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THE EFFECT OF A PERIODIC LATTICE POTENTIAL ON THE OPTICAL PROPERTIES AND OTHER INTEGRAL CHARACTERISTICS OF CUBIC MULTI-VALENT METALS

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Analytic expressions are obtained which allow one to estimate the effect of a periodic lattice potential on the concentration of conduction electrons as determined by optical methods, N_{opt}, and also on the magnitude of the Fermi surface S_F and the electron state density on the Fermi surface γ_F. The expressions apply to cubic nontransition multivalent metals. The calculation is performed to first-order terms with respect to $|V_g|/E_F$ where V_g is the Fourier component of the pseudopotential and E_F is the electron energy on the Fermi surface. The formulas are employed to determine N_{opt} for lead and aluminum. The considered effect leads to a much smaller value of N_{opt} than that of N_{val} (N_{val} is the concentration of valence electrons). However, it does not completely explain the difference $N_{\text{val}} - N_{\text{opt}}$ observed experimentally.

FOR multivalent nontransition metals, such as aluminum, lead, and tin, there is a large discrepancy between the concentration of conduction electrons N_{opt} determined by the optical method and the concentration of valence electrons N_{val}. For these metals N_{opt} is close to one electron per atom, which is several times less than N_{val}. At the same time, for the same metals in the liquid or amorphous state N_{opt} is approximately equal to N_{val}. This fact has already been considered in[1] where the question of the possible effect of Fermi-liquid effects on N_{opt} has been discussed. It was noted that the interelectron interactions effect N_{opt} differently in the case of the crystalline and liquid or amorphous state. One can therefore expect that Fermi-liquid effects can at least partly explain the observed difference between N_{opt} and N_{val}. In[1] it was assumed that the Fourier components of the pseudopotential for the above metals are so small that they cannot explain the discrepancy between N_{opt} and N_{val}. At the same time, it was emphasized in[1] that it is still necessary to refine from experimental data the actual value of N_{opt} obtained without allowance for interelectron interaction.

Using results pertaining to the van Alphen—de Haas effect, it has recently been possible to determine the Fourier components of the pseudopotential for lead.[2] These turned out to be rather large. One should, therefore, estimate first the effect of the periodic lattice potential on the optical properties of multivalent nontransition metals. This is the purpose of this paper. At the same time, we estimate the effect of the lattice on the total Fermi surface S_F and on the density of states on the Fermi surface γ_F.

1. CUBIC MULTIVALENT METALS

A. Let us consider the cubic lattice. As is well known,[3] in this case optical measurement of the complex index of refraction in the infrared region make it possible to determine the quantity

$$\frac{N_{\text{opt}}}{m} = \frac{2}{3(2\pi\hbar)^3}\oint v_F dS_F. \tag{1}$$

Here m is the mass of a free electron, v_F is the electron velocity on the Fermi surface, and dS_F is an element of the Fermi surface in momentum space. We must, therefore, estimate the effect of the periodic lattice potential on the quantity

$$\oint v_F dS_F \tag{1'}$$

B. We use the pseudopotential method.[4,5] We expand the pseudopotential in a Fourier series:

$$V(\mathbf{r}) = \sum_{\mathbf{g}} V_{\mathbf{g}} \exp(2\pi i \mathbf{g}\mathbf{r}). \tag{2}$$

The summation is over all the reciprocal lattice vectors **g**. Assuming that $|V_g| \ll E_F$ (E_F is the Fermi energy), we use the weak-coupling method. In the calculation we shall take into account only first-order terms in the small parameter $|V_g|/E_F$. In this approximation each component of the pseudopotential V_g yields an independent contribution and is effective only in the vicinity of the corresponding Bragg plane.

