Indirect interaction between impurity atoms in paramagnetic metals

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Indirect exchange of impurity atoms via the conduction band of a paramagnetic metal is investigated. Exactly solvable two-center models of impurity centers are considered. The method developed is used also to study indirect interaction between adsorbed atoms via the metallic surface-electron band of a substrate crystal. The effective interaction between electrons localized on impurity centers is evaluated.

INTRODUCTION

The structure of an alloy is known to be greatly influenced by the long-range interaction between the impurity atoms. In particular, the onset of long-period superstructures in binary alloys is apparently due just to the presence of some form of long-range interaction between the atoms.[1] In metal alloys, in which the electrostatic interaction is screened at interatomic distances, a particular role is assumed, besides elastic interactions, by indirect exchange between the impurity atoms.

Indirect interaction plays no less an important role on the metal surfaces on which adsorbed films have been produced.[2] In this case electric dipole interaction takes place between charged adatoms, and falls off in proportion to $1/R^3$. Indirect interaction, however, which has in many cases a slower decrease with distance,[2–4] can compete with the electric-dipole interaction and determine the structure of the adsorbed film.

The indirect interaction between impurity atoms in paramagnetic metals is usually determined by calculating the electron-density polarization induced in a metal by impurity atoms. Solving the problem of electron-wave scattering by impurities

$$\psi_{\mathbf{k}}\rightarrow e^{i\mathbf{kr}}+f_k(\theta)e^{ikr}/r,$$

it is easy to obtain for the Fourier component $\Delta\rho_{\mathbf{k}}(\mathbf{r}) = \psi_k^*\psi_k - 1$ of the electron density an expression averaged over the angles:

$$\langle\Delta\rho_{\mathbf{k}}(\mathbf{r})\rangle=f_k(\pi)e^{2ikr}/2kr^2i+\text{H.c.},$$

which makes it possible to determine the electron-density polarization[5]:

$$\Delta\rho(\mathbf{r})=\frac{2}{(2\pi)^3}\int d^3\mathbf{k}\langle\rho_{\mathbf{k}}(\mathbf{r})\rangle=C_F\frac{\cos(2k_Fr+\varphi_F)}{r^3}.$$

If another impurity atom is present at the point **r**, it interacts with this induced electron density, and this produces between the impurities an effective interaction that falls off with distance in accordance with the law cited above.

A more consistent approach to the determination of an indirect interaction is to use perturbation theory in a small parameter such as the interaction of the impurity with the electron of the metal (or the potential produced for the electrons by the impurity). In second-order perturbation theory, electron exchange is produced between two impurity centers via the electron band of the metal. Using such an approach for impurities having a magnetic moment, an effective Hamiltonian that describes the indirect (RKKY) interaction between magnetic moment was obtained in Ref. 2. The magnitude of this interaction depends on the distance R between the impurity centers and is proportional to $[(k_F R)\cos 2k_F R - \sin 2k_F R]/(k_F R)^4$ (Ref. 6).

Description of indirect interaction by perturbation theory, however, is not always possible. The most obvious case is when the potential produced by the impurity is not low in energy. Another case, considered in an as yet unpublished paper by the author and V. Ya. Chernyak, occurs in the study of the interaction of two nonmagnetic impurity atoms with like electron levels located near the Fermi energy of the metal. In this situation, perturbation theory in the small parameter V, the amplitude of the electron transition from an impurity level to the conduction band of the metal, diverges and cannot be used for this system. An exact solution of the problem was therefore obtained for the case of a weak intranucleon repulsion of the electrons by the impurity center.

We describe here this case in greater detail, and focus attention on the unusual behavior of the indirect interaction at intermediate distances R between the impurities ($V^2 \ll R^{-1} \ll k_F$). For the same model, we obtain the effective indirect electron-electron interaction, and study also the influence of neighboring impurities on the occupation of the electronic levels. We show next how the method of Ref. 7 is generalized for a description of indirect interaction adsorbed on the surface of a crystal having a metallic surface band of electronic states. The presence of an indirect interaction leads to mutual polarization of the adatoms and, as a consequence, to a change of the surface work function.

We consider in addition two other cases (models of a point potential) in which an exact expression can be obtained for the indirect interaction between impurity atoms regardless of the size of the potential produced by the impurity atoms for the metal electrons.

Finally, in the last section we dwell on the size of the indirect interaction between impurity atoms that have a localized magnetic moment, and compare it with the interelectron (RKKY) interaction of these atoms.

1. INDIRECT INTERACTION OF NONMAGNETIC IMPURITY ATOMS IN THE ANDERSON MODEL

This section reports the result of a joint study by the author and V. Ya. Chernyak, with some details of the calculations made more accurate. Certain physical consequences of the use of the model are also considered. The simplest model is investigated, that of two nonmagnetic impurity

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centers whose levels are located near the Fermi energy of a metal with an isotropic electron spectrum.

In standard notation, the Hamiltonian of such a model takes the form of the Anderson Hamiltonian for two impurity centers:

$$H=\sum_{\mathbf{k},\sigma}[\varepsilon(\mathbf{k})-\mu]c^+_{\mathbf{k},\sigma}c_{\mathbf{k},\sigma}+\varepsilon_d\sum_{\sigma}(d^+_{1,\sigma}d_{1,\sigma}+d^+_{2,\sigma}d_{2,\sigma})$$
$$+V\Big(\sum_{\sigma}\Psi_\sigma^+(\mathbf{r}_1)d_{1,\sigma}+\Psi_\sigma^+(\mathbf{r}_2)d_{2,\sigma}+\text{H.c.}\Big)$$
$$+U\sum_{i=1,2}d_{i,\uparrow}d_{i,\uparrow}d^+_{i,\downarrow}d_{i,\downarrow}, \tag{1}$$

where

$$\Psi_\sigma^+(\mathbf{r})=\int e^{i\mathbf{k}\mathbf{r}}c_{\mathbf{k}}^+\,d^3\mathbf{k}.$$

Since the localized moment on an individual level is produced at sufficiently large values of U (the Anderson criterion), we shall assume U for impurities without a magnetic moment to be the smallest energy quantity in the problem. We shall therefore investigate the Hamiltonian (1) in two stages: we first put $U=0$ and then take into account the finiteness of this quantity by perturbation theory.

