Faktorgruppe zu besseren Ergebnissen führt, als wenn nur die Punktgruppe des Moleküls in Betracht gezogen wird. Dies stellten bereits Hooper und James bei Raman-Messungen von polykristallinem AsJ_3 und SbJ_3 fest. Ihre Ergebnise konnten aber erst durch die Polarisationsmessungen an einem Einkristall von AsJ_3 bestätigt werden. Obwohl alle drei Trijodidkristalle verschiedenen Kristall-Charakter zeigen (AsJ_3 reiner Molekülkristall, SbJ_3 Übergang zwischen Molekül- und Ionenkristall, BiJ_3 vorwiegend Ionencharakter), gehören sie mit ihrer rhomboedrischen Einheitszelle, die jeweils zwei „Moleküle" enthält, zur Raumgruppe C_{3i}, und die Schwingungsanalyse läßt sich somit gemeinsam für alle drei durchführen. Die jeweils getroffene Zuordnung wird für die Fundamental- (innere und äußere) Schwingungen in Tab. 8 nochmals gemeinsam aufgeführt. Bei fast allen Schwingungen wird beim Übergang von AsJ_3 zu BiJ_3 eine Wellenzahlerniedrigung beobachtet. Eine Ausnahme bilden hierbei die entarteten Deformationsschwingungen (ν_6 und ν_8).

		AsJ_3 ν (cm^{-1})	SbJ_3 ν (cm^{-1})	BiJ_3 ν (cm^{-1})	Lit.
äußere Schwingungen:					
Rot.	ν_{p1} (E_g)	33,3	~33	~25	
	ν_{p2} (A_g)	39,0	38	36	
Transl.	ν_{p3} (E_g)	37,9	67,5(?)	?	
	ν_{p4} (A_g)	85 (?)	73 (?)	?	
innere Schwingungen:					
Molekül	*Kristall*				
ν_1 (A_1) <	ν_1 (A_g)	187,1	161,5	140	
	ν_3 (A_u)	201	177	145	(3)
ν_2 (A_1) <	ν_2 (A_g)	84,6	67,5	65	
	ν_4 (A_u)	102	89	90	(3)
ν_3 (E) <	ν_5 (E_g)	208,2	139	116	
	ν_7 (E_u)	216	147	115	(3)
ν_4 (E) <	ν_6 (E_g)	56,0	45,5	54(?)	
	ν_8 (E_u)	74	71	71	(3)

Tab. 8. Innere und äußere Schwingungen der Trijodide von Arsen, Antimon und Wismut in festem Zustand.

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Current Fluctuations of Hot Electrons

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In order to calculate the spectral density of current fluctuations in a high d. c. electrical field, a method using the one-electron density matrix is proposed. The nonperturbed problem is considered to be that of the electrons in an external field. The other interactions of electrons are expressed by means of a relaxation time matrix. To fit the expression of the current, given by the Boltzmannian formalism, a form of the diagonal terms of this matrix for electron-phonon interaction is suggested and closed formulae for the current fluctuations spectrum are obtained.

1. Introduction

In the current literature there are two principal ways in dealing with hot electron conduction, and related current fluctuations. One way is to modify the usual Boltzmann approach in order to account for the non-linear behaviour of hot electrons. A fluctuation theory was thus designed by **Gurevich**[1] and **Schlup**[2]. A semi-phenomenological point of view was used by **Price**[3]. The second way is based on the density matrix technique like in the Kubo's method, taking as many orders in the electrical field, as possible. This method was used mainly in conduction problems. If, for the steady-state current,

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[1] V. L. **Gurevich**, J. Exp. Theor. Phys. USSR **43**, 1771 [1962]. — V. L. **Gurevich** and R. **Katilius**, J. Exp. Theor. Phys. USSR **49**, 1145 [1965]. — S. V. **Gantsevich**, V. L. **Gurevich**, and R. **Katilius**, Fiz. Tver. Tela **11**, 308 [1969].

[2] W. A. **Schlup**, Phys. Kondens. Mat. **8**, 167 [1968].

[3] P. J. **Price**, Fluctuation Phenomena in Solids, ed. by R. E. **Burgess**, Academic Press, New York and London 1965, Chapter 8.

the results are quite satisfactory, in the case of the current noise spectral density the results are either crude or foamy and hard to understand and compare with experimental data.

The main idea of the present attempt, inspired from unpublished work by BÁNYAI[4], is to take exactly into account the electric field, by using the eigenfunctions of free electrons in an external field. The scattering interactions are treated as a perturbation. A formal expression is then obtained for the current fluctuation spectrum in the relaxation time approximation.

By means of a number of approximations and phenomenological speculations upon the relaxation time, as well as of an unorthodox cut-off of the integrals over the energy spectrum, we obtained a simple and plausible formula in the case of acoustic mode scattering at low and high fields.

2. The Steady State Current

Let us consider N electrons in a box of volume Ω, interacting with a scattering system and with an external electric Field E, chosen in the z-direction and assumed uniform. The total Hamiltonian of the problem will be:

$$\mathcal{H} = \boldsymbol{H}_0 + \boldsymbol{H}_{\mathrm{E}}' + \boldsymbol{V} \tag{2.1}$$

where $\boldsymbol{H}_0$ is the Hamiltonian of free electrons without field, $\boldsymbol{H}_{\mathrm{E}}'$ is the interaction with the electric field and $\boldsymbol{V}$ is the scattering potential. If the density of electrons is not too great, then the electron-electron interacting may be taken as negligible.

