

On the theory of Raman scattering of light in superconductors

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The modifications in the theory of Raman scattering of light in superconductors, which appear as a result of taking into account the anisotropy of the electronic spectrum and the electron Coulomb interaction, are considered. It is shown that the scattering probability is strongly anisotropic and varies from 10^{-3} up to a value exceeding by several times that previously obtained for an isotropic model and without account of Coulomb interaction.

During the period elapsed since the publication of the theory of the Raman effect in superconductors,^[1] interest in this phenomenon has grown considerably (see^[2,3]). This is undoubtedly related to the improved experimental possibilities; there is reason to hope that the effect will be investigated experimentally in the near future. In this connection we encounter the question of the accuracy of the calculation carried out in^[1] for the simplest model.

The model adopted in^[1] for the electrons is in fact the model of a neutral isotropic Fermi gas. Long-wave and low-frequency fluctuations of the electron density are the fundamental cause of the light scattering. If the Coulomb forces are taken into consideration, then, as is well known, such low-frequency oscillations turn out to be impossible because the longitudinal electric field (which arises in this connection) leads to a screening of the charge, and consequently also leads to oscillations of the electron density over distances of the order of interatomic distances. This fact might produce an appreciable decrease in the amplitude of the effect ($\sim (qa)^4$, where a is the interatomic distance and q denotes the wave vector of light in the metal) if the metal were actually isotropic.

However, the situation is different in an anisotropic metal, since in actual fact the question is not that of fluctuations of the density but fluctuations of the quantity corresponding to the operator

$$\sum_p a_p^+ \frac{\partial^2 \epsilon}{\partial p_i \partial p_k} a_p,$$

evaluated on the Fermi surface, and which is certainly not equal to $(1/m) \sum_p a_p^+ a_p \delta_{ik}$, as would be true in an isotropic metal. It is seen therefore that to obtain a correct estimate of the amplitude of the Raman effect it is necessary to investigate simultaneously the effects due to anisotropy and due to the Coulomb interaction. This will be done in the present article.

First let us write down the Hamiltonian describing the interaction of the electrons with the electromagnetic field. The simplest procedure is to write down the energy operator of an electron in a lattice as a function of the generalized momentum $\mathbf{p} - (e/c)\mathbf{A}$ and expand it in powers of \mathbf{A} up to terms of second order. Then the interaction corresponds to the operator

$$H_{int} = \int \left[-\frac{e}{c} \psi^+ \frac{\partial \epsilon}{\partial p_i} \psi A_i + \frac{e^2}{2c^2} \psi^+ \frac{\partial^2 \epsilon}{\partial p_i \partial p_k} \psi A_i A_k \right] dV. \quad (1)$$

But whereas such a procedure seems natural to first order in \mathbf{A} , doubts may arise with regard to the second-order terms.¹⁾ Let us show that this is actually so for not too large frequencies. We consider the model of

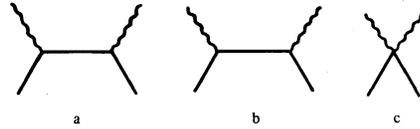


FIG. 1

mutually non-interacting electrons in a periodic field, and we apply the effective-mass approximation.

Let the energy of an electron with quasi-momentum \mathbf{p} in a certain band (we are, of course, interested in the conduction band) be $\epsilon_n(\mathbf{p})$, and let the corresponding Bloch function be $e^{i\mathbf{p} \cdot \mathbf{r}} u_{n\mathbf{p}}(\mathbf{r})$. We represent the function at a nearby point $\mathbf{p} + \mathbf{k}$ in the form

$$e^{i(\mathbf{p}+\mathbf{k}) \cdot \mathbf{r}} \sum_n C_n u_{n\mathbf{p}}(\mathbf{r}).$$

By substituting this expression in the Schrödinger equation with the Hamiltonian $H = -\nabla^2/2m + U(\mathbf{r})$, we verify that the "perturbation" operator is given by $\hat{v} \cdot \mathbf{k} + k^2/2m$ for small \mathbf{k} , where $\hat{v} = -i\nabla/m$. From this we can obtain the following formula:

$$\frac{\partial^2 \epsilon_n(\mathbf{p})}{\partial p_i \partial p_k} = \frac{1}{m} + \sum_{m \neq n} \frac{(\hat{v}_i)_{mn} (\hat{v}_k)_{nm} + (\hat{v}_i)_{nm} (\hat{v}_k)_{mn}}{\epsilon_n(\mathbf{p}) - \epsilon_m(\mathbf{p})}, \quad (2)$$

where the summation goes over states with quasi-momentum \mathbf{p} in different bands.