Let us consider the effect of one component of V_g. We shall use the extended-zone scheme. We denote the distance from the center of the zone Γ to the corresponding Bragg plane by p_g. We split the electron momentum into components—parallel and perpendicular to the Bragg plane: $p_{\|}$ and $p_\perp$. The electron energy will be

$$E(\mathbf{p}) = p_{\|}^2 + p_\perp^2 - 2(p_\perp - p_g)p_g \pm [4(p_\perp - p_g)^2 p_g^2 + |V_g|^2]^{1/2}. \tag{3}$$

We have, for simplicity, chosen a system of units for which $2m = 1$, where m is the free electron mass. We introduce no other mass, except that of the free electron. On the Bragg plane $p_\perp - p_g = 0$ and the electron energy is

$$E = E_0 \pm |V_g|. \tag{4}$$

Here E_0 is the energy of the free electron.

For convenience we introduce the dimensionless quantities (see the figure):

$$w = \frac{E(\mathbf{p})}{p_g^2}, \quad \xi = \frac{|V_g|}{p_g^2}, \quad x = \frac{p_\perp - p_g}{p_g}, \quad y = \frac{p_{\|}}{p_g}. \tag{5}$$

In terms of these variables the equal-energy surface will be of the following form

$$w = y^2 + x^2 + 1 + \operatorname{sign}(x)\sqrt{4x^2 + \xi^2}. \tag{6}$$

The Bragg plane changes the velocity component of the electron perpendicular to this plane. In terms of our variables we shall have the following expressions for the electron velocity:

$$v_{\|} = 2p_g\, y,$$

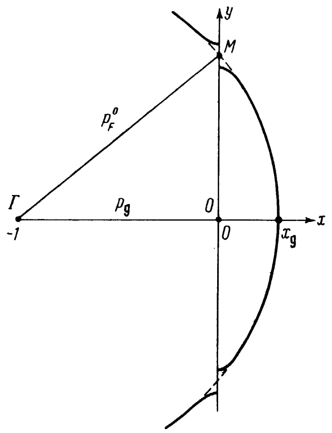
$$v_\perp = 2p_g\,[x + \operatorname{sign}(x)\cdot 2x / \sqrt{4x^2 + \xi^2}],$$

$$v^2(x) = v_{\|}^2 + v_\perp^2 = 4p_g^2 \left[w - \frac{\xi^2}{4x^2 + \xi^2} - \operatorname{sign}(x)\frac{\xi^2}{\sqrt{4x^2 + \xi^2}} \right]. \tag{7}$$

The presence of a Bragg plane leads also to a change in the shape of the Fermi surface. The figure shows the initial free-electron sphere and the changes in it due to the presence of one Bragg plane. The radius of the free-electron sphere is given by the expression

$$p_F{}^0 = 2\pi\hbar \left(\frac{3}{8\pi} \frac{\Delta n}{\Delta\tau} \right)^{1/3}. \tag{8}$$

Here Δn is the number of valence electrons contained in a volume Δτ.



The Fermi surface near the region of intersection of the Bragg plane OM with the free-electron sphere. The plane of the diagram is perpendicular to the Bragg plane and passes through the center of the sphere Γ.

Assuming that the Bragg plane intersects the free-electron sphere, we find that the Fermi surface will be a surface of revolution with an axis passing through the center of a sphere Γ perpendicular to the Bragg plane. The area element of the Fermi surface is, as can be readily shown,

$$dS_F = 2\pi p_g{}^2 y(x)\,[1 + (dy(x)\,/\,dx)^2]^{1/2} dx = \pi p_g\, v_F(x)\, dx. \tag{9}$$

The cited relations (7) and (9) allow us to calculate readily the integral characteristics of the Fermi surface.[1] We confine ourselves to first-order terms in ξ. It should, however, be borne in mind that the distance to the Bragg plane p can be close to the Fermi momentum for free electrons $p_F^0 = (E_F^0)^{1/2}$, i.e., $x_g = (p_F^0 - p_g)/p_g \ll 1$. The ratio ξ/x_g will therefore be assumed to be arbitrary. We also note that in the expression for v(x) the term containing sign(x) leads, as can be readily shown, to small corrections of the order of $\xi^2 \ln \xi$ and can therefore be discarded.

C. Let us consider the effect of a periodic potential on the optical electron concentration N_{opt}. It was already noted above that

$$N_{\text{opt}} \sim \oint v_F dS_F.$$

Obviously,

$$N_{\text{val}} \sim v_F{}^0 S_F{}^0.$$

The superscript 0 refers to free electrons. In our units $S_F^0 v_F^0 = 4\pi(p_F^0)^2 2p_F^0$.

