

ELECTRICAL CONDUCTIVITY OF ISOTOPICALLY DISORDERED METALS

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We consider the electric conductivity of metals due to isotopic disorder. We show that the residual resistivity appears already in the Born approximation with respect to the electron–phonon interaction if account is taken of the actual amplitude of the elastic scattering of electrons in the vibrating crystal. The temperature-dependent part of the resistivity is analyzed.

1. INTRODUCTION

IN an earlier paper<sup>[1]</sup> we developed the theory of electric conductivity of metals with nonmagnetic impurities, when the concentration of the latter is small. This theory can, naturally, be directly extended to include the case when the impurity atoms are isotopes. This, however, affords an opportunity of considering an arbitrary isotopic concentration, for now it is possible to use in the problem of a second small parameter, namely the ratio of the difference of the isotope masses to the average mass.

The dependence of the electric conductivity on the isotopic composition is physically due to two causes. First, the phonon spectrum of the metal changes with changing composition, and with it the resistance due to the scattering of the electrons by the phonons. On the other hand, although it can be assumed that the amplitude for the scattering of the electrons by an individual ion has the same value for the different isotopes, and consequently static ordering is present, nonetheless, owing to the difference in the isotope masses, dynamic disorder appears. This leads to an additional source of electron scattering, and consequently to an additional resistance. The presence of an isotopic dynamic disorder should lead, in particular, to the appearance of a residual resistance in an ideally pure metal.

This fact was first pointed out by Pomeranchuk<sup>[2]</sup>. He found that the residual resistance appears only if account is taken of an approximation higher than the Born approximation in the electron-phonon interaction, and by virtue of this his final result depended on the constant of this interaction to the fourth power.

Actually, the residual resistance appears already in the Born approximation. This is connected with the fact that the true amplitude of the elastic scattering of the electron in the n-th ion,  $b_n(\mathbf{q})$ , is not the amplitude of scattering by the fixed ion,  $a_n(\mathbf{q})$ , but the product

$$b_n(\mathbf{q}) = a_n(\mathbf{q}) e^{-W_n(\mathbf{q})/2}, \tag{1.1}$$

where the factor  $\exp(-W_n(\mathbf{q})/2)$  determines the amplitude of the probability of non-excitation of the phonons when a momentum  $\mathbf{q}$  is transferred to the ion ( $W_n(\mathbf{q})$  is the usual Debye-Waller factor). Here

$$b_n(\mathbf{q}) - b_m(\mathbf{q}) = a_n(\mathbf{q}) (e^{-W_n(\mathbf{q})/2} - e^{-W_m(\mathbf{q})/2}). \tag{1.2}$$

But when  $T = 0$  the Debye-Waller factor differs from zero as a result of the zero-point oscillations and depends on the mass of the oscillating atom. Thus, for different isotopes the difference (1.2) turns out to be

different from zero, and the residual resistance appears already in the first Born approximation.

In the present paper we develop a theory which takes into account in explicit form the causes of the influence of the isotopic composition on the electric conductivity of the metal. For the interaction between the electron and the individual ion we use here the ordinary concept of the pseudopotential, and we solve the problem under the same assumptions as in<sup>[1]</sup>. We note, however, that the two main important assumptions used in<sup>[1]</sup>, namely the invariance of the electron spectrum and the invariance of the force constants in the dynamic oscillation matrix upon introduction of the impurities, are satisfied automatically in the isotopic case.

2. DETERMINATION OF THE SCATTERING CORRELATION FUNCTION

The general expression for the resistance is

$$\rho = \frac{1}{2\tau} \frac{\int d\mathbf{k} d\mathbf{k}' (\varphi_{\mathbf{k}} - \varphi_{\mathbf{k}'})^2 f_{\mathbf{k}}^{(0)} (1 - f_{\mathbf{k}'}^{(0)}) W_{\mathbf{k}\mathbf{k}'}(\mathbf{q}, \omega)}{\left| \int d\mathbf{k} e^{i\mathbf{q}\cdot\mathbf{r}_\mathbf{k}} \varphi_{\mathbf{k}} (\partial f_{\mathbf{k}}^{(0)} / \partial \mathbf{e}_{\mathbf{k}}) \right|^2}, \tag{2.1}$$