To diagonalize (1) under the condition $U=0$ we break up the space $\mathscr{H}_{\mathbf{k}}$ of the one-electron functions of a band with a specified energy $\varepsilon=\varepsilon(\mathbf{k})$ into a direct sum of the half-space $\mathscr{H}^{(1)}_{\mathbf{k}}$ of the wave functions that vanish at the points $\mathbf{r}_1$ and $\mathbf{r}_2$ where the impurities are located, and its band supplement $\mathscr{H}^{(0)}_{\mathbf{k}}$:

$$\mathscr{H}_{\mathbf{k}}=\mathscr{H}_{\mathbf{k}}^{(0)}+\mathscr{H}_{\mathbf{k}}^{(1)}.$$

The wave functions

$$\varphi_{i,k}(\mathbf{r})=\sin(k|\mathbf{r}-\mathbf{r}_i|)/k|\mathbf{r}-\mathbf{r}_i|,\quad i=1,\ 2$$

constitute the basis of $\mathscr{H}^{(0)}_{\mathbf{k}}$ since, on the one hand, they are orthogonal to the wave functions that vanish at the point $\mathbf{r}_i$, and on the other, it is possible to choose for any φ from $\mathscr{H}_{\mathbf{k}}$ numbers c_1 and c_2 such that $\varphi-c_1\tilde{\varphi}_{1k}-c_2\tilde{\varphi}_{2k}$ vanish at $\mathbf{r}_1$ and $\mathbf{r}_2$. Then $\{\varphi_{1,k},\varphi_{2k},\varphi_{n,k}\}_{n>2,k>0}$ make up the orthonormalized basis of the space of single-electron wave functions. Here $\{\varphi_{n\mathbf{k}}\}_{n>2}$ (the orthonormalized basis of $\mathscr{H}^{(1)}_{\mathbf{k}}$, while $\varphi_{\mathbf{k}_{1,2}}$ take the form

$$\varphi_{\mathbf{k}_{1,2}}=\Big(\frac{\sin k|\mathbf{r}-\mathbf{r}_2|}{k|\mathbf{r}-\mathbf{r}_2|}\pm\frac{\sin k|\mathbf{r}-\mathbf{r}_1|}{k|\mathbf{r}-\mathbf{r}_1|}\Big)k\Big(1\pm\frac{\sin kR}{kR}\Big)^{-1/2}.$$

where $R=|\mathbf{r}_2-\mathbf{r}_1|$. Electrons with wave functions φ_{nk}, $n>2$ do not interact with the impurities, since $\varphi_{n\mathbf{k}}(\mathbf{r}_i)=0$ $(i=1,2)$, and at $U=0$ the Hamiltonian of the system, in the chosen basis, takes following the transformation $d_1\to2^{-1/2}(d_1+d_2)$ $d_2\to2^{-1/2}(d_1-d_2)$ the form

$$H=\sum_{\mathbf{k},\sigma;n=1,2}[\varepsilon(k)-\mu]c^+_{n,\mathbf{k},\sigma}c_{n,\mathbf{k},\sigma}+\sum_{\sigma;n=1,2}\varepsilon_d d^+_{n,\sigma}d_{n,\sigma}$$
$$+\sum_{k,\sigma;n=1,2}(V_{n,k}c^+_{n,\mathbf{k},\sigma}d_{n,\sigma}+\text{H.c.}), \tag{2}$$

$$V_{1,k}=Vk[1+\sin(kR)/kR]^{1/2},\qquad V_{2,k}=-Vk[1-\sin(kR)/kR]^{1/2}.$$

We have thus reduced the initial Hamiltonian to a one-dimensional and one-center form, thereby substantially simplifying the calculation of the Green's functions

$$G^{\sigma,n}_{\mathbf{k},\mathbf{k}'}(\varepsilon)=\frac{\delta_{\mathbf{k},\mathbf{k}'}}{\varepsilon-\varepsilon_{\mathbf{k}}+\mu+i\delta\operatorname{sgn}\varepsilon}$$
$$-\frac{V_{n,\mathbf{k}}V_{n,\mathbf{k}'}G^{\sigma,n}_{dd}}{(\varepsilon-\varepsilon_{\mathbf{k}}+\mu+i\delta\operatorname{sgn}\varepsilon)(\varepsilon-\varepsilon_{\mathbf{k}'}+\mu+i\delta\operatorname{sgn}\varepsilon)}, \tag{3}$$

$$G^{\sigma,n}_{dd}(\varepsilon)=\Big[\varepsilon-\varepsilon_d+\mu+\sum_{\mathbf{q}}\frac{V^2_{n,q}}{\varepsilon-\varepsilon_{\mathbf{q}}+\mu+i\delta\operatorname{sgn}\varepsilon}\Big]^{-1}. \tag{4}$$

For the density-of-state function $\rho(\varepsilon)=\rho_1(\varepsilon)+\rho_2(\varepsilon)$ we have accordingly from the relation

$$\rho_n(\varepsilon)=\sum_{\sigma}\frac{1}{\pi}\operatorname{Im}\operatorname{Tr}G^n(\varepsilon).$$

In the case $\varepsilon(k)=k^2/2m$ (note that the final result for the interaction between the impurities does not depend on the particular choice of the form of the spectrum) we obtain

$$\rho_{1,2}(\varepsilon)=\operatorname{Im}\Big\{\Big\{1-\frac{mV^2}{2\pi v_F}I_0\mp\frac{V^2}{2v_F{}^2R}(\cos k_\varepsilon R-k_\varepsilon R\sin k_\varepsilon R)$$
$$+i\operatorname{sgn}\varepsilon\Big[\frac{mV^2}{v_F}\pm\frac{V^2}{2v_F{}^2R}(\sin k_\varepsilon R+k_\varepsilon R\cos k_\varepsilon R)\Big]\Big\}$$
$$\times\Big[\varepsilon-\varepsilon_d^{(r)}\mp\frac{mV^2}{2v_FR}\cos k_\varepsilon R+i\frac{mV^2k_\varepsilon}{2v_F}\Big(1\pm\frac{\sin k_\varepsilon R}{k_\varepsilon R}\Big)\operatorname{sgn}\varepsilon\Big]^{-1}\Big\}, \tag{5}$$

where $k_\varepsilon(k^2_F+2m\varepsilon)^{1/2}$; $\varepsilon^{(r)}_d$ is the renormalized value of ε_d; I_0 is the renormalization constant and is determined, just as $\varepsilon^{(r)}_d$, by the form of the spectrum (we assume below that $v_F=1$).

