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CALCULATION OF THE ENERGY CHANGE IN A SYSTEM OF ELECTRONS IN A LATTICE WHEN DEFECTS ARE FORMED

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A system of non-interacting electrons in a lattice is considered. In the single-band approximation the changes of energy and thermal capacity of this system when defects are formed are calculated.

In the theory of local perturbations in crystals the most important problems are, on the one hand, finding the discrete levels and the scattering problem,[1,2] and, on the other hand, the calculation of the changes in the various thermodynamic quantities. The latter problem was first posed and solved in the general case by I. Lifshitz[3] (see also references 4 and 5).

We consider the change of the electronic energy of a crystal when defects are formed. This problem is of particular interest in connection with the possibility of thus finding the contribution to the electronic thermal capacity of the crystal made by lattice defects. We use the one-electron approximation, and neglect electron interactions. We write the Schrödinger equation for the wave function of an electron in an ideal lattice as

$$H_0\psi_{\mathbf{k}} = \varepsilon_{\mathbf{k}}\psi_{\mathbf{k}}; \tag{1}$$

H_0 includes the kinetic energy and the periodic potential averaged over the lattice, $\psi_{\mathbf{k}}$ is a Bloch function. We limit the spectrum of $\epsilon_{\mathbf{k}}$ to one band.

For a lattice with a defect we have

$$(H_0 + V)\varphi_{\mathbf{k}} = \varepsilon'_{\mathbf{k}}\varphi_{\mathbf{k}}. \tag{2}$$

Here V is the perturbing potential localized about the same point $\mathbf{r}_0$; $\epsilon'_{\mathbf{k}}$ and $\varphi_{\mathbf{k}}$ are the perturbed eigenvalues and eigenfunctions.

Our problem consists in calculating the energy change of the electron system ΔE, which, using the invariance of the trace of operators, we will write in the form

$$\Delta E = \operatorname{Sp}\{\Omega(H_0 + V) - \Omega(H_0)\}, \tag{3}$$

$$\Omega(\varepsilon) = -kT\ln(1 + e^{(\mu-\varepsilon)/kT}), \tag{4}$$

where μ is the chemical potential, T is the temperature, k is Boltzmann's constant. If P_ϵ and $P_{\epsilon'}$ (the projection operators into the states $\psi_{\mathbf{k}}$ and $\varphi_{\mathbf{k}}$) are introduced, then

$$\Delta E = \int \operatorname{Sp}(P_\varepsilon - P'_\varepsilon)\,\Omega'(\varepsilon)\,d\varepsilon. \tag{5}$$

The trace of the difference of projection operators has been calculated in the case of a degenerate regular perturbation by I. Lifshitz.[3] We use for the perturbation operator the first order approximation. With this aim we expand $\psi_{\mathbf{k}}$, normalized to a δ-function, in terms of the Wannier functions $a_{\mathbf{n}}(\mathbf{r})$, localized at the lattice sites:

$$\psi_{\mathbf{k}}(\mathbf{r}) = (2\pi)^{-3/2}\sum_{\mathbf{n}} e^{i\mathbf{k}\mathbf{n}}a_{\mathbf{n}}(\mathbf{r}). \tag{6}$$

The diagonal matrix elements of V in $\psi_{\mathbf{k}}$ space, which are of interest to us in this approximation, will have the form

$$\langle\psi_{\mathbf{k}}|V|\psi_{\mathbf{k}}\rangle = (2\pi)^{-3}\sum_{\mathbf{n},\mathbf{n}'}\langle a_{\mathbf{n}}|V|a_{\mathbf{n}'}\rangle e^{i\mathbf{k}(\mathbf{n}-\mathbf{n}')}. \tag{7}$$

Limiting ourselves to the largest of all the elements $\langle a_{\mathbf{n}}|V|a_{\mathbf{n}'}\rangle$

$$\alpha = (2\pi)^{-3}\alpha_0 = (2\pi)^{-3}\langle a_{\mathbf{n}_0}|V|a_{\mathbf{n}_0}\rangle \tag{8}$$

($\mathbf{n}_0$ is the site closest to $\mathbf{r}_0$), we obtain

$$\langle\psi_{\mathbf{k}}|V|\psi_{\mathbf{k}}\rangle = \alpha. \tag{9}$$

It is now possible to use the results of reference 3 for the case of a one-dimensional first-order perturbation. We have

$$\operatorname{Sp}(P_\varepsilon - P'_\varepsilon) = \frac{1}{\pi}\arg\left(1 + \int\frac{c(\varepsilon')}{\varepsilon' - \varepsilon - i0}\,d\varepsilon'\right),$$

$$c(\varepsilon) = \int\limits_{\varepsilon_{\mathbf{k}}=\varepsilon}\frac{d\omega}{|\nabla\varepsilon_{\mathbf{k}}|}. \tag{10}$$

The last integral is taken over a surface of constant energy, $d\omega$ is the element of its area.

The Stieltjes integral (5) gives

$$\Delta E = 2[\Omega(\varepsilon_0) - \Omega(\varepsilon_g)] + \frac{2}{\pi}\int\tan^{-1}\Big[\pi\alpha c(\varepsilon)\Big/\Big(1 + \alpha\mathrm{P}\int\frac{c(\varepsilon')}{\varepsilon' - \varepsilon}\,d\varepsilon'\Big)\Big]\,\Omega'(\varepsilon)\,d\varepsilon. \tag{11}$$

Here the spin degeneracy has already been taken into account, and the level of the localized state ϵ_0

is determined from the equation

$$1+\alpha\int d\varepsilon c(\varepsilon)/(\varepsilon-\varepsilon_0)=0; \qquad (12)$$

ϵ_g is the upper or lower edge of the band, depending upon the sign of α.