where the probability  $W_{\mathbf{k}\mathbf{k}'}$  of the transition of the electron from the state  $\mathbf{k}$  to the state  $\mathbf{k}'$  upon scattering is defined by

$$W_{\mathbf{k}\mathbf{k}'} = \frac{(2\pi)^2}{m_e^2 V_0} a^2(\mathbf{q}) S(\mathbf{q}, \omega), \tag{2.2}$$

$$S(\mathbf{q}, \omega) = \frac{1}{N} \sum_{nn'} \exp\{i\mathbf{q}(\mathbf{R}_n^{(0)} - \mathbf{R}_{n'})\} \langle \exp\{-(W_n + W_{n'})/2\} \{2\pi\delta(\omega) + \langle (\mathbf{q}u_n(t) | \mathbf{q}u_{n'}(0) \rangle_\omega\} \rangle_c \equiv S_1(\mathbf{q}, \omega) + S_2(\mathbf{q}, \omega), \tag{2.3}$$

$$W_n(\mathbf{q}) = \langle (\mathbf{q}u_n(0))^2 \rangle. \tag{2.4}$$

For  $\varphi_{\mathbf{k}}$  we assume the usual first-approximation value  $\varphi_{\mathbf{k}} = \kappa \cdot \mathbf{k}$ . We use throughout the same notation as in<sup>[1]</sup>. The angle brackets  $\langle \dots \rangle_c$  denote averaging over the configurations of the isotopes, and we consider an arbitrary isotopic composition.

We have left out from (2.3) the terms corresponding to multiphonon scattering of the electrons. It is easy to show, however, that even the two-phonon term contains, when compared with the single-phonon term retained in (2.3), so small a parameter as  $\sqrt{m/M}$ , where  $m$  and  $M$  are the masses of the electron and the ion.

Let us consider the term  $S_1(\mathbf{q}, \omega)$  corresponding to pure elastic scattering of the electrons. Recognizing that  $W_n \ll 1$ , we expand the exponential in a series, retaining the first three terms of the expansion. It is easy to see that all terms of the expansion, with the exception of the one containing the mixed product  $W_n W_{n'}$ , leads to the appearance of  $\delta(\mathbf{q})$ . But those terms of  $W_{\mathbf{k}\mathbf{k}'}$

which contain simultaneously  $\delta$  functions in the energy and in the momentum will of course lead to no resistance whatever. Thus, the only term responsible for the actual scattering of the electrons is

$$S_1(\mathbf{q}, \omega) = \frac{1}{N} \sum_{nn'} \exp\{i\mathbf{q}(\mathbf{R}_n^{(0)} - \mathbf{R}_{n'}^{(0)})\} 2\pi\delta(\omega) \frac{1}{4} \langle W_n W_{n'} \rangle. \quad (2.5)$$

Thus, to determine the resistance we have to find correlators of two types—the ordinary correlator contained in (2.3) and responsible for the inelastic single-phonon scattering of the electrons, and the correlator in (2.5), which actually determines the residual resistance.

We introduce the retarded Green's function, defined in terms of the displacements:

$$G_{nn'}^{\alpha\beta}(t) = -i\Theta(t) \langle [u_n^\alpha(t) u_{n'}^\beta(0)] \rangle, \quad (2.6)$$

where  $\Theta(t)$  is the usual step function. The Hamiltonian of the vibrational problem has in our case the form

$$H = \sum_n \frac{\mathbf{p}_n^2}{2M_n} + \frac{1}{2} \sum_{nn'} \Phi^{\alpha\beta}(\mathbf{n} - \mathbf{n}') u_n^\alpha u_{n'}^\beta. \quad (2.7)$$