It can be easily shown that the total energy of the system $\int\varepsilon\rho(\varepsilon)d\varepsilon$, in the region of the largest distances, $k_F R\gg1$, $[\min(V^2,\varepsilon_d)]R\gg1$, is proportional to

$$\mu(A_1\cos2k_FR+A_2\sin2k_FR)/(k_FR)^3, \tag{6}$$

where

$$A_1=[(\pi V^2)^2\varepsilon_d{}^2-(\pi V^2)^4]/[\varepsilon_d{}^2+(\pi V^2)^2]^2,$$
$$A_2=2(\pi V^2)^3\varepsilon_d/[\varepsilon_d{}^2+(\pi V^2)^2]^2.$$

At intermediate distances $V^2,\varepsilon_d\ll R^{-1}\ll k_F$ the interaction decreases more slowly:

$$\propto V^4\frac{\cos2k_FR}{k_FR}\ln[\min(V^2,\varepsilon_d)R]. \tag{7}$$

The term added to the Hamiltonian (2) to account for the correlation energy U is of the form

$$\tfrac{1}{2}U[(d^+_{1,\uparrow}d_{1,\uparrow}+d^+_{2,\uparrow}d_{2,\uparrow})(d^+_{1,\downarrow}d_{1,\downarrow}+d^+_{2,\downarrow}d_{2,\downarrow})$$
$$+(d^+_{1,\uparrow}d_{2,\uparrow}+d^+_{2,\uparrow}d_{1,\uparrow})(d^+_{1,\downarrow}d_{2,\downarrow}+d^+_{2,\downarrow}d_{1,\downarrow}). \tag{8}$$

The first perturbation-theory corrections to the energy are given by the diagrams of Fig. 1, which make a contribution proportional to $U/\varepsilon_d)^2R^{-3}$. Diagrams of higher orders also consist only of vertices and of the zeroth-order impurity Green's functions $G^{\sigma,n}_{dd}$ [Eq. (4)] that join the vertices. There is therefore no integration over the momenta at all in such diagrams, and no divergences appear in any order of perturbation theory. We find as a result that in the limit as $U\to0$ allowance for the corrections leads only to an arbitrarily small renormalization of the system energy. This means that the nonmagnetic impurities can interact at low tem-

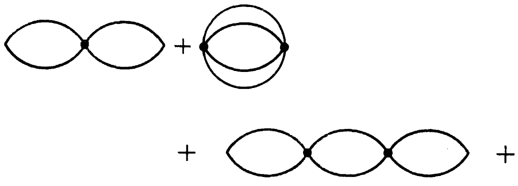


FIG. 1.

peratures via indirect exchange through the conduction electrons of the metal in accordance with Eqs. (6) and (7).

Also noteworthy is the result for the occupation of the electronic levels of the impurity atoms. The point is that in the situation considered, owing to the transitions of the electrons from an impurity atom to the electron band of the metal, the level spreads out into a quasilevel of width $\sim V^2$, and in the case $\varepsilon_d \sim V^2$ the occupation of the level at low temperatures may not be complete. This recalls the behavior of systems with intermediate valency, observed in a number of transition and rare-earth metals,[8] in which complete occupation of the localized f level at the atomic center takes place. The substantial difference is that in the case of a system with intermediate valency the intra-Coulomb repulsion of the electron at the f center is large. The simplest approximation to such a system is a zero-spin model,[8] in which it is assumed that $U\to\infty$ and the electron spins are not considered (this approximation is justified in those cases when the scattering by impurity with spin flip can be neglected, for example in the case of strong anisotropy of the scattering amplitude). Such a system can be described by the Hamiltonian (1) without the last term that describes the intra-Coulomb repulsion at the center, and without the spin indices of all the remaining terms. The formal procedures reported above remain unchanged, so that the mutual influence of the f centers on the quasilevels that occupy them can be determined. Calculation of the quantity

$$\int \rho_d(\varepsilon)\,d\varepsilon, \quad \rho_d(\varepsilon)=\sum_{n=1,2}\frac{1}{\pi}\,\mathrm{Im}\,\mathrm{Tr}\,G^{n,\sigma}_{dd}(\varepsilon),$$

and of $G^{n,\sigma}_{dd}(\varepsilon)$ defined by Eq. (4) makes it possible to determine the change of the occupation of an f level in the presence of another center at a distance R:

$$\Delta\rho_d \propto V^2/\mu(k_F R)^2, \quad V^2R\gg 1, \quad k_F R\gg 1. \tag{9}$$

The value of the "intermediate valency" is thus determined also by the positions of the other centers.

2. INDIRECT INTERACTION OF ELECTRONS OF NONMAGNETIC IMPURITY ATOMS

We have discussed so far the interaction between impurity atoms, which is produced even at zero value of the parameter U, by calculating the total-energy corrections that depend on the distances between the atoms. No less important is the question of the size of the indirect interaction between impurity-level electrons, which sets in at nonzero values of the parameter U. If the atom has a localized magnetic moment (the case of large $U\gg\varepsilon_d$ and $U\gg V^2$) the electrons interact in accordance with the known RKKY law. We calculate in the present section the form of the interaction for the case of nonmagnetic atoms ($U\ll\varepsilon_d$, V^2).

To this end we return to the study of the Hamiltonian (1) and consider the matrix element of the indirect interactions between impurity electronic states, which occur in second-order perturbation theory in the parameter U/ε_d. These matrix elements are described by the Feynman diagrams of Fig. 2. The diagram 2a describes two-particle excitation on centers, which are of no interest to use at present. We consider therefore the two remaining diagrams. The indices 1 and 2 on these diagrams are the numbers of the impurities, and the internal lines, over the energies of which the integration is carried out, describe "mixed" electronic propagators

$$\mathcal{G}^{\sigma}_{12}=-i\langle Td_{1,\sigma}d^{+}_{2,\sigma}\rangle, \quad \mathcal{G}^{\sigma}_{21}=-i\langle Td_{2,\sigma}d^{+}_{1,\sigma}\rangle.$$

Their Fourier components can be easily determined from the Green's functions (4) calculated in the preceding section:

$$\mathcal{G}^{\sigma}_{12}(\varepsilon)=\mathcal{G}_{21}(\varepsilon)=G^{1,\sigma}_{dd}(\varepsilon)-G^{2\sigma}_{dd}(\varepsilon)\approx\frac{V^2}{R}\,\frac{\cos k_\varepsilon R-i\sin(k_\varepsilon R)\,\mathrm{sgn}\,\varepsilon}{(\varepsilon-\varepsilon_d+iV^2\,\mathrm{sgn}\,\varepsilon)^2-(V^2/R)^2[\cos k_\varepsilon R-i\sin(k_\varepsilon R)\,\mathrm{sgn}\,\varepsilon]^2}. \tag{10}$$

Since the states $d_i^+|0\rangle$, $i=1, 2$ are not eigenstates of the Hamiltonian (1), the interaction deduced from the diagram data has an imaginary part. This difficulty can be avoided by considering the limit $V^2\ll\varepsilon_d$.

