For example, let us assume that dislocations form on the average a regular structure described by a set of radius vectors $\mathbf{R}_\alpha$ and that small deviations of the dislocation coordinates from the sites $\mathbf{R}_\alpha$ are described by a Gaussian distribution which is isotropic and the same at all sites:

$$\varphi(r)=\varphi_0\exp(-r^2/r_0^2),\quad \mathbf{r}=\mathbf{r}_\alpha-\mathbf{R}_\alpha;$$

$$\varphi_0=\begin{cases}\pi^{-1}r_0^{-2}\text{ — for rectilinear dislocations;}\\ \pi^{-3/2}r_0^{-3}\text{ — for loops.}\end{cases}$$

We shall assume that the dispersion of this distribution is fairly small ($r_0\ll\min\mathbf{R}_\alpha$) and, for simplicity, we shall assume that

$$U_0=\sum_\alpha U(\mathbf{R}_\alpha)=0.$$

Then, the expressions describing the characteristic function for quasiregular structures form the following chain of equalities:

$$\begin{gathered}F(x)=\left\langle\exp\left[ix\sum_\alpha U(\mathbf{R}_\alpha+\mathbf{r})\right]\right\rangle\\ =\prod_\alpha\int d\mathbf{r}\varphi(r)\exp\left[ix\frac{\partial U(\mathbf{R}_\alpha)}{\partial\mathbf{R}_\alpha}\mathbf{r}\right]=\exp\left\{-\frac{x^2r_0^2}{4}\sum_\alpha\left[\frac{\partial U(\mathbf{R}_\alpha)'}{\partial\mathbf{R}_\alpha}\right]^2\right\}.\end{gathered} \tag{32}$$

We shall now consider each of the above dislocation entities separately.

### Isolated rectilinear dislocations

Using Eqs. (29) and (30), we readily obtain the following expressions for the density of the distribution of shifts of the energy levels in the case of a uniformly random distribution of dislocations:

$$\begin{gathered}P_1(\sigma)=\begin{cases}\pi^{-1/2}\eta_0^{-1}\exp(-\sigma^2/\eta_0^2), & \sigma\leqslant\eta_0\\ c_1\lambda^2b^2/\sigma^3, & \eta_0\ll\sigma\ll\lambda\end{cases},\\ \eta_0=\lambda[2c_1b^2\ln(Lc_1^{1/2})]^{1/2}.\end{gathered} \tag{33}$$

Here, $L$ is the characteristic size of a sample. This distribution differs from that obtained earlier[3] by the nature of the asymptotic expressions for the wings, i.e., in the range where $\sigma\gg\eta_0$. The reasons for the deviation of $P_1(\sigma)$ from the Gaussian function are discussed in detail in the work of Krivoglaz *et al.* (see Ref. 14, p. 229).

In the case of a quasiregular distribution of rectilinear isolated dislocations, we find that Eqs. (29) and (32) yield the following expression for $P_1(\sigma)$:

$$\begin{gathered}P_1(\sigma)=\frac{1}{\pi^{1/2}\eta_1}\exp\left(-\frac{\sigma^2}{\eta_1^2}\right),\quad \eta_1=A_1\lambda br_0c_1,\\ A_1^2=2\sum_{k=1}^{\infty}\left[\frac{1}{k^4}+2\sum_{n=1}^{\infty}\frac{n^2}{(n^2+k^2)^3}\right]\approx 3.\end{gathered} \tag{34}$$

Comparing Eqs. (33) and (34) with Eq. (10), we can easily see that the concentration broadening conserves the energy band structure of the dislocation spectrum when dislocation densities satisfy the inequality

$$c_1\ll(\varepsilon_k-\varepsilon)^4/\lambda^2\varepsilon_0^2b^2 \tag{35}$$

in the case of a uniformly random distribution and

$$c_1\ll(\varepsilon_k-\varepsilon)^2/\varepsilon_0\lambda br_0 \tag{36}$$

in the case of quasiregular distribution.

### Dislocation dipoles

We shall first consider a uniformly random distribution of dipoles and assume that the density of these dipoles $c_2$ is quite low: $c_2d^2\ll 1$. At these densities the width of the distribution $P(\sigma)$ is governed by the values of the function $f(x)$ in the range $|x|z_d=\lambda|x|b/d\gg 1$. Then, the value of the function $f(x)$ itself is found by integration in Eq. (30) over the regions of space separated from a dipole by distances which are large compared with $d$:

$$f_2(x)\approx\frac{x^2}{2}\int d\rho|U_2(\rho)|^2\approx 2^{3/2}\lambda bd|x|.$$

Using this expression, we can easily obtain the following formula for $P_2(\sigma)$:

$$P_2(\sigma)=\frac{1}{\pi}\frac{\gamma_2}{\gamma_2^2+\sigma^2},\quad \gamma_2=2^{3/2}\lambda bdc_2,\quad \sigma\ll z_d. \tag{37}$$