We then obtain directly for the Dyson equation corresponding to the Green's function (2.6)

$$G_{nn'}^{\alpha\beta}(\omega) = G_{nn',0}^{\alpha\beta}(\omega) + \omega^2 \sum_{n_1} G_{nn_1,0}^{\alpha\gamma}(\omega) (M_c - M_{n_1}) G_{n_1 n'}^{\gamma\beta}(\omega), \quad (2.8)$$

$$G_{nn',0}^{\alpha\beta}(\omega) = \frac{1}{M_c N} \sum_{ij} \frac{v_{ij}^\alpha v_{ij}^\beta \exp\{i\mathbf{q}(\mathbf{R}_n^{(0)} - \mathbf{R}_{n'}^{(0)})\}}{\omega^2 - \omega_{ij}^2}. \quad (2.9)$$

Here  $M_c = \langle M_n \rangle_c$ , and the Green's function (2.9) corresponds to an ideal lattice with  $M = M_c$ .

The solution of (2.8) can be represented in the form of an iteration series, which is in fact a series in powers of the relative change of the isotope mass—the small parameter of the problem. Retaining terms quadratic in this parameter, we have

$$G_{nn'}^{\alpha\beta}(\omega) = G_{nn',0}^{\alpha\beta}(\omega) + \omega^2 \sum_{n_1} G_{nn_1,0}^{\alpha\gamma}(\omega) (M_c - M_{n_1}) G_{n_1 n'}^{\gamma\beta}(\omega) + \omega^4 \sum_{n_1} G_{nn_1,0}^{\alpha\gamma}(\omega) (M_c - M_{n_1}) G_{n_1 n_2,0}^{\gamma\delta}(\omega) (M_c - M_{n_2}) G_{n_2 n'}^{\delta\beta}(\omega). \quad (2.10)$$

To calculate the correlator contained in  $S_2(\mathbf{q}, \omega)$  it is necessary to average the Green's function over the configurations of the isotopes. It is important that when the zeroth Green's function is chosen in the form (2.9), the linear term of (2.10) disappears. We have

$$\langle G_{nn'}^{\alpha\beta}(\omega) \rangle_c = G_{nn',0}^{\alpha\beta}(\omega) + \omega^4 M_c^2 \sum_{n_1} G_{nn_1,0}^{\alpha\gamma}(\omega) G_{n_1 n',0}^{\gamma\delta}(\omega) G_{n_2 n'}^{\delta\beta}(\omega), \quad (2.11)$$

where

$$\xi^2 = \frac{\langle M_n^2 \rangle_c - M_c^2}{M_c^2}. \quad (2.12)$$

To determine the correlator in  $S_1(\mathbf{q}, \omega)$  we shall use the usual connection between the correlation functions and the imaginary part of the Green's function

$$\langle u_n^\alpha(t) u_{n'}^\beta(0) \rangle_\omega = -\frac{2\text{Im} G_{nn'}(\omega)}{1 - e^{-\omega/T}}. \quad (2.13)$$

(Here and below  $\hbar = 1$  and  $T$  is in energy units.) Then, taking into consideration the explicit form of (2.3),

$$\langle W_n W_{n'} \rangle_c = \frac{q^\alpha q^\beta q^\gamma q^\delta}{(2\pi)^2} \iint d\omega_1 d\omega_2 \frac{1}{1 - e^{-\omega_1/T}} \times \frac{1}{1 - e^{-\omega_2/T}} \langle \text{Im} G_{nn}^{\alpha\beta}(\omega_1) \text{Im} G_{n'n'}^{\gamma\delta}(\omega_2) \rangle_c, \quad (2.14)$$

we use the expansion (2.10). Here, however, none of the Green's functions which enter into the obtained expressions can be replaced by the zeroth function, again because in this case a  $\delta$  function in the momentum transfer appears in  $S_1$  of (2.5). Therefore the first nonvanishing approximation for the residual resistance corresponds to a replacement of both Green's functions in (2.12) by the terms linear in the mass difference of (2.10). Then

$$\langle \text{Im} G_{nn}^{\alpha\beta}(\omega_1) \text{Im} G_{n'n'}^{\gamma\delta}(\omega_2) \rangle_c \rightarrow \omega_1^2 \omega_2^2 M_c^2 \times \sum_{n_1} (\text{Im} G_{nn_1,0}^{\alpha\gamma}(\omega_1) G_{n_1 n',0}^{\gamma\delta}(\omega_1)) (\text{Im} G_{n'n_1,0}^{\gamma\delta}(\omega_2) G_{n_1 n',0}^{\alpha\beta}(\omega_2)).$$