The effective Hamiltonian of the interacting impurity electronic states at various centers, obtained from an analysis of these processes, has the form of an exchange operator:

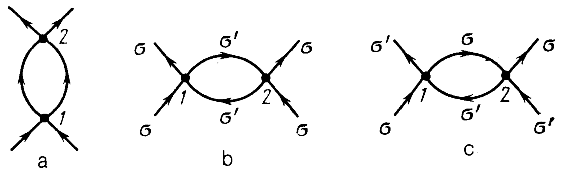


FIG. 2.

$$H_{\text{eff}}=J(R)\left(\frac{1}{4}+\hat{\mathbf{S}}_1\hat{\mathbf{S}}_2\right), \tag{11}$$

where, as usual the operator $\hat{\mathbf{S}}_i$, $i=1, 2$, stands for

$$\sum_{\sigma,\sigma'}\frac{1}{2}\,d^{+}_{i,\sigma}\hat{\sigma}_{\sigma\sigma'}d_{i,\sigma},$$

$\hat{\sigma}^x$, σ^y, $\hat{\sigma}^z$ are Pauli matrices, and

$$J(R)\propto\mathrm{Im}\int\mathcal{G}_{12}(\varepsilon+\omega)\mathcal{G}_{21}(\varepsilon)\,d\varepsilon. \tag{12}$$

We are not interested in the retarded part of the interaction, and put $\omega=0$. The asymptotic form of $J(R)$ at large distances $\varepsilon_d R\gg 1$, $k_F R\gg 1$, (U, $V^2\ll\varepsilon_d$) is then

$$J(R)\propto\mu\frac{U^2V^4}{\varepsilon_d^4}\frac{\cos 2k_F R}{(k_F R)^3}, \tag{13}$$

while at intermediate distances $\varepsilon_d\ll R^{-1}\ll k_F$ we have

$$J(R)\propto\frac{U^2V^4}{\varepsilon_d^{\,3}}\frac{\sin 2k_FR}{(k_FR)^2}. \qquad (14)$$

Note that the same dependence of the interaction on the distance was obtained in Ref. 9 for the intermediate region in the case of indirect exchange between localized magnetic moments of rare-earth impurity atoms.

Indirect exchange between impurity electronic states is thus also an oscillatory effect and decreases like a power law with distance. In contrast to the interatomic interaction [Eqs. (6) and (7)] the interelectron interaction vanishes in the limit as $U\to 0$.

It should also be noted that the presence of other impurity atoms alters the interelectron interaction only in the next order in the parameter V^2/ε_d, i.e., (11) describes a pair interaction in the considered limit $V^2\ll\varepsilon_d$. This permits the result to be applied to a lattice of impurity atoms.

3. IMPURITY INTERACTION IN THE MODEL OF POINT POTENTIALS WITH SHALLOW LEVEL

For a comprehensive study of indirect exchange between impurities, it would be of interest to investigate also other possible models that describe impurity atoms. We consider in this section the interaction of two impurity atoms that produce for the electrons a deep potential well with a shallow level. Such a potential is characterized by a ratio $|E_0|/U\to 0$, where $E=-|E_0|$ is the bound electronic level of the well, and U is the depth of the well. At fixed E_0 it is necessary to make $U\to\infty$, in which case $R\to 0$ in such a way that $UR^2\to\text{const}$, or $\int U(\mathbf{r})d^3\mathbf{r}\sim U_0R^3\to 0$. The solution of the problem of scattering by one such well is well known. We shall consider two wells simulating the potential produced by the impurities, and investigate the scattering, from them, of electrons from the metallic band of the crystal, which occupy at low temperatures all the band states below the Fermi level μ. Just as before, the electron spectrum is assumed isotropic and quadratic.

The problem of particle motion in the field of one such δ-well can be formulated in the language of the boundary conditions imposed on the wave function at the location $\mathbf{r}_i$ of the well[10]:

$$d\ln(|\mathbf{r}-\mathbf{r}_i|\psi(\mathbf{r}))/d|\mathbf{r}-\mathbf{r}_i|=z. \qquad (15)$$

The general expression for the solution of the Schrödinger equation for small $|\mathbf{r}-\mathbf{r}_i|$ and $l=0$ (l is the orbital momentum) is $\psi=\alpha+\beta/|\mathbf{r}-\mathbf{r}_i|$, where $\alpha/\beta=z$. The entire reasoning of Sec. 1, based on the assumption of a point interaction between the electron and the impurity, is applicable also in this case. We need only take into account in addition the presence of a singularity of the wave function at the impurity center.

This allows us to write down directly the form of the wave functions that constitute the complete basis of the electronic states that interact with the two impurity centers:

$$\psi_k^{\pm}\propto[\sin(k|\mathbf{r}-\mathbf{r}_1|+\delta_0^{\pm})/|\mathbf{r}-\mathbf{r}_1|\pm\sin(k|\mathbf{r}-\mathbf{r}_2|+\delta_0^{\pm})/|\mathbf{r}-\mathbf{r}_2|]. \qquad (16)$$

From the boundary conditions on the impurity centers (15) we can easily determine for $i=1, 2$ the phase shift:

$$\delta_0^{\pm}=\operatorname{arctg}\left[\left(k\pm\frac{\sin kR}{R}\right)\Big/\left(z\mp\frac{\cos kR}{R}\right)\right]. \qquad (17)$$

The asymptotic form of the wave functions (16) at large distances r from both centers ($r\gg R$) is

$$\begin{aligned}\psi_k^{+}&\to(C/r)\cos(kR\cos\varphi)\sin(kr+\delta_0^{+}),\\ \psi_k^{-}&\to(C/r)\sin(kR\cos\varphi)\cos(kr+\delta_0^{-}),\end{aligned} \qquad (18)$$

where $\cos\varphi=\mathbf{R}\cdot\mathbf{r}/Rr$. Imposing at infinity the boundary conditions $\psi(L)=0$ as $L\to\infty$, we obtain from (18) for the density of states $\rho_i^{k\pm}=1/L(k_{i+1}-k_i)$, in the continuous limit,

$$\rho_k^{\pm}=\frac{1}{\pi}\left(1+\frac{1}{L}\frac{d\delta_0^{\pm}}{dk}\right). \qquad (19)$$

The R-dependent correction to the total energy of the system takes the form

$$\begin{aligned}\Delta E&=\frac{1}{L}\sum_{k\leqslant k_F}[\varepsilon(k)-\mu]\frac{1}{\pi}\left(\frac{d\delta_0^{+}}{dk}+\frac{d\delta_0^{-}}{dk}\right)\\ &=\frac{1}{\pi}\int_0^{k_F}\left(\frac{k^2}{2m}-\mu\right)\left(\frac{d\delta_0^{+}}{dk}+\frac{d\delta_0^{-}}{dk}\right)dk.\end{aligned} \qquad (20)$$

The first nonvanishing term in the expansion of this energy in the parameter $(k_F R)^{-1}\ll 1$ is proportional to (at $|E_0|\ll\mu$)

$$\mu\cos(2k_FR)/(k_FR)^3 \qquad (21)$$

and describes the magnitude of the indirect interaction of two impurity centers.