In the case of a quasiregular distribution of dipoles of low density $c_2d^2 \ll 1$, we find from Eqs. (32) that the distribution of energy shifts is given by

$$P_2(\sigma)=\frac{1}{\pi^{1/2}\eta_2}\exp\left(-\frac{\sigma^2}{\eta_2^2}\right), \quad \eta_2=A_2\lambda bdr_0c_2^{3/2},$$
$$A_2^2=64\sum_{n=0}^{\infty}\sum_{k=1}^{\infty}\frac{1}{(n^2+k^2)^3}\approx 10^2. \tag{38}$$

A comparison of Eq. (14) with Eqs. (37) and (38) shows that the concentration broadening conserves the band structure of the dislocation spectrum at dipole densities satisfying the following inequalities:

$$\begin{gathered} c_2\ll(\varepsilon_k-\varepsilon)/\lambda bdN_0, \quad \varepsilon_k-\varepsilon\ll z_d; \\ c_2\ll(\varepsilon_k-\varepsilon)^2/\varepsilon_0\lambda bd, \quad z_d\ll\varepsilon_k-\varepsilon\ll\mu \end{gathered} \tag{39}$$

in the case of a uniformly random distribution and

$$\begin{gathered} c_2\ll((\varepsilon_k-\varepsilon)/A_2N_0\lambda bdr_0)^{2/3}, \quad \varepsilon_k-\varepsilon\ll z_d; \\ c_2\ll[(\varepsilon_k-\varepsilon)^2/A_2\varepsilon_0\lambda bdr_0]^{2/3}, \quad z_d\ll\varepsilon_k-\varepsilon\ll\mu \end{gathered} \tag{40}$$

for a quasiregular distribution.

### Dislocation loops

Finally, we shall estimate the concentration broadening of the energy levels of electrons localized on circular prismatic loops of sufficiently low density $c_3R^3 \ll 1$. In the case of a uniformly random distribution of loops, it follows from Eqs. (16), (29), and (31) that $P_3(\sigma)$ is given by:

$$P_3(\sigma)=\frac{\gamma_3}{\gamma_3^2+\sigma^2}, \quad \gamma_3=\frac{4\pi^2}{3^{5/2}}\lambda bR^2c_3, \quad \sigma\ll\lambda\frac{b}{R}. \tag{41}$$

In the case of a quasiregular distribution of loops, it follows from Eqs. (16), (29), and (32) that

$$P_3(\sigma)=\frac{1}{\pi^{1/2}\eta_3}\exp\left(-\frac{\sigma^2}{\eta_3^2}\right), \quad \eta_3=A_3\lambda bR^2r_0c_3^{4/3},$$
$$A_3^2=(3\pi)^2\left[\frac{1}{2}\sum_{k=1}^{\infty}\sum_{n,m=-\infty}^{\infty}\frac{(n^2+m^2-2k^2)^2}{(n^2+m^2+k^2)^6}+\sum_{n=1}^{\infty}\sum_{m=0}^{\infty}\frac{1}{(n^2+m^2)^4}\right]\sim 10^2. \tag{42}$$

The loop densities $c_3$ at which the broadening of the levels remains less than the separation between them should obey—according to Eqs. (19), (24), (41), and (42)—the inequalities

$$c_3\ll\begin{cases} ((\varepsilon_k-\varepsilon)z_l)^{1/2}/N_0\lambda bR^2, & \varepsilon_k-\varepsilon\ll\lambda b/R \\ (\varepsilon_k-\varepsilon)^{3/2}/N_1\lambda^{3/2}bR^2, & \lambda b/R\ll\varepsilon_k-\varepsilon\ll\lambda(b/R)^{1/2} \\ (\varepsilon_k-\varepsilon)^2/\varepsilon_0\lambda bR^2, & \lambda(b/R)^{1/2}\ll\varepsilon_k-\varepsilon\ll\mu \end{cases} \tag{43}$$

in the case of a uniformly random distribution and

$$c_3\ll\begin{cases} [z_l(\varepsilon_k-\varepsilon)]^{3/8}/(A_3N_0\lambda bR^2r_0)^{3/4}, \\ (\varepsilon_k-\varepsilon)^{9/8}/(A_3N_1\lambda^{3/2}bR^2r_0)^{3/4}, & \lambda b/R\ll\varepsilon_k-\varepsilon\ll\lambda(b/R)^{1/2} \\ (\varepsilon_k-\varepsilon)^{3/2}/(A_3\varepsilon_0\lambda bR^2r_0)^{3/4}, & \lambda(b/R)^{1/2}\ll\varepsilon_k-\varepsilon\ll\mu. \end{cases} \tag{44}$$

in the case of a quasiregular distribution.

