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Abstract

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OPTICAL PROPERTIES OF POLYVALENT METALS AND INTERELECTRON INTERACTION

Recently it has become clear (^{1}) that even for polyvalent metals the approximation of weakly bound electrons is, in a number of respects, quite good. Specifically, the Fermi surface proves to be close to a sphere, if one disregards the regions directly adjacent to the lines of its intersection with the planes bounding the Brillouin zones. The effective mass m_{ef} and the velocity $v = |\partial\varepsilon/\partial p|$, averaged over the Fermi surface, are also close to the free-electron mass m and the velocity p_F/m, where p_F is the momentum on the Fermi surface (apparently the agreement is to within tens of percent). Thus a certain return becomes possible to the ideas that prevailed at the first stage in the development of the quantum electron theory of metals (see, for example, (^{2})) and that for a time (approximately from 1955 on) seemed completely unsuitable in the case of polyvalent metals, in connection with the discovery of a number of effects caused by the nonsphericity of the Fermi surface (see, for example, the review (^{3})). These effects, however, are connected either with small regions of the Fermi surface or with the reflection of electrons from zone boundaries, i.e., they in no way yet testify against the use of the approximation of weakly bound electrons. From this point of view, if one speaks of the optical properties of metals, they would seem to have to be close (^{4,5}) to those corresponding to the free-electron model (see, for example, (^{6})).

In the infrared part of the spectrum (outside the absorption band), in the one-electron approximation the dielectric constant of a metal with a lattice of cubic symmetry is

$$\varepsilon \simeq -\frac{4\pi e^2 N_{\text{opt}}}{m\omega^2} \equiv -\frac{e^2 \oint v\,dS}{3\pi^2\hbar^3\omega^2}, \tag{1}$$

where e and m are the charge and mass of the free electron and, by assumption, $|\varepsilon| \gg 1$.

For free electrons the integral over the Fermi surface is $\oint v\,dS = v_F \cdot 4\pi p_F^2 = 4\pi p_F^3/m$, and the electron concentration, equal to the concentration of valence electrons, is

$$N_{\mathrm{val}} = \frac{8\pi}{3}\,\frac{p_F^3}{(2\pi\hbar)^3}.$$

Thus, in this case, of course, $N_{\mathrm{opt}} = N_{\mathrm{val}}$, and under the conditions of applicability of the weakly bound electron approximation one might expect that for metals

$$N_{\mathrm{opt}} \simeq N_{\mathrm{val}}. \tag{2}$$

For Au, indeed, $N_{\mathrm{val}} = N_{\mathrm{at}} = 5.9 \cdot 10^{22}\ \mathrm{cm}^{-3}$, and from optical measurements (^{5}) $N_{\mathrm{opt}} = (5.54 \pm 0.08) \cdot 10^{22}$. Apparently, an analogous situation also holds for other monovalent metals (we do not give the corresponding data, since the available measurements were not sufficiently careful (see (^{5,6})). However, for polyvalent metals relation (2) is already clearly violated, as is seen from Table 1.

Thus, the model of weakly bound electrons, without any additional refinements, proves unsuitable for calculating N_{opt}. On the other hand, as was noted quite long ago $^{(10-12)}$, in Fermi-liquid theory $^{(13)}$, in which the electron-electron interaction is taken into account more fully (in the model of weakly bound electrons some part of the electron-electron interaction may be regarded as being taken into account in the choice of the self-consistent potential), the equality (2) is no longer valid. Specifically, in the Fermi-liquid model, in formula (1)

$$N_{\mathrm{opt}} = \frac{m}{12\pi^3\hbar^3}\int \frac{(\mathbf{v}\mathbf{V})}{v}\,dS, \tag{3}$$

where

$$\mathbf{V}(\mathbf{p}) = \mathbf{v}(\mathbf{p}) - \int f(\mathbf{p},\mathbf{p}')\,\frac{\partial n_0'}{\partial \mathbf{p}'}\,d\tau'. \tag{4}$$

In (3) the integration is carried out over the Fermi surface, n_0' is the equilibrium distribution function, $d\tau' = 2dp'/(2\pi\hbar)^3$, and $f(\mathbf{p},\mathbf{p}')$ is the second variational derivative of the system energy with respect to the quasiparticle distribution function (see $^{(10-13)}$). If the quasiparticle energy ε does not depend on the distribution function, which corresponds to the gas approximation, then $f(\mathbf{p},\mathbf{p}') = 0$, $\mathbf{V} = \mathbf{v} = \partial\varepsilon/\partial\mathbf{p}$, and formula (3) goes over into (1).