4. IMPURITY INTERACTION IN THE MODEL OF DEEP POINT POTENTIALS

We consider one more two-center problem that admits of an exact solution. The potential produced by an individual impurity has in this model the form of a point well, but deeper than in the preceding case: $\int Ud^3\mathbf{r}=\text{const}$. Such a well can be described by the limiting expression

$$U(\mathbf{r}-\mathbf{r}_i)=V\delta(x-x_i)\delta(y-y_i)\delta(z-z_i).$$

The Hamiltonian of such a two-center system takes in the second-quantization representation the form

$$\begin{aligned}H=\int d^3\mathbf{r}\Big\{&-\frac{\hbar^2}{2m}\hat{\psi}^{+}(\mathbf{r})\nabla^2\psi(\mathbf{r})\\ &+[U(\mathbf{r}-\mathbf{r}_1)+U(\mathbf{r}-\mathbf{r}_2)-\mu]\hat{\psi}^{+}(\mathbf{r})\hat{\psi}(\mathbf{r})\Big\}\end{aligned} \qquad (22)$$

(we put below, as usual $\hbar=2m=1$).

We expand the operators $\hat{\psi}^{+}(\mathbf{r})$ in a basis of standing plane waves that are symmetric and antisymmetric relative to the symmetry plane of the system:

$$\hat{\psi}^{+}(\mathbf{r})=\int_{k_x\geqslant 0}\frac{d^3\mathbf{k}}{(2\pi)^3}(\overset{+}{a}_{1,\mathbf{k}}\cos k_xx+\overset{+}{a}_{2,\mathbf{k}}\sin k_xx)e^{i\mathbf{k}_\perp\mathbf{r}},$$

$$\mathbf{k}_\perp=(k_y,k_z),$$

where the origin of the coordinate frame is taken to be the midpoint of the segment joining the two impurities, while the x axis is directed along this segment. In this frame, the impurity positions are described by the points ($\pm R/2$, 0, 0). The Hamiltonian (22) takes in the new basis the form

$$H=\sum_{\mathbf{k}}(k^2-\mu)(\overset{+}{a}_{1,\mathbf{k}}a_{1,\mathbf{k}}+\overset{+}{a}_{2,\mathbf{k}}a_{2,\mathbf{k}})$$

$$+V\sum_{\mathbf{k},\mathbf{p}}\Bigl(\cos\frac{p_xR}{2}\cos\frac{k_xR}{2}\overset{+}{a}_{1,\mathbf{k}}a_{1,\mathbf{p}}$$

$$+\sin\frac{p_xR}{2}\sin\frac{k_xR}{2}\overset{+}{a}_{2,\mathbf{k}}a_{2,\mathbf{p}}+\text{H.c.}\Bigr)\quad(k_x,p_x\geqslant 0).\tag{23}$$

The equations for the temperature Green's functions

$$G_{p'p}(\tau)=-\langle T\tilde{a}_p(\tau)a_p(0)\rangle,\quad \tilde{a}_p(\tau)=e^{\tau H}a_pe^{-\tau H}$$

take the form

$$\sum_{\nu}(i\omega_n-H)_{\mu\nu}G_{\nu\lambda}=\delta_{\mu\lambda}.\tag{24}$$

For the Hamiltonian (23) this means that

$$[i\omega_n-\varepsilon(k)+\mu]G^{(1)}_{kk}-V\cos\frac{k_xR}{2}\sum_{\mathbf{q},q_x\geqslant 0}\cos\frac{q_xR}{2}G^{(1)}_{qk}=1,$$

$$[i\omega_n-\varepsilon(k')+\mu]G^{(1)}_{kk'}-V\cos\frac{k_x'R}{2}\sum_{\mathbf{q},q_x\geqslant 0}\cos\frac{q_xR}{2}G^{(1)}_{qk}=0,\tag{25}$$

$\mathbf{k}'\neq\mathbf{k}$,

and analogously

$$[i\omega_n-\varepsilon(k)+\mu]G^{(2)}_{kk}-V\sin\frac{k_xR}{2}\sum_{\mathbf{q},q_x\geqslant 0}\sin\frac{q_xR}{2}G^{(2)}_{qk}=1,$$

$$[i\omega_n-\varepsilon(k)+\mu]G^{(2)}_{k'k}-V\sin\frac{k_x'R}{2}\sum_{\mathbf{q},q_x\geqslant 0}\sin\frac{q_xR}{2}G^{(2)}_{qk}=0,\tag{26}$$

$\mathbf{k}'\neq\mathbf{k}$,

where $\varepsilon(k)=k^2$. The solutions of (25) and (26) at $T=0$ are

$$G^{(1,2)}_{kk}=\frac{1}{\varepsilon-\varepsilon_k+\mu-i\delta\operatorname{sgn}\varepsilon}$$

$$+\frac{V}{2}(1\pm\cos kR)(\varepsilon-\varepsilon_k+\mu-i\delta\operatorname{sgn}\varepsilon)^{-2}$$

$$\times\Bigl(1-\frac{V}{2}\sum_{\mathbf{k}',k_x'\geqslant 0}\frac{1+\cos k'R}{\varepsilon-\varepsilon_{k'}+\mu-i\delta\operatorname{sgn}\varepsilon}\Bigr)^{-1}.\tag{27}$$

For the R-dependent part of the density of states

$$\rho(\varepsilon)=\frac{1}{\pi}\operatorname{Im}\sum_{\substack{n=1,2\\ \mathbf{k},k_x\geqslant 0}}G^{(n)}_{kk}(\varepsilon)$$

we obtain accordingly

$$\Delta\rho(\varepsilon)\propto\frac{V}{1+V^2}\Bigl[\frac{V(1-V^2)}{1+V^2}\frac{\cos 2k_\varepsilon R}{R}-\frac{2V^2}{1+V^2}\frac{\sin 2k_\varepsilon R}{R}\Bigr],$$

$$k_\varepsilon=(k_F{}^2+\varepsilon)^{1/2}.\tag{28}$$

As a result we get for $k_F\gg 1$ the R-dependent correction to the total energy $E=\int\varepsilon\rho(\varepsilon)d\varepsilon$:

$$\Delta E\propto\frac{V^2(1-V^2)}{(1+V^2)^2}\frac{\cos 2k_FR}{(k_FR)^3}-\frac{2V^3}{(1+V^2)^2}\frac{\sin 2k_FR}{(k_FR)^3}$$

$$=V^2\frac{\cos(2k_FR+\varphi_F)}{(k_FR)^3},\tag{29}$$

$$\varphi_F=\arccos\frac{1-V^2}{(1+V^2)^2},$$

which is in fact the law governing the decrease of the indirect interaction of two impurity centers with increase of distance.