Let the electric field be switched on suddenly at $t=0$. Then

$$\boldsymbol{H}_{\mathrm{E}}' = \begin{cases} 0 & \text{at} \quad t \leqq 0\,, \\ \boldsymbol{H}_{\mathrm{E}} = e\,\boldsymbol{E}\,\boldsymbol{r} & \text{at} \quad t > 0\,. \end{cases} \tag{2.2}$$

We shall look for the stationary current, given by the virtual average

$$\langle I_{\mathrm{i}} \rangle = N \operatorname{Tr}\{\varrho_{\mathrm{st}}\, \boldsymbol{j}_{\mathrm{i}}\} \tag{2.3}$$

where $\boldsymbol{j}_i$ is the one-particle current operator in the i-direction and ϱ_{st} is the value of the density matrix in the steady-state regime. ϱ_{st} is gotten as the limit (i. e. when the transitory effects will be removed) of the solution of Liouville's equation:

$$i\,\frac{\partial \varrho}{\partial t} = [\mathcal{H}, \varrho] + i\,s(\varrho_0 - \varrho) \quad (s \to +0) \tag{2.4}$$

(units $\hbar = k_{\mathrm{B}} = 1$) with the initial condition

$$\varrho(0) = \varrho_0(\boldsymbol{H}_0 + \boldsymbol{V}) = Z^{-1}\, e^{-\beta(\boldsymbol{H}_0 + \boldsymbol{V})}\,, \qquad Z = \operatorname{Tr}\{e^{-\beta(\boldsymbol{H}_0+\boldsymbol{V})}\} \quad \text{and} \quad \beta = T^{-1}.$$

The last term in Eq. (2.4) represents a small interaction with the environment and amortises the oscillating terms in $\varrho(t)$.

The results obtained with the above form of the density matrix are equivalent to those obtained both in the many-body representation with variable number of particles, and in the one-body representation with Fermi statistics[5].

The solution of Eq. (2.4) may be written as:

$$\varrho(t) = \varrho_0 + \frac{1}{i} \lim_{s \to +0} \int_0^t \mathrm{d}t'\, e^{-st'}\, e^{-i\mathcal{H}t'}\, [\mathcal{H}, \varrho_0]\, e^{i\mathcal{H}t'} \tag{2.5}$$

so that the current is

$$\langle I_i \rangle = N \operatorname{Tr}\left\{ \frac{1}{i} \lim_{s \to +0} \int_0^\infty \mathrm{d}t [\mathcal{H}, \varrho_0]\, \boldsymbol{j}_i^{\mathcal{H}}(t)\, e^{-st} \right. \tag{2.6}$$

[$A^{\mathcal{H}}(t)$ being the operator $\boldsymbol{A}$ in the Heisenberg representation.]

At this stage of the problem we introduce two essential assumptions:

(i) The interaction term $\boldsymbol{V}$ is small in comparison with the free particle Hamiltonian – the so-called weak coupling.

(ii) The possibility of description, in the representation of eigenfunctions corresponding to $\boldsymbol{H}_0 + \boldsymbol{H}_{\mathrm{E}}$ also, of the scattering by means of a relaxation time matrix $\boldsymbol{\tau}$ which can be calculated from the quantum theory of perturbations.

The first assumption will allow us to make the approximation

$$\varrho_0(\boldsymbol{H}_0 + \boldsymbol{V}) \approx \varrho_0(\boldsymbol{H}_0) \tag{2.7}$$

and therefore

$$[\mathcal{H}, \varrho_0(\boldsymbol{H}_0 + \boldsymbol{V})] = [\boldsymbol{H}_{\mathrm{E}}, \varrho_0(\boldsymbol{H}_0 + \boldsymbol{V})] \approx [\boldsymbol{H}_0 + \boldsymbol{H}_{\mathrm{E}}, \varrho_0(\boldsymbol{H}_0)]\,. \tag{2.8}$$

Due to the second hypothesis, taking the matrix elements of the Laplace transform

$$\boldsymbol{J}_i(s) = \int_0^\infty \mathrm{d}t\, e^{-st}\, \boldsymbol{j}_i^{\mathcal{H}}(t) \tag{2.9}$$

between the eigenfunctions of $\boldsymbol{H}_0 + \boldsymbol{H}_{\mathrm{E}}$, with eigenvalues W_α, we can write

$$\lim_{s \to i\omega} (\boldsymbol{J}_i(s))_{\alpha\beta} = i\, \frac{(j_i)_{\alpha\beta}}{W_\alpha - W_\beta - \omega + i\,\tau_{\alpha\beta}^{-1}(\omega)}\,. \tag{2.10}$$

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[4] L. BANYAI, unpublished.

[5] M. LAX, Phys. Rev. **109**, 1921 [1958].

Hence, the expression of the current (2.6) becomes

$$\langle I_i \rangle = N \sum_{\alpha\beta} \frac{(W_\alpha - W_\beta)\,(\varrho_0)_{\alpha\beta}\,(j_i)_{\beta\alpha}}{W_\beta - W_\alpha + i\,\tau_{\beta\alpha}^{-1}\,(0)}\,. \tag{2.11}$$

Making use of the expressions for the matrix elements from the appendix (A.7 – 10) one obtains for the current densities

$$\langle J_x \rangle = \langle J_y \rangle = 0\,,$$

$$\langle J_z \rangle = \frac{N\,e^2\,E}{m\,\Omega} \sum_{\varepsilon} \sum_{\boldsymbol{K}_\perp} (\varrho_0)_{\varepsilon \boldsymbol{K}_\perp}\,\tau_{\varepsilon \boldsymbol{K}_\perp} \tag{2.12}$$

$$= \frac{n\,e}{2\,\pi\,m^2\,T\,L_z} \int \mathrm{d}\varepsilon \int \mathrm{d}\boldsymbol{K}_\perp \exp\{-K_\perp^2/2\,m\,T\}\,\tau_{\varepsilon \boldsymbol{K}_\perp} \tag{2.13}$$

and hence the electrical conductivity is

$$\sigma_{ij} = \delta_{ij} \frac{e^2\,n}{m} \sum_{\varepsilon} \sum_{\boldsymbol{K}_\perp} (\varrho_0)_{\varepsilon \boldsymbol{K}_\perp}\,\tau_{\varepsilon \boldsymbol{K}_\perp}\,. \tag{2.14}$$

For abrigdement we noted the diagonal elements by a simple index [e. g. $(\varrho_0)_{\varepsilon \boldsymbol{K}_\perp} \equiv (\varrho_0)_{\varepsilon \boldsymbol{K}_\perp,\, \varepsilon \boldsymbol{K}_\perp}$].