The operator describing the interaction of an electron with an electromagnetic field is of the form

$$\int \left[-\frac{e}{c} \psi^+ \hat{v} \psi \mathbf{A} + \frac{e^2}{2mc^2} \psi^+ \psi \mathbf{A}^2 \right] dV. \quad (3)$$

Let us imagine that the field contains a component with frequency ω_1 and amplitude A_1 and another component with frequency ω_2 and amplitude A_2 . We are interested in the part of the electron scattering amplitude which is proportional to $A_{1i} A_{2k}$. It is expressed by the diagrams shown in Fig. 1 and is described by the expression

$$\left[\sum_{m \neq n} \frac{(\hat{v}_i)_{nm} (\hat{v}_k)_{mn'}}{\epsilon_n - \epsilon_m + \omega_1} + \sum_{m \neq n} \frac{(\hat{v}_k)_{nm} (\hat{v}_i)_{mn'}}{\epsilon_n - \epsilon_m - \omega_2} + \frac{1}{m} \right] \frac{e^2}{c^2} A_{1i} A_{2k}. \quad (4)$$

Here the states n and m have different quasi-momenta, and therefore they may pertain to a single band.

We assume that the bands are non-degenerate or, if degeneracy exists, then $(\hat{v}_i)_{nm} = 0$ for such bands. Since we are interested in small changes of the frequency, i.e., $\omega_1 \approx \omega_2$, the initial and final states (n and n') refer to a single band. From the summation in Eq. (4) we separate the term in which the state m refers to the same band as n does (in this case the condition $m \neq n$ is satisfied be-

cause of the change in the value of the quasi-momentum). In this term (correct to within terms of order v/c) $\epsilon_n = \epsilon_m' (\hat{v}_i)_{nm} = (\hat{v}_i)_{mn}$ and therefore relative to the remaining terms it is of order²⁾

$$\frac{\omega_1 - \omega_2}{\omega} \sim \frac{\Delta}{\omega} \ll 1.$$

Thus, only the terms involving interband transitions are left in the sum. If $|\epsilon_n - \epsilon_m| \gg \omega_1 \approx \omega_2$ for these terms, then by comparing with expression (2) we obtain the expression $\partial^2 \epsilon / \partial p_i \partial p_k$ inside the brackets in (4).

Thus, calculation of the interband transitions in second-order perturbation theory from the first term in (3) is equivalent (for the case under consideration) to the replacement of $(1/m)\delta_{ik}$ in the second term of (3) by $\partial^2 \epsilon / \partial p_i \partial p_k$. Hence one can actually use the Hamiltonian (1) and consider only the conduction band.

There is no reason to repeat here the derivation given in^[1]. We only note the differences. In evaluating the function f (formula (5) in^[1]) it is necessary to divide the integration into an integration over ξ and over the equal-energy surface. Since $vq \gg q_0$ (q_0 is the energy transfer), the surface integration reduces to (as always happens in connection with the anomalous skin effect) an integration over a narrow strip $\mathbf{v} \cdot \mathbf{q} \approx 0$. In addition, it is necessary to take into consideration that $\partial^2 \epsilon / \partial p_i \partial p_k$ appears in our calculation instead of $1/m$. Thus, in the anisotropic case it is necessary to make the following substitution in formula (4) of^[1]

$$\frac{1}{m^2} R(q_0) \rightarrow \left(\frac{\partial^2 \epsilon}{\partial p_i \partial p_k} \right)^2 |A_{2i} A_{2k}'(q_0)|^2,$$

and the following substitution should be made in formula (7)

$$\frac{1}{m^2} f(q_0) \rightarrow \frac{1}{2\pi} \int d\varphi f(q_0, \Delta(\varphi), \varphi) \theta(q_0 - 2\Delta(\varphi)) \left(\frac{\partial^2 \epsilon}{\partial p_i \partial p_k} \right)^2 \quad (5)$$

($\theta(x) = 1$ for $x > 0$, $\theta(x) = 0$ for $x < 0$). In this formula the integration is performed over the strip $\mathbf{g} \cdot \mathbf{v} = 0$, and only over that region where $2\Delta(\varphi) < q_0$. The explicit $f(\varphi)$ dependence is associated with the factor $[\pi^2 v^2(\varphi) K(\varphi)]^{-1}$, where $K(\varphi)$ denotes the Gaussian curvature of the Fermi surface.³⁾ This factor replaces the expression $p_0^2/v^2 \pi^2$ appearing in formula (7) of^[1].