Using (7) and (9) one readily obtains

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[1] It is easy to show that a change in the volume of momentum space enclosed within the Fermi surface is given by quantities of second-order in smallness and it can be assumed that far from a Bragg plane the Fermi surface is a sphere of radius p_F^0 and that $E_F = E_F^0$.

$$\frac{N_{\mathrm{val}} - N_{\mathrm{opt}}}{N_{\mathrm{val}}} \equiv \left(v_F{}^0 S_F{}^0 - \oint v_F dS_F\right) \Big/ v_F{}^0 S_F{}^0$$

$$= \sum_{\mathbf{g}} \frac{\pi}{4} \frac{p_{\mathbf{g}}}{p_F{}^0} \frac{|V_{\mathbf{g}}|}{E_F{}^0} \left(\frac{1}{2} + \frac{\varphi_{\mathbf{g}}}{\pi}\right), \tag{10}$$

$$\varphi_{\mathbf{g}} = \operatorname{arc\,tg} \frac{2\,(p_{\mathbf{g}}/p_F{}^0)\,(1 - p_{\mathbf{g}}/p_F{}^0)}{(|V_{\mathbf{g}}|/E_F{}^0)}. \tag{11*}$$

Summation is over all Bragg planes intersecting the free-electron sphere. We note that for

$$(p_F{}^0 - p_{\mathbf{g}}) / p_{\mathbf{g}} \gg {}^1\!/_2 (|V_{\mathbf{g}}| / E_F{}^0)\,(p_F{}^0 / p_{\mathbf{g}})^2$$

we get $1/2 + \varphi_{\mathbf{g}}/\pi \approx 1$.

D. Let us consider the effect of a periodic potential on the area of the Fermi surface. Using the same expressions (7) and (9), we obtain

$$\frac{S_F{}^0 - S_F}{S_F{}^0} = \sum_{\mathbf{g}} \frac{1}{2} \frac{|V_{\mathbf{g}}|}{E_F{}^0} \left[f\left(\frac{p_{\mathbf{g}}}{p_F{}^0}\right) - \frac{1}{2} \tilde{f}\left(\frac{p_{\mathbf{g}}}{p_F{}^0}, \varphi_{\mathbf{g}}\right) \right], \tag{12}$$

where

$$f(z) = \frac{1}{z} E(z) - \left(\frac{1}{z} - z\right) K(z),$$

$$\tilde{f}(z, \varphi) = \frac{1}{z} E\left(z, \frac{\pi}{2} - \varphi\right) - \left(\frac{1}{z} - z\right) F\left(z, \frac{\pi}{2} - \varphi\right)$$

$$- \frac{1}{z} [1 - (1 - z^2 \cos^2 \varphi)^{1/2}] \operatorname{tg} \varphi,$$

$$E(z, \psi) = \int_0^\psi d\theta\,(1 - z^2 \sin^2 \theta)^{1/2},$$

$$F(z, \psi) = \int_0^\psi \frac{d\theta}{(1 - z^2 \sin^2 \theta)^{1/2}},$$

$$E(z) \equiv E\left(z, \frac{\pi}{2}\right), \quad K(z) \equiv F\left(z, \frac{\pi}{2}\right). \tag{13†}$$

Here $F(z, \psi)$ and $E(z, \psi)$ are elliptic integrals of the first and second kind respectively (see, for example,[6]). We note that for $x_{\mathbf{g}} \gg \xi$, i.e., when

$$[(p_F{}^0 / p_{\mathbf{g}}) - 1] \gg (|V_{\mathbf{g}}| / E_F{}^0)\,(p_F{}^0 / p_{\mathbf{g}})^2$$

we have

$$\tilde{f}\left(\frac{p_{\mathbf{g}}}{p_F{}^0}, \varphi_{\mathbf{g}}\right) \cong \frac{p_{\mathbf{g}}}{p_F{}^0} \frac{\xi}{4x_{\mathbf{g}}} = \frac{1}{4} \frac{|V_{\mathbf{g}}|}{E_F{}^0} \frac{1}{1 - p_{\mathbf{g}}/p_F{}^0} \tag{13'}$$

and the formula is thus appreciably simplified.