If τ is constant, then Eq. (2.13) reduces to

$$\langle J_z \rangle = \frac{n\,e\,\tau}{m\,L_z} \int \mathrm{d}\varepsilon$$

which for a domain of integration $-e\,E\,L_z/2 \leqq \varepsilon \leqq e\,E\,L_z/2$ gives the well known expression for the ohmic range

$$\langle J_z \rangle = n\,e^2\,\tau\,E/m\,. \tag{2.15}$$

It would also be possible, instead of the above form of Liouville's Eq. (2.4), to introduce directly a relaxation time expressing all the interactions with the scattering system

$$i(\partial\varrho/\partial t) = [\boldsymbol{H}_0 + \boldsymbol{H}_\mathrm{E}, \varrho] + i(\varrho_0 - \varrho)/\boldsymbol{\tau}$$

with the solution

$$\varrho_\mathrm{st} = \varrho_0 + \frac{1}{i} \int_0^\infty \mathrm{d}t\, e^{-t/\tau}\, e^{-i(\boldsymbol{H}_0 + \boldsymbol{H}_\mathrm{E})t}$$

$$\cdot [\boldsymbol{H}_0 + \boldsymbol{H}_\mathrm{E}, \varrho_0]\, e^{i(\boldsymbol{H}_0 + \boldsymbol{H}_\mathrm{E})t}$$

that leads to

$$\langle I_i \rangle = N \sum_{\alpha\beta} \frac{(W_\alpha - W_\beta)\,(\varrho_0)_{\alpha\beta}\,(j_i)_{\beta\alpha}}{W_\beta - W_\alpha + i\,\tau_{\alpha\alpha}^{-1}}$$

and then to the final expression (2.12).

3. The Current Fluctuations Spectral Density

The Wiener-Khintchine theorem for the fluctuation of the current operator $\delta\boldsymbol{I}_i(t) = \boldsymbol{I}_i(t) - \langle I_i \rangle$ may by written as:

$$S_{ik}(\nu) = \int_{-\infty}^{\infty} e^{-i\omega T}\,[\langle \delta\boldsymbol{I}_i(t+T)\,\delta\boldsymbol{I}_k(t) \rangle + \langle \delta\boldsymbol{I}_k(t)\,\delta\boldsymbol{I}_i(t+T) \rangle]\,\mathrm{d}T \tag{3.1}$$

$$= \int_0^\infty e^{-i\omega T}\,[\langle \delta\boldsymbol{I}_i(t+T)\,\delta\boldsymbol{I}_k(t) \rangle + \langle \delta\boldsymbol{I}_k(t)\,\delta\boldsymbol{I}_i(t+T) \rangle]\,\mathrm{d}T$$

$$+ \int_0^\infty e^{-i\omega T}\,[\langle \delta\boldsymbol{I}_i(t)\,\delta\boldsymbol{I}_k(t+T) \rangle + \langle \delta\boldsymbol{I}_k(t+T)\,\delta\boldsymbol{I}_i(t) \rangle]\,\mathrm{d}T$$

$$= S_{ik}^{\mathrm{I}}\,(\nu) + S_{ik}^{\mathrm{II}}\,(\nu) + S_{ik}^{\mathrm{III}}\,(\nu) + S_{ik}^{\mathrm{IV}}\,(\nu)\,. \tag{3.2}$$

The averaging is done over the stationary state, so that

$$\langle \delta\boldsymbol{I}_i(t+T)\,\delta\boldsymbol{I}_k(t) \rangle = \mathrm{Tr}\{\varrho_\mathrm{st}\, e^{i\mathcal{H}T}\,\delta\boldsymbol{I}_i\, e^{-i\mathcal{H}T}\,\delta\boldsymbol{I}_k\} \tag{3.3}$$

and use was made of the relation $\langle \delta\boldsymbol{I}_i(t-T)\,\delta\boldsymbol{I}_k(t) \rangle = \langle \delta\boldsymbol{I}_i(t)\,\delta\boldsymbol{I}_k(t+T) \rangle$. The terms in Eq. (3.2) obviously obey the relations

$$S_{ik}^{\mathrm{IV}}\,(\nu) = S_{ki}^{\mathrm{I}}\,(-\nu) \quad \text{and} \quad S_{ik}^{\mathrm{III}}\,(\nu) = S_{ki}^{\mathrm{II}}\,(-\nu)\,. \tag{3.4}$$

In the same sense as in the preceeding paragraph, that is using the expression (2.5) for the density matrix, the Laplace transform (2.9) of the current operators and in addition the assumption on the statistical independence of electrons [i. e. $\langle \delta\boldsymbol{I}_i(t+T)\,\delta\boldsymbol{I}_k(t) \rangle = N \langle \delta\boldsymbol{j}_i(t+T)\,\delta\boldsymbol{j}_k(t) \rangle$] we obtain

$$S_{ik}^{\mathrm{I}}\,(\nu) = \lim_{s_1 \to i\omega} N \int_0^\infty e^{-s_1 T}\,\mathrm{Tr}\{\varrho_\mathrm{st}\,\delta\boldsymbol{j}_i^{\mathcal{H}}(T)\,\delta\boldsymbol{j}_k\}\,\mathrm{d}T = \lim N\,\mathrm{Tr}\{\varrho_0\,\delta\,\boldsymbol{J}_i(s_1)\,\delta\boldsymbol{j}_k\} \tag{3.5}$$

$$+ \frac{1}{i} \lim_{\substack{s_1 \to i\omega \\ s_2 \to +0}} N\,\mathrm{Tr}\{[\mathcal{H}, \varrho_0] \int_0^\infty \mathrm{d}t\, e^{-s_2 t}\, e^{i\mathcal{H}t}\,\delta\boldsymbol{J}_i(s_1)\,\delta\boldsymbol{j}_k\, e^{-i\mathcal{H}t}\}\,.$$