Now let us consider what the role of the Coulomb interaction reduces to. The strongest effect due to the longitudinal electric field can be taken into account if, instead of diagram c on Fig. 1, we sum the chain of diagrams shown in Fig. 2, where the Coulomb interaction $4\pi e^2/q^2$ is denoted by the dotted lines. In the present case we are interested in the case $qv \gg q_0 \sim \Delta$, $q \ll p_0$. It is easy to verify that taking superconductivity into account in the loops leads to corrections of order

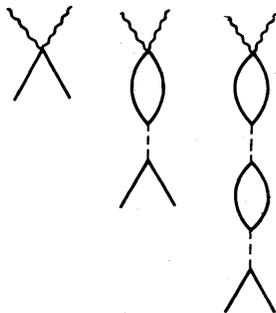


FIG. 2

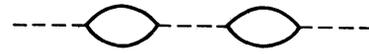


FIG. 3

$(\Delta/qv)^2 \ll 1$. In view of this, we can carry out the calculation for the normal metal. In the case under consideration all of the loops (with the exception of the very last) are given by

$$\bar{\Pi} = -2 \int \frac{dS}{v(2\pi)^3} = -\frac{\kappa^2}{4\pi e^2},$$

where κ is the reciprocal Debye radius, which is of the order of $1/a$; a is the atomic spacing.⁴⁾ The summation of the loops shown in Fig. 3 leads to the appearance of a screened Coulomb interaction

$$\frac{4\pi e^2}{q^2 + \kappa^2} \approx \frac{4\pi e^2}{\kappa^2},$$

because $\kappa \gg q$.

The outermost loop in the diagrams shown in Fig. 2 except in the first diagram is given by

$$-2 \int \frac{dS}{v(2\pi)^3} \frac{\partial^2 \epsilon}{\partial p_i \partial p_k} = -\frac{\overline{\partial^2 \epsilon}}{\partial p_i \partial p_k} \frac{\kappa^2}{4\pi e^2},$$

where the bar denotes averaging over the Fermi surface. The sum of all the diagrams in Fig. 2 leads to the result that the difference $\partial^2 \epsilon / \partial p_i \partial p_k - \overline{\partial^2 \epsilon} / \partial p_i \partial p_k$ appears instead of $\partial^2 \epsilon / \partial p_i \partial p_k$. Therefore, the complete formula, including the Coulomb interaction, is not given by Eq. (5) but rather by

$$\frac{1}{m^2} f(q_0) \rightarrow \frac{1}{2\pi} \int d\varphi f(q_0, \Delta(\varphi), \varphi) \theta(q_0 - 2\Delta(\varphi)) \left(\frac{\partial^2 \epsilon}{\partial p_i \partial p_k} - \frac{\overline{\partial^2 \epsilon}}{\partial p_i \partial p_k} \right)^2 \quad (6)$$

Now let us analyze the obtained formula. The anisotropy $\Delta(\varphi)$ appears most strongly near the absorption threshold. Let us assume that the minimum point of $\Delta(\varphi)$ on the strip $\mathbf{q} \cdot \mathbf{v} = 0$ does not coincide with an extremum of the remaining part of formula (6) or, if it does, then this extremum is not steep. Near the minimum $\Delta = \Delta_0 [1 + a(\varphi - \varphi_0)^2]$, where $a \sim 1$ ($a > 0$). Substituting this result into (6) and taking into consideration that $f \propto q_0 - 2\Delta$ for $q_0 - 2\Delta \ll \Delta$, we find that the function given by Eq. (6) is proportional to $(q_0 - 2\Delta_0)^{3/2}$ near the threshold $q_0 = 2\Delta_0$. From here it is seen that although the anisotropy smears somewhat the behavior of the scattering near threshold, the growth nevertheless remains rather abrupt.

We shall see below that cases are possible when a small range of angles near the maximum of the integrand gives the major contribution to the integral (6). If the minimum of $\Delta(\varphi)$ coincides with this point, then in view of the fact that $\Delta(\varphi)$ is usually a smooth function, in this case the previous dependence near threshold is preserved in practice: $f(q_0) \propto (q_0 - 2\Delta_0)$.

According to formula (6) the scattering probability is equal to zero in an isotropic metal, but the alkali metals, where superconductivity does not exist, are the only such examples. In all remaining metals the anisotropy is quite substantial.

Let us attempt to estimate the change in the probability of the Raman effect due to the anisotropy. If the idea of a small pseudo-potential can be used as a guide, then far away from the intersection of the Fermi surface with the edge of the Brillouin zone the correction to ϵ will be of the order of $V^2/\epsilon p$. But it is precisely this correction which is anisotropic. Therefore, if the directions i and k are not "special," namely, if they do not

coincide with the normal to the boundary of the Brillouin zone, then the scattering probability obtained in^[1] should be reduced by a factor $(V/\epsilon_F)^4$, which is usually of the order of 10^{-3} to 10^{-4} .