Substituting here (2.9), we obtain after appropriate calculations the final expression for

$$S_1(\mathbf{q}, \omega) = 2\pi\delta(\omega) \frac{\xi^2}{16M_c^2} \left[ \frac{1}{N} \sum_{ijj'} (\mathbf{q}v_{ij}) (\mathbf{v}_{ij}\mathbf{v}_{i+q,j'}) (\mathbf{q}\mathbf{v}_{i+q,j'}) \times \frac{\omega_{ij}(2n_{ij} + 1) - \omega_{i+q,j}(2n_{i+q,j'} + 1)}{\omega_{ij}^2 - \omega_{i+q,j'}^2} \right]^2 \equiv 2\pi\delta(\omega) S_1(\mathbf{q}). \quad (2.15)$$

We now determine  $S_2(\mathbf{q}, \omega)$ . Using (2.13), (2.11), and (2.9), we get

$$S_2(\mathbf{q}, \omega) = \frac{2\pi \text{sign } \omega}{1 - e^{-\omega/T}} \frac{1}{M_c} \sum_j (\mathbf{q}v_{qj})^2 \left\{ \delta(\omega^2 - \omega_{qj}^2) - \xi^2 \omega^4 \frac{1}{\pi} \text{Im} \left( Z(\omega^2) \frac{d}{d\omega^2} \frac{1}{\omega^2 - \omega_{qj}^2 + i\varepsilon} \right) \right\}, \quad (2.16)$$

$$Z(\omega^2) = I(\omega^2) - i\pi g(\omega^2),$$

$$I(\omega^2) = f d\omega_1^2 \frac{g(\omega_1^2)}{\omega^2 - \omega_1^2}$$

Expressions (2.15) and (2.16) define, in accordance with (2.2) and (2.3), the scattering probability  $W_{\mathbf{k}\mathbf{k}'}$  in an approximation which is quadratic in the isotope mass difference, and at the same time determine also the value of the resistance (2.1) in an isotopically disordered metal.

### 3. RESISTANCE OF ISOTOPICALLY DISORDERED METAL. DISCUSSION OF RESULTS

1. When  $T \rightarrow 0$ , the contribution made to  $\rho$  by the term (2.16) vanishes, and the residual resistance is determined only by the term (2.15). Let us write down the explicit form of this correlation function for  $T = 0$ :

$$S_1^{(0)}(\mathbf{q}, \omega) = 2\pi\delta(\omega) \frac{\xi^2}{16M_c^2} \times \left[ \frac{1}{N} \sum_{ijj'} \frac{(\mathbf{q}v_{ij}) (\mathbf{v}_{ij}\mathbf{v}_{i+q,j'}) (\mathbf{q}\mathbf{v}_{i+q,j'})}{\omega_{ij} + \omega_{i+q,j'}} \right]^2 \equiv 2\pi\delta(\omega) S_1^{(0)}(\mathbf{q}). \quad (3.1)$$

Calculating (3.1), we get approximately

$$S_1^{(0)}(\mathbf{q}) \approx \frac{\xi^2 q^4}{32M_c^2 \omega_D^2} \beta^2(\mathbf{q}), \quad \beta^2(\mathbf{q}) \lesssim 1, \quad (3.2)$$

where  $\omega_D$  is the end-point frequency of the phonon spectrum.