Similarly to Eq. (2.10) we have for the Laplace transform of the current fluctuations

$$\lim_{s\to i\omega} \delta J_{\alpha\beta}(s) = i \frac{(\delta j)_{\alpha\beta}}{W_\alpha - W_\beta - \omega + i\,\tau_{\alpha\beta}^{-1}(\omega)} \tag{3.6}$$

and

$$\lim_{s\to +0} \int_0^\infty \mathrm{d}t\, e^{-st}\, [e^{i\mathcal{H}t}\, \delta\boldsymbol{j}_i\, \delta\boldsymbol{j}_k\, e^{-i\mathcal{H}t}]_{\alpha\beta} = i \frac{[\delta\boldsymbol{j}_i\, \delta\boldsymbol{j}_k]_{\alpha\beta}}{W_\alpha - W_\beta + i\,\tau_{\alpha\beta}^{-1}(0)} \tag{3.7}$$

respectively. Introducing again the approximations (2.7) and (2.8) we can write finally

$$S_{ik}^{\mathrm{I}}(\nu) = -N \sum_{\alpha\beta\gamma} \frac{\tau_{\beta\alpha}^{-1}(0)\, (\varrho_0)_{\alpha\beta} (\delta j_i)_{\beta\gamma} (\delta j_k)_{\gamma\alpha}}{[W_\beta - W_\gamma - \omega + i\,\tau_{\beta\gamma}^{-1}(\omega)]\,[W_\beta - W_\alpha + i\,\tau_{\beta\alpha}^{-1}(0)]} \tag{3.8}$$

and in the same way

$$S_{ik}^{\mathrm{II}}(\nu) = -N \sum_{\alpha\beta\gamma} \frac{\tau_{\beta\alpha}^{-1}(0)\, \varrho_0)_{\alpha\beta} (\delta j_k)_{\beta\gamma} (\delta j_i)_{\gamma\alpha}}{[W_\gamma - W_\alpha - \omega + i\,\tau_{\gamma\alpha}^{-1}(\omega)]\,[W_\beta - W_\alpha + i\,\tau_{\beta\alpha}^{-1}(0)]}$$

Summing now the four terms from Eq. (3.2) with the aid of Eq. (3.4) we obtain

$$\begin{aligned} S_{ik}(\nu) = -N \sum_{\alpha\beta\gamma} & \frac{\tau_{\beta\alpha}^{-1}(0)\, (\varrho_0)_{\alpha\beta}}{W_\beta - W_\alpha + i\,\tau_{\beta\alpha}^{-1}(0)} \\ & \times \Bigg\{ (\delta j_i)_{\beta\gamma} (\delta j_k)_{\gamma\alpha} \left[\frac{1}{W_\beta - W_\gamma - \omega + i\,\tau_{\beta\gamma}^{-1}(\omega)} + \frac{1}{W_\gamma - W_\alpha + \omega + i\,\tau_{\gamma\alpha}^{-1}(-\omega)} \right] \\ & + (\delta j_k)_{\beta\gamma} (\delta j_i)_{\gamma\alpha} \left[\frac{1}{W_\beta - W_\gamma + \omega + i\,\iota_{\beta\gamma}^{-}(-\omega)} + \frac{1}{W_\gamma - W_\alpha - \omega + i\,\tau_{\gamma\alpha}^{-1}(\omega)} \right] \Bigg\}. \end{aligned} \tag{3.9}$$

Taking into account the definition of fluctuation

$$(\delta j_i)_{\alpha\beta} \equiv (j_i)_{\alpha\beta} - \frac{1}{N} \langle I_i \rangle\, \delta_{\alpha\beta}$$

and the symmetry $S_{ik}(\nu) = S_{ki}(\nu)$, the current noise spectral density takes the form

$$\begin{aligned} S_{ik}(\nu) = -\frac{N}{2} & \sum_{\alpha\beta\gamma} \frac{\tau_{\beta\alpha}^{-1}(0)\, (\varrho_0)_{\alpha\beta}}{W_\beta - W_\alpha + i\,\tau_{\beta\alpha}^{-1}(0)} \,[(j_i)_{\beta\gamma} (j_k)_{\gamma\alpha} + (j_k)_{\beta\gamma} (j_i)_{\gamma\alpha}] \\ & \times \Bigg[\frac{1}{W_\beta - W_\gamma - \omega + i\,\tau_{\beta\gamma}^{-1}(\omega)} + \frac{1}{W_\gamma - W_\alpha - \omega + i\,\tau_{\gamma\alpha}^{-1}(\omega)} \\ & \qquad + \frac{1}{W_\beta - W_\gamma + \omega + i\,\tau_{\beta\gamma}^{-1}(-\omega)} + \frac{1}{W_\gamma - W_\alpha + \omega + i\,\tau_{\gamma\alpha}^{-1}(-\omega)} \Bigg] \\ & + \tfrac{1}{2} \sum_{\alpha\beta} \frac{\tau_{\beta\alpha}^{-1}(0)\, (\varrho_0)_{\alpha\beta}}{W_\beta - W_\alpha + i\,\tau_{\beta\alpha}^{-1}(0)} \,[\langle I_i \rangle (j_k)_{\beta\alpha} + \langle I_k \rangle (j_i)_{\beta\alpha}] \\ & \times \Bigg[\frac{2}{W_\beta - W_\alpha - \omega + i\,\tau_{\beta\alpha}^{-1}(\omega)} + \frac{2}{W_\beta - W_\alpha + \omega + i\,\tau_{\beta\alpha}^{-1}(-\omega)} \\ & \quad + \frac{1}{\omega + i\,\tau_{\alpha\alpha}^{-1}(-\omega)} - \frac{1}{\omega - i\,\tau_{\alpha\alpha}^{-1}(\omega)} + \frac{1}{\omega + i\,\tau_{\beta\beta}^{-1}(-\omega)} - \frac{1}{\omega - i\,\tau_{\beta\beta}^{-1}(\omega)} \Bigg] \\ & - \frac{2}{iN} \langle I_i \rangle \langle I_k \rangle \sum_\alpha (\varrho_0)_{\alpha\alpha} \left[\frac{1}{\omega + i\,\tau_{\alpha\alpha}^{-1}(-\omega)} - \frac{1}{\omega - i\,\tau_{\alpha\alpha}^{-1}(\omega)} \right]. \end{aligned} \tag{3.10}$$

In a large domain of frequencies, the relaxation time does practically not depend on frequencey, i. e. $\tau_{\alpha\beta}(\omega) \approx \tau_{\alpha\beta}(0) \equiv \tau_{\alpha\beta}$ and the above expression becomes considerably simpler. However this limitation in frequency will exclude the appearence on any quantum correction factor.