5. INDIRECT INTERACTION OF ADSORBED ATOMS VIA THE ELECTRONS OF THE SURFACE BAND OF A SUBSTRATE CRYSTAL

It was already indicated in the Introduction that indirect interaction of atoms plays no less important a role on the surfaces of crystals on which adsorption monolayers are produced, and in the formation of the structure of clean faces of single crystals. In the present section we use the method developed to determine the interaction of two nonmagnetic adatoms that exchange electrons via a metallic surface band with a quasi-two-dimensional isotropic spectrum. We study for this purpose a two-dimensional model described by a Hamiltonian of the Anderson-Newns type, which is similar for two centers to the analogous expression (2) in standard notation (see, e.g., Ref. 11):

$$H=-\sum_{\sigma}\int\hat{\Psi}_\sigma{}^+(\mathbf{r})\nabla^2\hat{\Psi}_\sigma(\mathbf{r})d^2\mathbf{r}+\varepsilon_d\sum_{\sigma;i=1,2}\overset{+}{d}_{i,\sigma}d_{i,\sigma}$$

$$+\sum_{\sigma}V(\hat{\Psi}_\sigma{}^+(\mathbf{r}_1)d_{1,\sigma}+\hat{\Psi}_\sigma{}^+(\mathbf{r}_2)d_{2,\sigma}+\text{H.c.})$$

$$+U\sum_{i=1,2}\overset{+}{d}_{i,\uparrow}d_{i,\uparrow}\overset{+}{d}_{i,\downarrow}d_{i,\downarrow},\tag{30}$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ are the coordinates of the adatoms, and the electron energy is reckoned from the Fermi level μ of the system. Just as in the investigation of the Hamiltonian (1), we consider first the case $U=0$, and then take into account the finite character of this quantity by perturbation theory.

By analogy with the arguments advanced in the preceding section, we expand the operators $\hat{\Psi}_0^+(\mathbf{r})$ in a basis of symmetric and antisymmetric waves:

$$\hat{\Psi}_\sigma{}^+(\mathbf{r})=\int_{k_x\geqslant 0}\frac{d^2\mathbf{k}}{(2\pi)^2}e^{ik_yr_y}(c^{+(1)}_{\mathbf{k},\sigma}\cos k_xr_x+c^{+(2)}_{\mathbf{k},\sigma}\sin k_xr_x).\tag{31}$$

Putting $r_1=-R/2$, $r_2=R/2$ and making the substitution $d^+_{1,2}\to 2^{-1/2}(d_1^+\pm d_2^+)$, we transform the Hamiltonian (30) at $U=0$ into

$$H=\sum_{\sigma;n=1,2}\int_{k_x\geqslant 0}d^2\mathbf{k}(\varepsilon_k-\mu)c^{+(n)}_{\mathbf{k},\sigma}c^{(n)}_{\mathbf{k},\sigma}+\sum_{\sigma;n=1,2}\varepsilon_d\overset{+}{d}_{n,\sigma}d_{n,\sigma}$$

$$+\sum_{\sigma,n=1,2}\int_{k_x\geqslant 0}d^2\mathbf{k}\,V_{n,\mathbf{k}}(c^{+(n)}_{\mathbf{k},\sigma}d_{n,\sigma}+\text{H.c.}),\tag{32}$$

where

$$\varepsilon_{\mathbf{k}}=k^2/2m,\quad V_{1,\mathbf{k}}=V(1+\cos kR)^{1/2},$$

$$V_{2,\mathbf{k}}=-V(1-\cos kR)^{1/2}.$$

For the Green's functions of such a Hamiltonian we obtain accordingly

$$G^{\sigma,n}_{dd}(\varepsilon)=\Bigl[\varepsilon-\varepsilon_d+\int\frac{\pi V^2[1\pm J_0(kR)]k\,dk}{\varepsilon-\varepsilon_{\mathbf{k}}+\mu-i\delta\operatorname{sgn}\varepsilon}\Bigr]^{-1},$$

$$G^{\sigma,n}_{\mathbf{k},\mathbf{k}}(\varepsilon)=\frac{1}{\varepsilon-\varepsilon_{\mathbf{k}}+\mu-i\delta\operatorname{sgn}\varepsilon}\tag{33}$$

$$-\frac{V^2_{n,\mathbf{k}}}{(\varepsilon-\varepsilon_{\mathbf{k}}+\mu-i\delta\operatorname{sgn}\varepsilon)^2}G^{\sigma,n}_{dd}(\varepsilon),\tag{34}$$

where $J_0(x)$ is a Bessel function of zero order.

Calculations similar to those of the preceding sections yield readily the form of the indirect interaction at large distances $k_F R \gg 1$, $R \min(V^2, \varepsilon_d) \gg 1$:

$$\propto \mu\left(A_1 \frac{\sin 2k_F R}{(k_F R)^2} + A_2 \frac{\cos 2k_F R}{(k_F R)^2}\right), \tag{35}$$

$$A_1 = [(\pi V)^8 - (\pi V)^4 \varepsilon_d^2]/[\varepsilon_d^2 + (\pi V)^4]^2,$$

$$A_2 = 2(\pi V)^6 \varepsilon_d/[\varepsilon_d^2 + (\pi V)^4]^2.$$

In the region of intermediate states $k_F^{-1} \ll R \ll V^{-2}, \varepsilon_d^{-1}$, whose density can cover, for actual values of the parameters V^2 and ε_d, a rather wide interval of submonolayer coatings, the interaction has a non-attenuating character:

$$\propto V^4 \sin(2k_F R) \ln[R \min(V^2, \varepsilon_d)]. \tag{36}$$

The first nonvanishing corrections to (35) in terms of the parameter U/ε_d are expressed by the same diagrams as in Fig. 1, are proportional to $U/(k_F R)^2$, and are consequently insignificant in the limit as $U \to 0$. This result may turn out to be important for the understanding of the causes of the reconstruction of a pure surface of a semiconductor crystal, particularly the Si(111) − (7×7) surface whose structure, according to the latest experiments (scanning of the Si surface with an electron microscope[12]) seems to contain 12 silicon adatoms or adatom clusters per unit surface cell of 49 atoms. The presence of a long-range alternating -sign interaction between such adatoms can stabilize the long-period superstructures.[13] In particular, the presence of interaction that falls off in accordance with (35) can stabilize the (7×7) structure.[14] No less important a question is that of the possibility of stabilizing a superstructure by an interaction that varies in accordance with (36). The existence of a surface band near the Fermi level for this face was reliably established in photo-electron-spectroscopy experiments.