Table 1

Metal	Number of valence electrons per atom n_{val}	$N_{\text{val}} \cdot 10^{-22}$	$N_{\text{opt}} \cdot 10^{-22}$	Number of optical electrons per atom $n_{\text{opt}} = \frac{N_{\text{opt}}}{N_{\text{val}}} \times n_{\text{val}}$	Source
Au	1	5.9	5.5	0.93	(5)
Al	3	18.1	6.8	1.1	(7)
Sn	4	14.8	4.8	1.30	(8)
Pb	4	13.2	4.0	1.21	(9)

It is also important to note that, with regard to the static properties of metals, Fermi-liquid theory introduces no changes in comparison with the gas approximation (3,10), except for the influence on the function $\varepsilon(\mathbf{p})$. In view of the above, we suppose that the inequality $N_{\text{opt}} < N_{\text{val}}$ for polyvalent metals (see Table 1) can be explained by electron-electron interaction.

Let us discuss this question in somewhat more detail.

One possible way of checking such an explanation of the experimental data for N_{opt} is to study the metal in the liquid state. The point is that in Fermi-liquid theory, in the absence of an external field (in particular, of the lattice field), by virtue of the principle of Galilean relativity, the equality (13)

$$\mathbf{V} = \mathbf{p}/m, \tag{5}$$

holds, where $\mathbf{p}$ is the quasiparticle momentum and m is the mass of a free electron. Hence, according to (3), it follows immediately that for a spherical Fermi surface (and for a liquid metal this is precisely the case) $N_{\text{opt}} = (8\pi/3)p_F^3/(2\pi\hbar)^3 = N_{\text{val}}$, since the total number of quasiparticles in a Fermi liquid is equal to the number of particles. This result has an obvious physical meaning. Indeed, in the absence of external forces the Coulomb interaction between electrons cannot change their total momentum, and therefore the center of mass of the ensemble of electrons in the external electric field of the wave will move just as if the electrons did not interact. Since the polarization $P = [(\varepsilon - 1)/4\pi]E$ of an ensemble of identical particles is proportional to the displacement of the center of mass under the influence of the field, it is clear that ε is determined by formula (1) with $N_{\text{opt}} = N_{\text{val}}$, the total electron concentration. The electron-electron interaction in this approx-

conditions as well, of course, has no effect (see, for example, (14)). Above, however, we assumed that the electrons in the liquid do not collide with the lattice, or, more precisely, that $\nu^2 \ll \omega^2$, where ν is the number of collisions with the lattice or impurities. When the interaction of the electrons with the lattice is taken into account, the electron-electron interaction already affects both ε and σ. However, the coefficient N_{opt} in the formula

$$\varepsilon = -4\pi e^2 N_{\text{opt}}/m(\omega^2 + \nu^2) \tag{6}$$

in the liquid must still be equal to N_{val} to an accuracy up to terms of order $\hbar/p_F l$, where $l = v_F/\nu$ is the mean free path of the electrons. Indeed, relation (5) characterizes the liquid itself, and its accuracy cannot depend on the frequency of a weak external field. Therefore the only dimensionless parameter characterizing the accuracy with which Galilean invariance holds can be the indicated ratio $\hbar/p_F l$, which in the cases of interest to us is small. This conclusion can be substantiated by considering concrete models, for example an electron liquid that interacts with chaotically located impurities (scattering by such impurities models the scattering of electrons by fields in a liquid metal).

Table 2

Liquid metal	n_{val}	n_{opt}	Source
Ag	1	1.1	(15)
Al	3	3.0	(7)
Sn	4	4.6	(16)
Pb	4	4.6	(16)

Thus, for liquid metals in the region where formula (1) or (6) is applicable, relation (2) must hold. The available data confirm this conclusion (see Table 2; for Al the measurements were carried out for an amorphous layer, whose average density was somewhat less than the mean density of the liquid metal. We note that under the conditions in which the value N_{opt} was determined in liquids, the relation $\nu \approx \omega$ was observed.