For an electric field directed along the z-axis, substituting the matrix elements of ϱ and $\boldsymbol{j}_i$ from the appendix, after some algebra we obtain the following formulae for the fluctuation spectrum matrix:

$$S_{xx}(\nu) = \frac{4e^2 N}{m^2 L_x^2} \sum_\varepsilon \sum_{\boldsymbol{K}_\perp} \frac{(\varrho_0)_{\varepsilon\boldsymbol{K}_\perp} \tau_{\varepsilon\boldsymbol{K}_\perp}}{1 + \omega^2 \tau_{\varepsilon\boldsymbol{K}_\perp}^2} K_x^2 \tag{3.11}$$

$$= \frac{2eN}{\pi m^3 T L_x^2 L_z E} \int \mathrm{d}\varepsilon \int \mathrm{d}\boldsymbol{K}_\perp\, K_x^2 \exp\{-K_\perp^2/2mT\} \frac{\tau_{\varepsilon\boldsymbol{K}_\perp}}{1 + \omega^2 \tau_{\varepsilon\boldsymbol{K}_\perp}^2}, \tag{3.11'}$$

$$S_{yy}(\nu) = \frac{4\,e^2\,N}{m^2\,L_y{}^2} \sum_{\varepsilon} \sum_{\boldsymbol{K}_\perp} \frac{(\varrho_0)_{\,\varepsilon\boldsymbol{K}_\perp}\,\tau_{\varepsilon\boldsymbol{K}_\perp}}{1+\omega^2\,\tau^2_{\varepsilon\boldsymbol{K}_\perp}}\,K_y{}^2 \tag{3.12}$$

[if the momentum $\mathbf{K}_\perp$ enters into the function $\tau_{\varepsilon\boldsymbol{K}_\perp}$ as $|\mathbf{K}_\perp|$ only, then the integrals in (3.11), (3.12) coincide]

$$S_{xy}(\nu) = S_{xz}(\nu) = S_{yz}(\nu) = 0\,, \tag{3.13}$$

$$\begin{aligned} S_{zz}(\nu) = {} & \frac{4\,N\,e^2\,T}{m\,L_z{}^2} \sum_{\varepsilon,\boldsymbol{K}_\perp} \frac{(\varrho_0)_{\,\varepsilon\boldsymbol{K}_\perp}\,\tau_{\varepsilon\boldsymbol{K}_\perp}}{1+\omega^2\,\tau^2_{\varepsilon\boldsymbol{K}_\perp}} + \frac{4\,N\,e^4\,E^2}{m^2\,L_z{}^2} \sum_{\varepsilon,\boldsymbol{K}_\perp} \frac{(\varrho_0)_{\varepsilon\boldsymbol{K}_\perp}\,\tau^3_{\varepsilon\boldsymbol{K}_\perp}}{1+\omega^2\,\tau^2_{\varepsilon\boldsymbol{K}_\perp}} \left[1+\frac{2}{1+\omega^2\,\tau^2_{\varepsilon\boldsymbol{K}_\perp}}\right] \\ & - \frac{4\,e^2\,E}{m\,L_z} \langle I_z\rangle \sum_{\varepsilon,\boldsymbol{K}_\perp} \frac{(\varrho_0)_{\,\varepsilon\boldsymbol{K}_\perp}\,\tau^2_{\varepsilon\boldsymbol{K}_\perp}}{1+\omega^2\,\tau^2_{\varepsilon\boldsymbol{K}_\perp}} \left[1+\frac{2}{1+\omega^2\,\tau^2_{\varepsilon\boldsymbol{K}_\perp}}\right] + \frac{4}{N} \langle I_z\rangle^2 \sum_{\varepsilon,\boldsymbol{K}_\perp} \frac{(\varrho_0)_{\,\varepsilon\boldsymbol{K}_\perp}\,\tau_{\varepsilon\boldsymbol{K}_\perp}}{1+\omega^2\,\tau^2_{\varepsilon\boldsymbol{K}_\perp}} \end{aligned} \tag{3.14}$$

or, turning the sums into integrals,

$$\begin{aligned} S_{zz}(\nu) = {} & \frac{2\,N}{\pi\,m\,T}\,\frac{1}{e\,E\,L_z} \left\{ \int \mathrm{d}\varepsilon \int \mathrm{d}\mathbf{K}_\perp \exp\{-K_\perp^2/2\,m\,T\} \frac{\tau_{\varepsilon\,\boldsymbol{K}_\perp}}{1+\omega^2\,\tau^2_{\varepsilon\boldsymbol{K}_\perp}} \left(\frac{e^2\,T}{m\,L_z{}^2}+\frac{\langle I_z\rangle^2}{N^2}\right) \right. \\ & \left. + \frac{e^2\,E\langle I_z\rangle}{m\,L_z\,N} \int \mathrm{d}\varepsilon \int \mathrm{d}\mathbf{K}_\perp \exp\{-K_\perp^2/2\,m\,T\} \frac{\tau^2_{\varepsilon\boldsymbol{K}_\perp}}{1+\omega^2\,\tau^2_{\varepsilon\boldsymbol{K}_\perp}} \left(1+\frac{2}{1+\omega^2\,\tau^2_{\varepsilon\boldsymbol{K}_\perp}}\right) \times \left(\frac{N\,e^2\,E}{m\,L_z\langle I_z\rangle}\,\tau_{\varepsilon\boldsymbol{K}_\perp}-1\right)\right\}. \end{aligned} \tag{3.15}$$

Comparing the transversal noise spectrum [Eq. (3.11), (3.12)] or the first term from the right of Eq. (3.14) with the conductivity [Eq. (2.14)] we see immediately that the classical fluctuation-dissipation theorem still applies.

If $\tau_{\varepsilon\boldsymbol{K}_\perp}$ is a constant, leading, as we have seen in § 2 to the ohmic behaviour of the current, then

$$L_x{}^2\,S_{xx}(\nu) = L_y{}^2\,S_{yy}(\nu) = \frac{4\,N\,e^2\,T\,\tau}{m(1+\omega^2\,\tau^2)}$$

and

$$S_{zz}(\nu) = \frac{4\,N\,e^2\,T\,\tau}{m\,L_z{}^2(1+\omega^2\,\tau^2)} + \frac{4}{N}\langle I_z\rangle^2 \frac{\tau}{1+\omega^2\,\tau^2} \tag{3.16}$$

that is in the longitudinal direction a supplementary term, proportional to the square of the current is added. The transversal noise spectrum, as well as the first term in $S_{zz}(\nu)$ is the usual Nyquist term with the frequency dependent conductivity.