E. Let us consider the effect of a periodic potential on the density of states on the Fermi surface

$$\gamma_F \sim \oint dS_F / v_F.$$

It follows from (9) that $dS_F/v_F = \pi p_{\mathbf{g}} dx$. The limits of integration also do not depend on ξ. Consequently, in the approximation under consideration, which is linear in $|V_{\mathbf{g}}|/E_F^0$, the periodic lattice potential does not alter the density of states of electrons on the Fermi surface:

$$\gamma_F = \gamma_F{}^0. \tag{14}$$

F. Utilizing Eqs. (10)—(13) one can estimate the effect of a periodic lattice potential on N_{opt} and S_F. Equations (12)—(14) are also applicable to noncubic crystals. Equations (10)—(11) yield the change of the quantity (1′) also for an arbitrary crystal lattice. However, for noncubic symmetry there is no simple relationship between $\{N_{\mathrm{opt}}\}_{ij}$ and (1′). Nevertheless it can be approximately assumed that for polycrystalline samples the average value of N_{opt} will be given by (1′).

The accuracy of the obtained expressions for $(N_{\mathrm{val}} - N_{\mathrm{opt}})/N_{\mathrm{val}}$ and $(S_F^0 - S_F)/S_F^0$ is determined by the average quantity $|\overline{V_{\mathbf{g}}}|/E_F^0$. Owing to the fact that we have neglected second-order quantities, it is to be expected that the relative error will be of the order of $|\overline{V_{\mathbf{g}}}|/E_F^0$.

Below we compare the results obtained from the equations of this paper with the experimental results obtained in[7-9], and also with the results of more accurate calculations by Anderson and Gold.[2]

2. TRI- AND TETRAVALENT METALS WITH A CUBIC FACE-CENTERED LATTICE

A. Let us apply the obtained formulas to a face-centered cubic lattice. For this type of lattice the only important Fourier components are V_{111} and V_{200} (cf.[2,10]). The corresponding Bragg planes pass at the following distances from the zone center Γ:

$$p_{111} = \frac{2\pi\hbar}{a} \frac{\sqrt{3}}{2}, \quad p_{200} = \frac{2\pi\hbar}{a}. \tag{15}$$

Here a is the lattice constant.

In calculating the sums in (10) and (12) one must take into account the fact that eight {111} and six {200} planes intersect the free-electron sphere.

B. Let us consider a tetravalent metal. The volume $\Delta\tau = a^3$ contains 16 valence electrons. Using (8), we obtain

$$p_F{}^0 / (2\pi\hbar / a) = 1.241. \tag{16}$$

As a result, in accordance with (10),

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*$\operatorname{arc\,tg} \equiv \tan^{-1}$.

†$\operatorname{tg} \equiv \tan$

$$\frac{N_{\text{val}}-N_{\text{opt}}}{N_{\text{opt}}}=4.40\frac{|V_{111}|}{E_F{}^0}\left(\frac{1}{2}+\frac{\varphi_{111}}{\pi}\right)$$
$$+3.80\frac{|V_{200}|}{E_F{}^0}\left(\frac{1}{2}+\frac{\varphi_{200}}{\pi}\right),$$
$$\varphi_{111}=\operatorname{arctg}\frac{0.420}{(|V_{111}|/E_F{}^0)},\quad \varphi_{200}=\operatorname{arctg}\frac{0.313}{(|V_{200}|/E_F{}^0)}. \tag{17}$$

Let us apply this formula to lead. According to[2] for lead $|V_{111}|/E_F^0 = 11.9 \times 10^{-2}$, and $|V_{200}|/E_F^0 = 5.5 \times 10^{-2}$. This yields

$$(N_{\text{val}}-N_{\text{opt}})/N_{\text{val}}=0.674.$$

Hence $N_{\text{opt}} = 1.30$ electrons per atom. Experiment[7] yields for lead $N_{\text{opt}} = 1.12 \pm 0.04$ electrons per atom[2)]. One can consider these values to coincide.