Taking into account the accuracy of determining n_{opt} (it probably did not exceed 10–20%), the equality $N_{\text{opt}} = \dfrac{n_{\text{opt}}}{n_{\text{val}}} N_{\text{val}} \simeq N_{\text{val}}$ for the liquid and amorphous metals investigated may be considered fully confirmed. This conclusion is in agreement with the supposition that the difference between N_{opt} and N_{val} in crystalline metals is associated with electron-electron interaction. From this point of view it is also natural that for Au and some other monovalent metals, even in the crystalline phase, $N_{\text{opt}} \simeq N_{\text{val}}$. The point is that in these cases a significant part, or even the whole, of the Fermi surface lies inside the first Brillouin zone. Therefore one may suppose that in this case the situation will differ comparatively little from that occurring in the liquid metal.

We note that, according to the data of (17), in liquid Bi and Sb, n_{opt} is respectively 5.4 and 6.1, whereas $n_{\text{val}} = 5$, and in the crystalline phase $n_{\text{opt}} \ll 1$. In these cases, of course, the matter is not in the electron-electron interaction, and the inequality $N_{\text{opt}} \ll N_{\text{val}}$ in the crystalline phase is connected simply with the smallness of the momentum p_F. The examples of Bi and Sb show, at the same time, that the increase of n_{opt} upon melting, and even the equality $n_{\text{opt}} = n_{\text{val}}$ in the liquid metal, still cannot be regarded as proof of the proposed explanation of the nature of the inequality $n_{\text{opt}} < n_{\text{val}}$ in crystalline polyvalent metals. From the comparison of the data for the crystalline and liquid phases in different metals, it undoubtedly follows only that the inequality $n_{\text{opt}} < n_{\text{val}}$ is caused by the influence of the boundaries of Brillouin zones, i.e., by the reflection of electrons from these boundaries, which disappear in the liquid state and play a small role (in measurements of N_{opt}) in monovalent metals. We do not see, however, any other possibility of explaining the observed decrease of N_{opt} in comparison with N_{val} in Al, Sn, and Pb, except by taking into account the influence of electron–electron interaction. In this case we

proceeded from the assumption that in the metals indicated

$$\oint v\,dS \simeq \frac{4\pi p_F^3}{m} \simeq \frac{3(2\pi\hbar)^3}{2m} N_{\text{val}};$$

verification of this relation is very important. At the same time, we would like to point out two points that are not sufficiently clear. First, as follows from Table 1, for all three polyvalent metals discussed, $n_{\text{opt}} \simeq 1$, which we cannot explain. It is quite possible, however, that this is a matter of accidental coincidence. Second, the conclusion that interelectron interaction has a strong influence on the ratio $n_{\text{opt}}/n_{\text{val}}$ is not supported by calculations for any models. We also cannot regard this circumstance as a serious objection, since even for the simplest models no simultaneous, at least somewhat consistent, treatment of both interelectron interaction and interaction with the lattice (under the conditions of polyvalent metals) has yet been carried out.

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CITED LITERATURE

1. W. A. Harrison, Phys. Rev., **118**, 1182, 1190 (1960); **129**, 2503 (1963); **131**, 2433 (1963); **136**, A1107 (1964).

2. A. Wilson, *Quantum Theory of Metals*, 1941.
3. I. M. Lifshits, M. I. Kaganov, UFN, **78**, 411 (1962).
4. G. P. Motulevich, ZhETF, **46**, 287 (1964).
5. G. P. Motulevich, A. A. Shubin, ZhETF, **47**, 840 (1964).
6. V. L. Ginzburg, G. P. Motulevich, UFN, **55**, 469 (1955).
7. G. P. Motulevich, A. A. Shubin, O. F. Shustova, Preprint, P. N. Lebedev Physical Institute, Academy of Sciences of the USSR, 1965.
8. A. I. Golovashkin, G. P. Motulevich, ZhETF, **47**, 64 (1964).
9. A. I. Golovashkin, G. P. Motulevich, ZhETF, **44**, 398 (1963); **48**, 825 (1965).
10. V. P. Silin, ZhETF, **33**, 1282 (1957); **34**, 707 (1958); *Soviet Physics—Solid State*, **1**, 705 (1959).
11. L. P. Pitaevskii, ZhETF, **34**, 942 (1958).
12. R. N. Gurzhi, ZhETF, **35**, 965 (1958).
13. L. D. Landau, E. M. Lifshits, *Statistical Physics*, Moscow, "Nauka," 1964.
14. V. L. Ginzburg, V. P. Silin, ZhETF, **29**, 64 (1955).
15. J. N. Hodgson, Phil. Mag., **5**, 272 (1960).
16. J. N. Hodgson, Phil. Mag., **6**, 509 (1961).
17. J. N. Hodgson, Phil. Mag., **7**, 229 (1962).

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