4. Estimations of the Current and the Current Noise Spectral Density

In order to obtain a clear dependence of both the current and noise on experimental parameters we would have to substitute into the Eq. (2.13) and (3.15) the adequate expressions for the relaxation time, connected with the probabality of transition for the corresponding type of interaction. Unfortunately, due to the form of the interaction potential and to the complications inherent to calculations with Airy functions, it was impossible to obtain a useful formula for the matrix elements of the relaxation time. Moreover, all the attempts clearly indicate a dependence of the results on the dimensions of the system, that renders difficult even the understanding of their physical meaning.

We shall try to remove these intricacies supposing that the diagonal elements of the relaxation time depend on the electron energy in the same way as in the plane wave representation. For scattering due to the acoustic modes of vibration only, we put then:

$$\tau_{\varepsilon\boldsymbol{K}_\perp} = \tau_1 \left(\varepsilon - \varepsilon_0 + \frac{K_\perp^2}{2\,m}\right)^{-1/2}. \tag{4.1}$$

Making use of the approximate integration formula

$$\int \mathrm{d}\mathbf{K}_\perp\, f(\mathbf{K}_\perp) \exp\{-K_\perp^2/2\,m\,T\} \approx 2\,\pi\,m\,T\,f(\mathbf{K}_\perp)|_{K_\perp^2=2mT} \tag{4.2}$$

the result of integrations in Eq. (2.13) for the current density on the intervals $\varepsilon_0 = -e\,E\,L_z/2 \leqq \varepsilon \leqq \varepsilon_0'$, $0 \leqq |\mathbf{K}_\perp| \leqq \infty$ is

$$\langle J_z\rangle \approx \frac{2\,n\,e\,\tau_1}{m\,L_z}\,[(\varepsilon_0' - \varepsilon_0 + T)^{1/2} - T^{1/2}]\,. \tag{4.3}$$

If the integration in ε were done over the whole spectrum, i. e. ε_0' were infinite, then the result would be divergent, which is obviously wrong. However, if we perform a cut-off at $\varepsilon_0' = e\,E\,L_z/2$, that is if the domain of variation of ε corresponds to the maximum energy transfer from the external field to electrons, the result in the limit situations (high and low applied field) is the following:

$$\langle J_z\rangle \sim \begin{cases} \dfrac{2\,n\,e\,\tau_1}{m\,L_z^{1/2}}\,(e\,E)^{1/2} \ldots & \text{for} \quad e\,E \gg T\,L_z^{-1} \\ \dfrac{n\,e^2\,\tau_1\,E}{m\,T^{1/2}} \quad \ldots & \text{for} \quad e\,E \ll T\,L_z^{-1} \end{cases} \tag{4.4}$$

The field dependence agrees qualitatively with that observed experimentally or resulting from Boltzmannian theories. In order to have also the expected dependence on the other parameters [6], the proportionality factor must be written as

$$\tau_1 = \tau_0\,(e\,E\,L_z/4 + T)^{1/2}\,(T/T_e)^{1/2} \tag{4.5}$$

where the relaxation time for ohmic conduction $\tau_0 = 4/3\,l\,m^{1/2}\,(2\,\pi\,T)^{-1/2}$, l is the mean free path for scattering by acoustic phonons.

The electron temperature T_e is given by [6]

$$\frac{T_e}{T} = \begin{cases} 1 & \ldots \text{ for } e\,E \gg m\,u_l\,\tau_0^{-1} \\ \dfrac{\pi\,3^{1/4}}{2\,\Gamma(3/4)}\,\dfrac{(m\,T)^{1/4}\,u_l^{1/2}}{(e\,E\,l)^{1/2}} & \ldots \text{ for } e\,E \ll m\,u_l\,\tau_0^{-1}, \end{cases} \tag{4.6}$$

(u_l is the longitudinal sound velocity).

Thus, from Eq. (4.4 – 6) we get

– in the low field limit

$$\langle J_z\rangle = \frac{4}{3}\,\frac{n\,e^2\,l\,E}{(2\,\pi\,m\,T)^{1/2}}$$

– in the high field limit

$$\langle J_z\rangle = \frac{(2\,\pi)^{1/2}}{3^{3/4}\,\Gamma(3/4)}\,\frac{e\,n\,(e\,E\,l\,u_l)^{1/2}}{m\,T^{1/4}}\,. \tag{4.7}$$

Using now the Eqs. (3.11 – 15) with the relaxation time (4.1) and the approximation (4.2) we are led to the following formulae for the noise spectral density

$$L_x^2\,S_{xx}(\nu) = L_y^2\,S_{yy}(\nu) \approx \frac{8\,N\,e\,T}{m\,E\,L_z}\,\tau_1 \Big[(e\,E\,L_z + T)^{1/2} - T^{1/2} - \omega\,\tau_1 \Big) \text{arc tg}\,\frac{(e\,E\,L_z+T)^{1/2}}{\omega\,\tau_1} - \text{arc tg}\,\frac{T^{1/2}}{\omega\,\tau_1}\Big)\Big]$$

$$L_z^2\,S_{zz}(\nu) \approx L_x^2\,S_{xx}(\nu) + \frac{8\,N\,e\,\tau_1^3}{m^2\,L_z^3\,E}\Big\{ 2\,\Big(\text{arc tg}\,\frac{(e\,E\,L_z+T)^{1/2}}{\omega\,\tau_1} - \text{arc tg}\,\frac{T^{1/2}}{\omega\,\tau_1}\Big) \tag{4.8}$$

$$\begin{aligned} &\times \Big[\frac{(e\,E\,L_z)^3}{\omega\,\tau_1} - 2\,\omega\,\tau_1\,\big((e\,E\,L_z+T)^{1/2} - T^{1/2}\big)^2 \Big] - 3\,e\,E\,L_z\,\big((e\,E\,L_z+T)^{1/2} - T^{1/2}\big)\ln\frac{e\,E\,L_z + T + (\omega\,\tau_1)^2}{T + (\omega\,\tau_1)^2} \\ &+ \frac{1}{[e\,E\,L_z + T + (\omega\,\tau_1)^2]\,[T + (\omega\,\tau_1)^2]} \cdot \big[(e\,E\,L_z+T)^{1/2}\,(16\,T^3 + 20\,e\,E\,L_z\,T^2 + 3\,(e\,E\,L_z)^2\,T) \\ &- T^{1/2}\,(16\,T^3 + 28\,e\,E\,L_z\,T^2 + 11\,(e\,E\,L_z)^2\,T - (e\,E\,L_z)^3) \\ &+ (\omega\,\tau_1)^2\,(e\,E\,L_z+T)^{1/2}\,(32\,T^2 + 24\,e\,E\,L_z\,T + 5\,(e\,E\,L_z)^2) \\ &- (\omega\,\tau_1)^2\,T^{1/2}\,(32\,T^2 + 40\,e\,E\,L_z\,T + 13\,(e\,E\,L_z)^2) \\ &+ 4\,(\omega\,\tau_1)^4\,\big((e\,E\,L_z+T)^{1/2}\,(4\,T + e\,E\,L_z) - T^{1/2}\,(4\,T + 3\,e\,E\,L_z)\big)\big]\Big\}\,. \end{aligned} \tag{4.9}$$