## CONCLUSIONS

In these conclusions it is desirable to consider at least briefly the physical phenomena in which electron states localize near dislocations can be observed. We shall begin by making some comments on the influence of dislocations on the thermodynamics of conduction electrons. This problem has been studied on many occasions[7,15-17] and it has been found that the classical (smooth) part of the dislocation contribution to the thermodynamic characteristics of an electron gas is usually small and does not have any interesting singularities. The exception to this rule is the case of an electronic transition of order 2.5 near which the dislocation contribution rises considerably.[16] The most interesting singularity is associated with the possibility of appearance of quantum oscillations of dislocation-induced corrections to the induced thermodynamic quantities.[17] This effect is possible in metals which have several inequivalent branches of the dispersion law $\varepsilon(\mathbf{p})$ in the conduction band (Fig. 4): in such cases the chemical potential level $\mu$ of electrons may lie within the part of the discrete spectrum split off under the influence of dislocations from the bottom of one of the valleys and the electronic characteristics may acquire an oscillatory dependence on the external parameters controlling the quantity $z = \varepsilon_k - \mu$ (one of such parameters can be pressure). Under certain conditions such oscillations can be giant. For example, at sufficiently low temperatures the amplitude of the specific heat oscillations for regular dislocation structures may exceed the smooth part.[17] We can show that similar oscillations are exhibited also by the paramagnetic susceptibility of the electron gas.

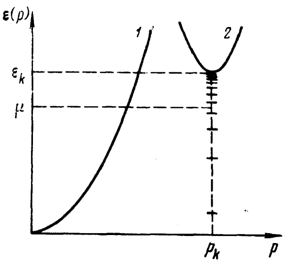

FIG. 4. Example of an electron spectrum of a metal in which the chemical potential level $\mu$ lies within the region of discrete levels of electrons localized at dislocations: 1) main branch of the dispersion law, whose population is governed by the chemical potential level; 2) secondary branch with dislocation levels split off from its bottom.

An interesting effect may also be observed in superconducting metals with the spectrum shown in Fig. 4. The temperature of the superconducting transition is known to be exponentially sensitive to the density of electron states at the Fermi level. In the presence of dislocations this density of states has an additional dislocation correction whose value at the Fermi level is an oscillatory function of the parameter $z$ [see, for example, Eq. (11) with $\varepsilon = \mu$]. This should result in oscillations of the superconducting transition temperature on variation of $z$ (i.e., on variation of the applied pressure).

It is shown in Ref. 18 that the absorption of ultrasound by electrons localized near dislocations in metals also has an oscillatory dependence on external parameters controlling the chemical potential level. Similar oscillations should occur also for other transport properties. We cannot exclude the possibility of the appearance of interesting singularities in view of possible resonance scattering of free electrons and thermal phonons by electrons localized at dislocations but this subject has not yet been investigated.

It should be pointed out that the oscillatory effects mentioned above are strongest at sufficiently low temperatures and for regular dislocation structures. Increase in temperature and the concentration broadening of a spectrum of localized electrons, analyzed in Sec. 2, broaden the oscillatory pattern. The estimates obtained in Refs. 17 and 18 show that these effects are fairly minute and attempts to discover them should be accompanied by special measures to produce ordered high-density dislocation structures.

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# High temperature ferromagnetism and the metal–semiconductor transition in an iron chromium sulfide spinel

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Results are presented of a comprehensive experimental and theoretical investigation of the metal–semiconductor phase transition in the Fe$_x$Cr$_{1-x}$S system at $x \simeq 0.5$. From an analysis of the structural, electrical, magnetic, thermal, and Mössbauer spectral characteristics it is concluded that the substance obtained, Fe$_2$Cr$_2$S$_4$, which possesses a record-high Curie temperature (940°K) in the semiconducting phase, is in reality the FeCr$_2$S$_4$ spinel with dissolved excess iron atoms. A model of the electronic structure is proposed and explains qualitatively the experimental data. The cause of the metal-semiconductor transition is splitting of the spin subbands upon ferromagnetic ordering.

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## 1. INTRODUCTION

The peculiarities of the electronic and crystalline structure of transition-metal sulfides are due to the rich diversity in their electrical and magnetic properties. The main cause of this diversity is the complexity and "mobility" of their electronic structure, which is primarily associated with the lower electronegativity of sulfur compared, for example, with oxygen. In particular, in a number of the indicated compounds a set of distinctive magnetic properties is observed; these are connected with the development of magnetic ordering and the presence of a metal–semiconductor phase transition. Since a basic reorganization of the electronic structure of the material occurs during the metal–semiconductor phase transition, investigation of compounds which combine magnetic ordering with such a transition provide unique opportunities—for example, for detailed study of the role of the electronic subsystem of the material in the development of magnetic ordering. The high-temperature character of the metal–semiconductor phase transition of sulfide compounds compared with vanadium oxides[1] makes the investigation of transition-metal sulfides important with a view toward applica-