To find the residual resistance  $\Delta\rho_0$  we substitute (3.1) in (2.1) and (2.2). The integral contained in the numerator of (2.1) can be transformed to

$$\frac{(2\pi)^3 T}{3m_*^2 V_0} \int_{\varepsilon_{\mathbf{k}} = \varepsilon_F} \int_{\varepsilon_{\mathbf{k}'} = \varepsilon_F} \frac{dS_{\mathbf{k}} dS_{\mathbf{k}'}}{|\mathbf{v}_{\mathbf{k}}| |\mathbf{v}_{\mathbf{k}'}|} a^2(\mathbf{q}) q^2 S_1^{(0)}(\mathbf{q}). \quad (3.3)$$

In the case of inelastic scattering by phonons in a regular monatomic crystal with  $M = M_c$ , the same integral will be determined by the first term of (2.16). The corresponding value is

$$\frac{(2\pi)^3}{3m_e^2 V_0} \int_{\epsilon_k = \epsilon_F} \int_{\epsilon_{k'} = \epsilon_F} \frac{dS_k dS_{k'}}{|\mathbf{v}_k| |\mathbf{v}_{k'}|} a^2(\mathbf{q}) q^2 \times \frac{1}{M_c} \sum_j (\mathbf{q}\mathbf{v}_{qj})^2 n(\omega_{qj}) (n(\omega_{qj}) + 1). \quad (3.4)$$

When  $T \gtrsim \omega_D$  we have  $n(\omega_{qj})(n(\omega_{qj}) + 1) \rightarrow T^2/\omega_{qj}^2$ . Comparing (3.3) with (3.4) and taking into consideration the form of the expression (2.1), we get directly

$$\Delta\rho_0 = \rho_0\gamma, \quad \rho_0 = \rho(T = \omega_D), \quad (3.5)$$

where the first factor is the resistance of the regular metal at  $T = \omega_D$ , and  $\gamma$  is a certain mean value of the ratio

$$S_1(\mathbf{q}) \Big|_{M_c} \frac{\omega_D}{\sum_j} \frac{(\mathbf{q}\mathbf{v}_{qj})^2}{\omega_{qj}^2}$$

over the phase volume involved in (3.3) and (3.4), with a weight corresponding to the integrand of (3.4). Taking into account (3.2) as well as the fact that the main contribution to (3.3) and to (3.4) (in the latter case when  $T > \omega_D$ ) is made by large momentum transfers  $q \sim 2k_F$ , we obtain as an estimate

$$\gamma \approx \frac{\xi^2 k_F^2}{8M_c \omega_D} \beta_1, \quad \beta_1 \lesssim 1 \quad (3.6)$$

Expressions (3.5) and (3.6), with allowance for (2.12), make it possible to estimate the residual resistance and, in particular, to estimate the limiting electron mean free path corresponding to the concrete isotopic composition. The resistance, of course, turns out to be quite small, since  $\gamma \sim \xi^2 \sqrt{m/M}$ .

We note that Pomeranchuk's result<sup>[2]</sup> contains, compared with (3.5) and (3.6), an additional small parameter of the order  $V_{2k_F}/\epsilon_F \ll 1$ , where  $V_{2k_F}$  is the Fourier component of the pseudopotential. However, the numerical estimates are close to those obtained on the basis of (3.5) and (3.6), since the parameter  $V_{2k_F}/\epsilon_F$  was assumed to be close to unity.

2. We consider now the temperature-dependent part of the resistance. The influence of the isotopic composition on the resistance is manifest most strongly in this case by the first term of (2.16), where the isotope concentration appears in explicit form via  $M_c$  and in implicit form via  $\omega_{qj}$ . The point is that in the derivation of (2.7) and (2.8) it was assumed that the lattice with atom mass  $M = M_c$  is ideal. Therefore, for any isotopic composition we have rigorously, for fixed  $\mathbf{q}$  and  $j$ ,

$$M_c \omega_{qj}^2 = \text{const.} \quad (3.7)$$

Taking this into consideration, we can easily determine the dependence of (3.4) on the isotopic composition. Let us assume for concreteness some fixed isotopic composition (index  $c_0$ ) and retain only the first term in (2.16); we get

$$\rho_c(T) = \rho_{c_0}(T') \sqrt{M_{c_0}/M_c}, \quad T' = T \sqrt{M_c/M_{c_0}} \quad (3.8)$$

At low temperatures, where Bloch's law is valid, this leads directly to

$$\rho_c(T) = a_{c_0} (M_c/M_{c_0})^2 T^5. \quad (3.9)$$

The coefficient of  $T^5$  is quite sensitive to the isotopic composition, since it depends linearly on the isotope mass difference, and not quadratically (this, of course, pertains to the general temperature dependence of (3.8)).