For low fields ($e\,E \ll T\,L_z^{-1}$, $m\,u_l\,\tau_0^{-1}$), the above expressions can be put into more closed forms

$$L_x^2\,S_{xx}(\nu) = L_y^2\,S_{yy}(\nu) \approx \frac{4\,N\,e^2\,T^{3/2}}{m}\,\frac{\tau_1}{T + (\omega\,\tau_1)^2} = \frac{4\,N\,e^2\,T}{m}\,\frac{\tau_0}{1 + \omega^2\,\tau_0^2}\,, \tag{4.10}$$

$$S_{zz}(\nu) \approx S_{xx}(\nu)\,\frac{L_x^2}{L_y^2} + \frac{4\,N\,e^4\,E^2}{m^2\,L_z^2}\,\frac{\tau_0^3}{1 + \omega^2\,\tau_0^2} \approx \frac{4\,N\,e^2\,T}{m\,L_z^2}\,\frac{\tau_0}{1 + \omega^2\,\tau_0^2} + \frac{\tau_0}{1 + \omega^2\,\tau_0^2}\,\frac{4\langle I_z^2\rangle}{N}\,. \tag{4.11}$$

The so called tensorial "noise temperature" defined in analogy with the usual Nyquist law

$$S_{ij}(\nu) = 4\,T_{ij}^{\mathrm{N}}\,\frac{\Omega}{L_i\,L_j}\,\mathrm{Re}\,\sigma_{ij}(\omega)$$

can be then expressed in a simple manner:

$$T_{ij}^{\mathrm{N}} = T\,\delta_{ij} + \frac{e^2\,E_i\,E_j\,\tau_0^2}{m}\,. \tag{4.12}$$

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[6] J. YAMASHITA and M. WATANABE, Progr. Theor. Phys. **12**, 443 [1954].

The noise temperature contains a convective term in addition to the lattice temperature, in agreement with GUREVICH[1], SCHLUP[2] and PRICE[3]. It does not depend on frequency, but probably this is a peculiarity of the parabolic bands.

In the high field limit $(e\,E \gg T\,L_z^{-1},\ m\,u_l\,\tau_0^{-1})$

$$L_x^2\,S_{xx}(\nu) = L_y^2\,S_{yy}(\nu) \approx \frac{8\,N\,e\,T}{m\,E\,L_z}\,\tau_1 (e\,E\,L_z)^{1/2}\,[1-\omega\,\tau_1 (e\,E\,L_z)^{-1/2} \operatorname{arc\,tg} (e\,E\,L_z)^{1/2}/\omega\,\tau_1]\,, \tag{4.13}$$

$$\begin{aligned} S_{zz}(\nu) \approx S_{xx}(\nu)\,\frac{L_x^2}{L_z^2} + \frac{8\,N\,e^2\,\tau_1^3}{m^2\,L_z^4}\,(e\,E\,L_z)^{1/2} \Bigg\{ 2\,\frac{e\,E\,L_z - 2(\omega\,\tau_1)^2}{\omega\,\tau_1 (e\,E\,L_z)^{1/2}} - 3\ln\frac{e\,E\,L_z + T + (\omega\,\tau_1)^2}{T + (\omega\,\tau_1)^2} \\ + \frac{(e\,E\,L_z)^{3/2}\,T^{1/2} + 3\,e\,E\,L_z\,T + (\omega\,\tau_1)^2\,[5\,e\,E\,L_z - 13\,(e\,E\,L_z\,T)^{1/2} + 4(\omega\,\tau_1)^4\,[1-3\,(T/e\,E\,L_z)^{1/2}]]}{e\,E\,L_z\,T + T^2 + (\omega\,\tau_1)^2 (e\,E\,L_z + 2\,T) + (\omega\,\tau_1)^4} \Bigg\}\,. \end{aligned} \tag{4.14}$$

These formulae become simpler for extreme frequenciens

A) For low frequencies $[\omega\,\tau_0 \ll 2\,(T_e/T)^{1/2}]$

$$L_x^2\,S_{xx}(\nu) = L_y^2\,S_{yy}(\nu) \approx \frac{4\,N\,e^2\,T}{m}\,\tau_0 (T/T_e)^{1/2} \tag{4.15}$$

$$S_{zz}(\nu) \approx \frac{4\,N\,e\,T}{m\,L_z^2}\,\tau_0 \left(\frac{T}{T_e}\right)^{1/2} + \frac{2\,\pi\,N\,e^4\,E^2}{m^2\,L_z^2}\,\tau_0^2\,\frac{T}{T_e}\,\frac{1}{\omega} = \frac{4\,N\,e\,T}{m\,L_z^2}\,\tau_0 \left(\frac{T}{T_e}\right)^{1/2} + \frac{2\,\pi \langle I_z \rangle^2}{N}\,\frac{1}{\omega}\,. \tag{4.16}$$