The possibility of approximating by a one-dimensional perturbation has no rigorous foundation, but we shall establish a criterion for its approximate feasibility. To do this we note that for sufficiently small values of α (in the three-dimensional case) Eq. (12) has no solutions at all, there is no localization due to the perturbation, and, consequently, the approximation is demonstrably inapplicable.

In order to obtain a more accurate estimate we write

$$\int\limits_{\varepsilon_k=\varepsilon} d\omega/\,|\nabla\varepsilon_k| = \int\delta(\varepsilon_k-\varepsilon)\,dk. \qquad (13)$$

It then becomes possible to introduce a new function

$$I_\varepsilon(\mathbf{n}-\mathbf{n}')=(2\pi)^{-3}\,\mathrm{P}\int dk e^{ik(\mathbf{n}-\mathbf{n}')}/(\varepsilon_k-\varepsilon-i0), \qquad (14)$$

which is the Green's function in the discrete space of lattice sites. We have

$$\mathrm{Re}\,I_\varepsilon(0)=(2\pi)^{-3}\mathrm{P}\int d\varepsilon' c(\varepsilon')/(\varepsilon'-\varepsilon),$$

$$\mathrm{Im}I_\varepsilon(0)=(2\pi)^{-2}c(\varepsilon). \qquad (15)$$

If we now consider that (in the three-dimensional case) $\mathrm{Re}\,I_\epsilon(0)$ is continuous through the boundary of the spectrum and attains a maximum (minimum) at it, then it is possible to write down the inequality

$$1/\alpha<\mathrm{P}\int d\varepsilon' c(\varepsilon')/(\varepsilon'-\varepsilon_g). \qquad (16)$$

We write $\epsilon=\epsilon^0+\beta f(\mathbf{k})$, where $\mathbf{k}$ is the quasi-momentum, and β determines the energy width of the band, then

$$1/\alpha_0<\mathrm{const}/\beta. \qquad (17)$$

The constant appearing here has a value of the order of unity. Thus, our approximation is most justified when

$$\alpha_0\gg\beta. \qquad (18)$$

We now turn to a study of the contribution of a small number of defects η to the electronic heat capacity at low temperatures. As is easily verified, the localized electrons give an exponentially small contribution and can, therefore, be ignored. For the energy change we find in the usual way[6]

$$\Delta E=\Delta E_0+\frac{\pi}{3}\eta(kT)^2\Phi'(\varepsilon_F),\ \Phi(\varepsilon)=\tan^{-1}\frac{\alpha_0\,\mathrm{Im}\,I_\varepsilon(0)}{1+\alpha_0\,\mathrm{Re}\,I_\varepsilon(0)}. \qquad (19)$$

Here ϵ_F is the Fermi energy, ΔE_0 is the energy change at $T=0$:

$$\Delta E_0=2(\varepsilon_0-\varepsilon_g)+\frac{2}{\pi}\int^{\varepsilon_F}\tan^{-1}\frac{\alpha_0\,\mathrm{Im}\,I_\varepsilon(0)}{1+\alpha_0\,\mathrm{Re}\,I_\varepsilon(0)}\,d\varepsilon. \qquad (20)$$

It must be pointed out that, in fact, in the nature of the problem, the integrals in (15) are taken over the unperturbed spectrum, but the integral in (20) over the perturbed. This becomes of particular importance near to the edges of the unperturbed spectrum, where it is not permissible to expand in terms of β/α_0 (see reference 7). In addition the relationships obtained are only valid when the band is not too full, because otherwise it is impossible to use the procedure of extending the integrals over ϵ from the distribution function to infinity. We do not consider here the complicated processes when there is a gap between two bands.

Thus we have, for the contribution to the heat capacity,

$$\Delta c=\frac{2}{3}(\pi k)^2\alpha_0\eta T$$

$$\times\frac{[\mathrm{Im}\,I_\varepsilon(0)]'+\alpha_0\{[\mathrm{Im}I_\varepsilon(0)]'\,\mathrm{Re}I_\varepsilon(0)-[\mathrm{Re}I_\varepsilon(0)]'\,\mathrm{Im}I_\varepsilon(0)\}}{[\alpha_0\,\mathrm{Im}I_\varepsilon(0)]^2+[1+\alpha_0\mathrm{Re}\,I_\varepsilon(0)]^2} \qquad (21)$$

We note that $\mathrm{Im}\,I_\epsilon(0)$ and $\mathrm{Re}\,I_\epsilon(0)$ possess characteristic singularities in their first derivatives at the boundary of the unperturbed spectrum.

When the inequality (18) is satisfied, the quantity Δc ceases to depend on the perturbation, and we obtain

$$\Delta c=\frac{2}{3}(\pi k)^2\eta T\Phi_0(\varepsilon_F),$$

$$\Phi_0(\varepsilon)=\{[\mathrm{Im}\,I_\varepsilon(0)]'\,\mathrm{Re}I_\varepsilon(0)-[\mathrm{Re}I_\varepsilon(0)]'\mathrm{Im}I_\varepsilon(0)\}/\,|\,I_\varepsilon(0)\,|^2 \qquad (22)$$

In the other limiting case ($\beta\gg\alpha_0$), provided the first order approximation remains applicable (for example, with modified α_0^*), we find

$$\Delta c=\frac{2}{3}(\pi k)^2\alpha_0^*\eta\,[\mathrm{Im}I_{\varepsilon_F}(0)]'\,T. \qquad (23)$$

These two possibilities are realized, apparently, in dielectrics and metals.

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