Thus the large observed difference between N_{opt} and N_{val} in lead is basically connected with the effect of the periodic lattice potential which is in this case rather large.

Let us calculate the area of the Fermi surface of lead. Assuming that condition (13′) is fulfilled (the error in assuming this is $\lesssim 3\%$), we obtain $(S_F^0 - S_F)/S_F^0 = 0.410$. An accurate calculation carried out by solving a fourth-order secular equation[2] yields $(S_F^0 - S_F)/S_F^0 = 0.411$. Thus, the results of both calculations coincide.

The total area of the Fermi surface has been determined experimentally[11] from measurements of surface conductivity in the case of the anomalous skin effect. The value obtained was $(S_F^0 - S_F)/S_F^0 = 0.45 \pm 0.05$ which is in good agreement with the calculation.

C. Let us consider a trivalent metal. In this case the volume $\Delta\tau = a^3$ contains 12 valence electrons. In accordance with (8) we obtain

$$p_F{}^0/(2\pi\hbar/a)=1.126. \tag{18}$$

As a result, according to (10),

$$\frac{N_{\text{val}}-N_{\text{opt}}}{N_{\text{val}}}=4.84\frac{|V_{111}|}{E_F{}^0}\left(\frac{1}{2}+\frac{\varphi_{111}}{\pi}\right)$$
$$+4.18\frac{|V_{200}|}{E_F{}^0}\left(\frac{1}{2}+\frac{\varphi_{200}}{\pi}\right),$$
$$\varphi_{111}=\operatorname{arctg}\frac{0.355}{(|V_{111}|/E_F{}^0)},\quad \varphi_{200}=\operatorname{arctg}\frac{0.199}{(|V_{200}|/E_F{}^0)}. \tag{19}$$

The Fourier components of the potential for aluminum are[10]: $|V_{111}|/E_F^0 = 2.09 \times 10^{-2}$, $|V_{200}|/E_F^0 = 6.57 \times 10^{-2}$. Using these values, we obtain $(N_{\text{val}} - N_{\text{opt}})/N_{\text{val}} = 0.346$, whence $N_{\text{opt}} = 1.96$ electrons per atom. Experiment yields for evaporated and unannealed films of aluminum[8] $N_{\text{opt}} = 1.33 \pm 0.06$ electrons per atom, and for sputtered and annealed films[9] $N_{\text{opt}} = 1.12 \pm 0.07$ electrons per atom. There is no agreement, although a considerable part of the difference between N_{opt} and N_{val} can be explained as being due to the periodic lattice potential.

Calculations of the area of the Fermi surface carried out with Eqs. (12) and (13) yield $(S_F^0 - S_F)/S_F^0 = 0.215$. Unfortunately, we cannot compare our results with the more accurate calculation of Ashcroft,[10] since he did not calculate the integral characteristics which interest us.

3. CONCLUSION

The obtained expressions which take into account the effect of the periodic lattice potential on the concentration of conduction electrons determined by the optical method, as well as on the area of the Fermi surface and on the density of states on the Fermi surface, make it possible to determine these quantities if the Fourier components of the pseudo-potential are known. At present, the latter are obtained experimentally from the results of measurements of the van Alphen—de Haas effect. We assume that the required Fourier components can also be obtained as a result of analyzing the results of optical measurements in the visible and infrared regions of the spectrum. However, the corresponding analysis of the experimental results has so far not been carried out.

The effect under consideration leads even without account of the interelectron interaction to an appreciable difference between N_{opt} and N_{val} for nontransition multivalent metals. The presence of a periodic potential leads to the inequality $N_{\text{opt}} < N_{\text{val}}$. However, for aluminum and with allowance for the action of the lattice, experiment yields a smaller value for N_{opt} than the calculated value. The reason for this discrepancy requires further study. It is quite possible that it is essentially related with the effect of the electron-electron interaction discussed in[1].

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[2)] We cite the value of N_{opt} obtained at T = 4.2°K, since the values of the potential refer to a temperature of this order.

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