To conclude this section, we wish to show how indirect interaction between adatoms can influence the work function of a crystal surface. It is known that electrostatic dipole interaction of charged adatoms can lead to their mutual depolarization, i.e., to a decrease of the charge, when the adatom quasilevels are located near the Fermi level of the substrate crystal.[15] Since the indirect interaction (35), (36) falls off more slowly than the dipole interaction, its influence on the occupation of the quasilevels can compete with the electrostatic interaction. When determining the change of the work function of a surface by adsorption, account must be taken of the total change of the surface charge, i.e., the occupation of the levels of the adatoms in the surface band of the substrate crystal.

Recognizing that the chemical potential μ of the system is determined by the substrate bulk electrons, the occupation $\Delta\sigma$ can be easily determined by substituting in the expression for the surface-charge density

$$\rho(\varepsilon) = \frac{1}{\pi} \operatorname{Im} \sum_{\sigma,n} \left[G_{dd}^{\sigma,n}(\varepsilon) + \sum_{\mathbf{k}} G_{\mathbf{kk}}^{\sigma,n}(\varepsilon) \right]$$

the Green's functions (33) and (34). It can be easily shown by calculation that the R-dependent correction $\Delta\sigma$ to the surface charge $\sigma = \int \rho(\varepsilon) d\varepsilon$ is given by ($k_F R \gg 1$, $V^2 R \gg 1$)

$$\Delta\sigma \propto (A_1 \cos 2k_F R + A_2 \sin 2k_F R)/k_F R, \tag{37}$$

$$A_1 = [(\pi V)^4 \varepsilon_d^2 - (\pi V)^8]/[\varepsilon_d^2 + (\pi V)^4]^2,$$

$$A_2 = -2(\pi V)^6 \varepsilon_d/[\varepsilon_d^2 + (\pi V)^4]^2.$$

The screening of such a surface charge in the case of a semiconductor crystal substrate (with a metallic surface band) occurs over a "Debye" distance, whose value can reach $l_D \sim 10^4$ Å. In this case the electrostatic energy stored in the space-charge region of the semiconductor may turn out to be appreciable and lead to a noticeable bending of the bands, $\Delta E \sim (4\pi/\varepsilon)\Delta\varepsilon e l_D$ (thus, at $\Delta\sigma \sim 10^{11}$ cm^{-2} the value of ΔE reaches ~ 1 eV). In the calculation of the surface charge, which determines the work function of the surface of a semiconductor crystal, it is therefore necessary to take into account the indirect interaction (via the electrons of the surface band) of the adsorbed atoms.

6. INDIRECT INTERACTION OF IMPURITY ATOMS HAVING A MAGNETIC MOMENT

We have discussed so far indirect interaction of nonmagnetic impurity atoms. In the present section we study the interaction of atoms having a localized magnetic moment. The manner of interaction of the electrons that make up the localized moment of the impurity is well known. The spin-dependent part of this interaction (the RKKY interaction), obtained in second-order perturbation theory in the parameter of the exchange-integral J of the impurity electrons in a metal,[6] is proportional to

$$J^2 \hat{\mathrm{S}}_1 \hat{\mathrm{S}}_2 (k_F R \cos 2k_F R - \sin 2k_F R)/(k_F R)^4, \tag{38}$$

where $\hat{\mathbf{S}}_1$ and $\hat{\mathbf{S}}_2$ are the spin operators of the electrons localized on two impurity centers (the exchange Hamiltonian from which this expression is obtained will be given below). According to an erroneous opinion, the same expression describes the interaction energy of impurity atoms, if the spin operators are replaced by their vacuum mean values $\langle 0|\hat{\mathbf{S}}_1 \hat{\mathbf{S}}_2|0\rangle$, where $|0\rangle$ is the unperturbed vacuum state of the system (see, e.g, Ref. 16). It is easily seen, however, that such a mean value vanishes in the absence of external field. To calculate the indirect interaction between impurity atoms it is therefore necessary to use the next higher orders of perturbation theory.

To this end, we consider the exchange Hamiltonian that describes the interaction of the electron of the impurities and of the metal:

$$H = -\sum_{\mathbf{k},\mathbf{k}'} \sum_{i=1,2} J \hat{\mathrm{S}}_i \hat{\boldsymbol{\sigma}}, \tag{39}$$

where

$$\hat{\boldsymbol{\sigma}} = \sum_{\sigma,\sigma'} c_{\mathbf{k},\sigma}^{\pm} \boldsymbol{\sigma}_{\sigma\sigma'} c_{\mathbf{k}',\sigma'}, \qquad \hat{\mathrm{S}}_i = \sum_{\mu,\mu'} d_{i,\mu}^{+} \mathrm{S}_{\mu\mu'} d_{i\mu'},$$

$\boldsymbol{\sigma} = (\sigma^x, \sigma^y, \sigma^z)$ are Pauli matrices, and $c_{\mathbf{k},\sigma}^{+}$ ($c_{\mathbf{k},\sigma}$) and $d_{i\mu}^{+}$ ($d_{i,\mu}$) are the creation (annihilation) operators for the electrons of the metal and impurity, respectively.

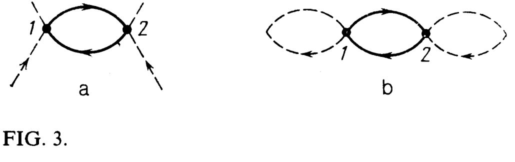
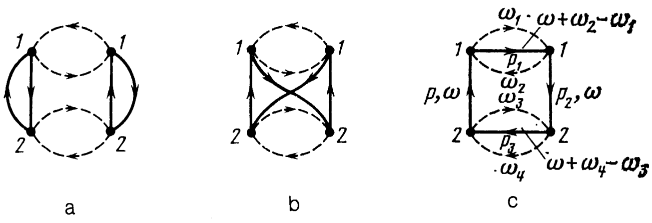


FIG. 3.



a b c

FIG. 4.

The matrix elements that describe the interaction of the impurity electrons, and appear in second-order perturbation theory, are expressed by the diagram (a) of Fig. 3 and lead to Eq. (38). The correction to the system energy, in the same order, is expressed by diagram (b) of Fig. 3 (the solid and dashed lines represent respectively the Green's functions of the metal and impurity electrons). The closed impurity loops denote taking the traces of the operators $\hat{\mathbf{S}}_i$, which are equal to zero by virtue of the properties of the Pauli matrices (meaning thereby that $\langle 0|\hat{\mathbf{S}}_1\hat{\mathbf{S}}_2|0\rangle = 0$).