Thus, in the case of a binary mixture ( $c$ —concentration of the first isotope), if we choose, for example,  $c_0 = 0$ , then

$$\rho_c(T) - \rho_{c_0}(T) \approx -2a_0 \frac{M_1 - M_2}{M_2} c T^5, \quad (3.10)$$

which coincides in the case of small concentration  $c$  with the result obtained in<sup>[1]</sup> for the case of equal amplitudes of electron scattering by the impurity ions and by the matrix.

In the classical limit with respect to temperature we have

$$\rho_c(T) \sim T' \sqrt{M_{c_0}/M_c},$$

and the resistance ceases to depend at all on the isotopic composition. We note that an analysis of (3.8) shows that the relative change of  $\rho$  with change of the composition decreases very sharply with increasing temperature.

3. The results obtained in the preceding section actually coincide with the result for a regular lattice, the mass of the atoms in which has a value  $M_c$  and changes with changing isotopic composition. The isotopic irregularity itself manifest and the coherent electron scattering that it produces become in those terms which are quadratic in the mass difference. The corresponding contribution to the resistance is made by both terms of (2.3). As to the elastic scattering of the electrons, this circumstance is already reflected in the residual resistance  $\Delta\rho_0$ . However, elastic scattering produces also a temperature-dependent resistance component  $\Delta\rho'$ , which can be determined from (2.1) by introducing in it  $S_1(\mathbf{q}, \omega) - S_1^{(0)}(\mathbf{q}, \omega)$ .

For the low-temperature region, taking into account the explicit form of (2.15) and (3.1) as well as (3.6), we get

$$\Delta\rho' \approx \rho_0 \delta\gamma_{\omega_T} / \omega_D, \quad (3.11)$$

where  $\omega_T$  is the energy of the phonon gas at the temperature  $T$  and is referred to the first mode. It follows therefore that  $\Delta\rho' \sim T^4$ .

The contribution of the inelastic scattering in the resistance component under consideration ( $\Delta\rho''$ ) is determined by the second term of (2.16). A direct analysis gives for the low-temperature region  $\Delta\rho'' \sim T^7$ . Thus, in an isotopically disordered metal, the low-temperature expansion of the resistance begins with a term proportional to  $T^4$ . It must be emphasized that this is of interest mostly from the fundamental point of view, since the term itself is small and it is very difficult to separate it against the background of the main term.

It follows from the form of (2.15) that in the classical region of temperatures  $\Delta\rho_0 + \Delta\rho' \rightarrow 0$ . On the other hand, it can be shown that in this region  $\Delta\rho'' \rightarrow 0$ . Thus, at high temperatures the influence of the isotopic disorder on the resistance of metals, and of the isotopic composition in general, disappears completely.

4. It is evident from the foregoing that in considering the dependence of the resistance of a metal on the isotopic composition we encounter two types of effects, one linearly and the other quadratically dependent on the isotope mass difference. At the present time the purity of crystals and the measurement accuracy have reached such a level that the quadratic effect should become manifest already in the case of a natural isotopic composition, let alone artificial isotopic mixtures. We have

in mind here principally the residual resistance  $\Delta\rho_0$ .

Naturally, measurement of the linear effects connected with the change of the temperature-dependent part of the resistance with changing composition, is much easier experimentally, primarily because of the much less stringent requirements with respect to the purity of the crystal. Indeed, in the three experimental studies performed to date of the dependence of the resistance on the isotopic composition (for Li<sup>[3,4]</sup> and Cd<sup>[5]</sup>), only the linear effect was analyzed. Special notice should be taken of<sup>[5]</sup>, where precision measurements were made for five isotopic compositions in a wide range of temperatures, and a specially detailed study was made of the low-temperature region. The observed results agree with the theory.

<sup>1</sup> Yu. Kagan and A. P. Zhernov, Zh. Eksp. Teor. Fiz. 50, 1107 (1966) [Sov. Phys.-JETP 23, 737 (1966)].

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