However, if we encounter a "special" direction, then the situation turns out differently. If the weak-coupling approximation is used, the formula for the energy has the following form near the intersection

$$\epsilon = \frac{p_x^2 + p_z^2 + (K/2)^2}{2m} \pm \left[\left(\frac{p_x K}{m} \right)^2 + V^2 \right]^{1/2}, \quad (7)$$

where p_z is measured from the zone boundary in the direction perpendicular to it, K is the corresponding period of the reciprocal lattice, and V is the pseudopotential. If $V \ll \epsilon_F \sim K^2/2m$, then $\partial^2 \epsilon / \partial p_x^2 = \partial^2 \epsilon / \partial p_y^2 = 1/m$, but $\partial^2 \epsilon / \partial p_z^2 = K^2/m^2 V$ provided $p_z < Vm/K$.

It is also necessary to recognize that the quantity $\alpha(\varphi) = [\pi^2 v^2(\varphi) K(\varphi)]^{-1}$ appears inside the integral in formula (5). In the neighborhood of the singular region the square of the velocity, $v^2(\varphi)$, is of the usual order of magnitude, but $K(\varphi) \sim \sqrt{Vm} \sim p_0 \sqrt{V/\epsilon_F}$.

If the strip $\mathbf{q} \cdot \mathbf{v} = 0$ does not pass near the intersection, then the neighborhood of the intersection only gives an appreciable contribution to $\partial^2 \epsilon / \partial p_z^2$. The probability of a contribution of order ϵ_F/V is of the order of V/ϵ_F . Therefore, the intersection region gives a contribution of the order of unity to $\partial^2 \epsilon / \partial p_z^2$. In this case for $i = k = z$ the small factor does not appear in Eq. (6), and the estimate of the amplitude given in^[1] remains valid.

Finally let us consider the case when the strip $\mathbf{q} \cdot \mathbf{v} = 0$ passes through the intersection region. Since $v_z = 0$ at the intersection itself, it would be best to take \mathbf{q} in the z direction. But in this case only the derivatives of ϵ with respect to p_x and p_y enter into expression (6). Therefore we take \mathbf{q} in the x direction and consider $i = k = z$. In the intersection region we have

$$\frac{\partial^2 \epsilon}{\partial p_x^2} \sim \frac{e_F}{mV}, \quad \frac{\partial^2 \epsilon}{\partial p_z^2} \sim \frac{1}{m}.$$

Therefore

$$\left(\frac{\partial^2 \epsilon}{\partial p_x^2} - \frac{\partial^2 \epsilon}{\partial p_z^2} \right)^2 \frac{1}{K(\varphi)} \sim \frac{e_F^{1/2}}{m^{1/2}} \left(\frac{e_F}{V} \right)^{1/2}.$$

This region itself has a probability V/ϵ_F of being in the belt.

After integration over φ we obtain the factor $(\epsilon_F/V)^{1/2}$ in comparison with the old estimate. Thus, in this case

the effect is enhanced by a factor of several times.

From what has been said it follows that taking account of the Coulomb interaction together with the anisotropy of the spectrum leads to a very strong anisotropy in the probability for the Raman effect, where this anisotropy may vary within the limits from 10^{-3} up to several times the value obtained in^[1]. The best condition for observation of this effect is when the incident and scattered light is polarized in the direction of the open orbits on the Fermi surface.

¹Such doubts were expressed by I. E. Dzyaloshinskiĭ, and the proof cited below appeared as a consequence.

²This has already been mentioned in [1]. The consideration of superconductivity does not change the situation. The difference between ϵ_n and ϵ_m leads to a correction of order $(v/c)^2$ in the summation (4).

³Since the momentum integration is restricted by the condition $\mathbf{q} \cdot \mathbf{v} = 0$, it is convenient to use the following transformation of the integral (see [4], Sec. 7.3):

$$\int d^3p \rightarrow \int d\epsilon \oint \frac{dS}{v} \rightarrow \int d\epsilon \int \frac{d\Omega_v}{vK(\theta, \varphi)}$$

where $\oint dS$ —the integral over the equal-energy surface—is expressed in terms of an integral over the angles of the normal vector to the surface, i.e., the velocity: $K(\theta, \varphi)$ denotes the Gaussian curvature of the surface at the point where the direction of the velocity is given by (θ, φ) . It is necessary to choose the polar axis along \mathbf{q} . After doing this one is left with an integral $\int d\phi$ in which $K(\pi/2, \phi) \equiv K(\phi)$ appears.

⁴The expression for Π is well known (see, for example, Sec. 22 of [5]). In the anisotropic case it is necessary to transform the momentum integral according to the rule indicated in the first footnote.

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