The next order corrections to the energy are expressed by the diagrams of Fig. 4 (we leave out diagrams with closed loops). Diagrams resulting from permutation of two vertices having the same number do not lead to new expressions. The diagram technique and the expressions for the impurity Green's functions are given in Ref. 17. Summation over the frequencies in diagrams 4a and 4b lead to a zero result. The only nonzero diagram is 4c, the analytic expression for which is, apart from a constant factor,

$$\lim_{\lambda\gg T}\left(\frac{e^{\lambda/T}}{2S+1}\right)^2 J^4\,\mathrm{Sp}(S_iS_k)\,\mathrm{Sp}(S_lS_m)\,\mathrm{Sp}(\sigma^i\sigma^k\sigma^m\sigma^l)$$
$$\times\int\frac{d^3\mathbf{p}_1}{(2\pi)^3}\int\frac{d^3\mathbf{p}_2}{(2\pi)^3}$$
$$\times\int\frac{d^3\mathbf{p}_3}{(2\pi)^3}\int\frac{d^3\mathbf{p}}{(2\pi)^3}T^5$$
$$\times\sum_{\omega\omega_1\omega_2\omega_3\omega_4}\frac{1}{i(\omega+\omega_2-\omega_1)-\xi(\mathbf{p}_1)}\,\frac{1}{i\omega_1-\lambda}\,\frac{1}{i\omega_2-\lambda}$$
$$\times\frac{1}{i(\omega+\omega_3-\omega_4)-\xi(\mathbf{p}_3)}\,\frac{1}{i\omega_3-\lambda}\,\frac{1}{i\omega_4-\lambda}\,\frac{1}{i\omega-\xi(\mathbf{p})}\,\frac{1}{i\omega-\xi(\mathbf{p}_2)}$$
$$\times\exp[i(\mathbf{p}-\mathbf{p}_2)\mathbf{R}], \tag{40}$$

where

$$\xi(\mathbf{p}_i)=\varepsilon(p_i)-\mu,\quad \omega=(2s+1)\pi T,\quad s=0,\pm1,\pm2,\ldots.$$

We shall not present here the details of the unwieldy albeit standard calculations. The result of these calculations for large R ($k_F R\gg 1$) is proportional to the quantity

$$\frac{\cos 2k_FR}{(k_FR)^3}\,\frac{J^4}{\mu^2}\,\frac{S^2(S+1)^2}{(2S+1)^2}\ln^2\frac{\mu}{T}, \tag{41}$$

which describes in fact the indirect interaction of two impurity atoms. Note that this equation is valid only for not too low temperatures ($T\gtrsim T_\mathrm{K}$, where T_K is the Kondo temperature), at which the perturbation theory does not lead to divergence. Thus, although the dependence on the distance between the impurities in this expression coincides with (38), the interaction is of the next lower order in $(J/\mu)^2$ at $T\gtrsim T_\mathrm{K}$. To obtain the spin-dependent part of the indirect interaction at low temperatures it is necessary to sum the divergent terms of all orders of perturbation theory.

CONCLUSION

We have considered in this paper various cases of indirect interaction of two impurity centers via electrons of the metallic band of a crystal. It was found that the exact solutions obtained for the interaction at large distances are derived quite simply from the simple qualitative considerations cited in the Introduction, which permit a correct description of the dependence of the indirect interaction on the distance R between impurity, namely, it is proportional to $C_F\cos(2k_F R + \varphi_F)/(k_F R)^3$. The expressions obtained in the paper can be used to refine the details of the interaction and to determine the parameters φ_F and C_F in cases when this cannot be done within the framework of perturbation theory.

A qualitatively similar dependence on the distance between the impurity centers is exhibited by indirect interaction of electrons localized on impurity levels, although the magnitude of the interelectron interaction can differ substantially from the interatomic interaction for both magnetic and nonmagnetic impurities.

Finally, the method developed can be used to determine the indirect interaction between atoms adsorbed on the surface of a crystal via the metallic surface band of the crystal. It turns out that this interaction can lead to mutual depolarization of adatoms and influence the work function from the crystal surface.

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[1] T. K. Vul and M. A. Krivoglaz, Phys. Met. Metall. **53**, 1 (1981).
[2] T. Grimley and S. Walker, Surf. Sci. **14**, 395 (1969).
[3] A. M. Gabovich and E. A. Pashitskiĭ, Fiz. Tverd. Tela (Leningrad) **18**, 377 (1976) [Sov. Phys. Solid State **18**, 220 (1976)].
[4] K. H. Lau and W. Kohn, Surf. Sci. **75**, 69 (1978).
[5] C. Kittel, *Quantum Theory of Solids*, Wiley, 1963.
[6] M. A. Ruderman and C. Kittel, Phys. Rev. **96**, 99 (1954).
[7] P. W. Anderson, Phys. Rev. **124**, 41 (1961).
[8] D. I. Khomskiĭ, Usp. Fiz. Nauk **129**, 443 (1979) [Sov. Phys. Usp. **22**, 879 (1979)].
[9] A. M. Tsvelik, Zh. Eksp. Teor. Fiz. **76**, 2260 (1979) [Sov. Phys. JETP **49**, 1142 (1979)].
[10] A. I. Baz', Ya. B. Zel'dovich, and A. M. Perelomov, *Scattering, Reactions, and Decay in Nonrelativistic Quantum Mechanics*, Wiley, 1969 (second Russian edition, Nauka, 1971).
[11] L. A. Bol'shov, A. P. Napartovich, A. G. Naumovets, and A. G. Fedorus, Usp. Fiz. Nauk **122**, 125 (1977) [Sov. Phys. Usp. **20**, 432 (1977)].
[12] G. Binnig, H. Rohrer, Ch. Gerber, and E. Weibel, Phys. Rev. Lett. **50**, 120 (1983).
[13] J. Kanamori, Sol. St. Commun. **50**, 363 (1984).
[14] K. Nakamura, Y. Nakahara, K. Ohtomi, and S. Sugana, Surf. Sci. **151/152**, 1020 (1985).
[15] L. A. Bol'shov, Fiz. Tverd. Tela (Leningrad) **13**, 1679 (1971) [Sov. Phys. Solid State **13**, 1404 (1971)].
[16] W. A. Harrison, *Solid State Theory*, McGraw, 1970, Chap. 5, § 7.
[17] A. A. Abrikosov, Physics 25 (1965).

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