B) For high frequencies $[\omega\,\tau_0 \gg 2\,(T_e/T)^{1/2}]$

$$L_x^2\,S_{xx}(\nu) = L_y^2\,S_{yy}(\nu) \approx \frac{16}{3}\,\frac{N\,e^2\,T}{m}\,\frac{1}{\omega^2\,\tau_0}\left(\frac{T}{T_e}\right)^{1/2} \tag{4.17}$$

$$S_{zz}(\nu) = \frac{L_x^2}{L_z^2}\,S_{xx}(\nu) + \frac{16}{3}\,\frac{N\,e^4\,E^2}{m^2\,L_z^2}\,\frac{\tau_0}{\omega^2}\left(\frac{T}{T_e}\right)^{1/2} = \frac{16}{3}\,\frac{N\,e^2\,T}{m\,L_z^2}\,\frac{1}{\omega^2\,\tau_0}\left(\frac{T}{T_e}\right)^{1/2} + \frac{16}{3}\,\frac{\langle I_z \rangle^2}{N}\,\frac{1}{\omega^2\,\tau_0}\left(\frac{T}{T_e}\right)^{1/2}. \tag{4.18}$$

Denoting $\tau_E = \tau_0 (T/T_e)^{1/2}$ we conclude that the pure Nyquist term looks like

$$\frac{4\,N\,e^2\,T}{m\,L_i^2}\,\frac{\tau_E}{1+\omega^2\,\tau_E^2} = \frac{4\,T\,\Omega}{L_i^2}\,\operatorname{Re}\sigma(\omega)$$

in disagreement with Gurevich and Price who obtain $T^N \approx T_e$.

The convective part of the noise temperature T^N behaves quite normally at high frequencies $(e^2\,E_i\,E_j\,\tau_E^2/m)$ and is proportional to the applied field $(\tau_E \sim E^{-1/2})$. On the contrary, at low frequencies the noise temperature depends on frequency and that does not seem to be an accident due to our approximations.

5. Final Remarks

Supposing that the various types of scattering of electrons may be described by means of specific relaxation times in the representation of the eigenfunctions corresponding to free electrons in an external field, we obtained some general formulae for the current density and for the spectral density of current fluctuations (§§ 2 and 3). However, it remains an open question to prove rigorously the validity of such a description and to calculate the relaxation time matrices for different processes.

Writing a special form of the diagonal elements of the relaxation time matrix for scattering on acoustic modes of vibration, analogous to that used in the plane waves representation, and introducing explicitely the maximum value of the energy transferred from the field to the electrons as a limit in integrations, the results for the current density agree in the low and high field limits with the experimental ones[7, 8].

When treating in the same way the general formula of the spectral density of fluctuations the results in both above limiting cases can be divided into a Nyquist-like term, with the noise temperature equal to the lattice one, and a convective term specific to the longitudinal direction and proportional to the square

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[7] E. J. RYDER, Phys. Rev. **90**, 766 [1953].

[8] W. SHOCKLEY, Bell Syst. Tech. J. **30**, 990 [1951].

of the current. The spectrum is white up to frequencies comparable with the inverse of the ohmic relaxation time.

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Appendix

The Wave Functions and Matrix Elements

The eigenfunctions of the operator $\boldsymbol{H}_0 + \boldsymbol{H}_{\mathrm{E}}$ obey the equation

$$\left(-\frac{1}{2\,m}\nabla^2 + e\,E\,z\right)\psi(\boldsymbol{r}) = W\,\psi(\boldsymbol{r}) \tag{A.1}$$

where e is the elementary charge and m the effective mass of the electron in the conduction band.

For free electrons or for a semiconductor with parabolic bands, if the dimension along the field direction is great, the wave function may be written as[9]

$$\psi_{\varepsilon_n K_x K_y}(\boldsymbol{r}) \equiv |\,\varepsilon_n\,\mathbf{K}_\perp\rangle = A_n\,\mathrm{Ai}(\xi_n)\exp[i(K_x x + K_y y)] \tag{A.2}$$

where $$W = \varepsilon_n + \frac{K_\perp^2}{2\,m}\,, \qquad \xi_n = \left(z - \frac{\varepsilon_n}{e\,E}\right)(2\,m\,e\,E)^{1/3}\,,$$

$\mathbf{K}_\perp$ is the momentum perpendicular to the field direction, and the Airy function is defined by

$$\mathrm{Ai}(\xi) = \frac{1}{\sqrt{\pi}}\int_0^\infty \cos\left(\frac{u^3}{3} + u\,\xi\right)\mathrm{d}u\,. \tag{A.3}$$

The constant A_i is gotten from the conditions of normalization on the volume $\Omega = L_x\,L_y\,L_z$ $(-L_x/2 \leqq x \leqq L_x/2$, etc.) and completeness on the discrete spectrum of ε_n.

$$A_n = \frac{(2\,m)^{1/3}}{\pi^{1/2}(e\,E)^{1/6}\,L_x^{1/2}\,L_y^{1/2}}\,[\eta(\varepsilon_n)]^{-1/2}\,. \tag{A.4}$$

The density of states $\eta(\varepsilon_n)$ (i. e. the inverse of the spacing between levels can be obtained from the vanishing at $-L_z/2$ of $\psi(\boldsymbol{r})$ which, for large negative z, behaves asymptotically like a sinus.

$$\eta(\varepsilon_n) \approx \frac{(2\,m)^{1/2}}{\pi\,e\,E}\left(\varepsilon_n + \frac{e\,E\,L_z}{2}\right)^{1/2}. \tag{A.5}$$

The same condition gives the lower limit of the spectrum, $\varepsilon_0 = -e\,E\,L_z/2$.

If the length of the box L_z is sufficiently great, $L_z(2\,m\,e\,E)^{1/3} \gg 1$, and the spacing between levels $\Delta\varepsilon_n = [\eta(\varepsilon_n)]^{-1}$ is small enough, then we can use a continuous density of states and integrate on the energy spectrum ε_n instead of summing $[\Sigma \ldots \to \int \mathrm{d}\varepsilon_n\,\eta(\varepsilon_n)\ldots]$. This corresponds to the semiclassical approximation when box normalized momentum eigenstates are used.

In order to calculate the matrix elements of ϱ and $\boldsymbol{j}_i$, we need the Fourier transform of $\psi(\boldsymbol{r})$

$$\Phi_{\varepsilon_n \mathbf{K}_\perp}(\boldsymbol{p}) = \frac{1}{\Omega^{1/2}}\int \exp\{-i\,\boldsymbol{p}\,\boldsymbol{r}\}\,\psi_{\varepsilon_n \mathbf{K}_\perp}(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r} = \frac{1}{[e\,E\,L_z\,\eta(\varepsilon_n)]^{1/2}}\exp\left[-\frac{i}{e\,E}\left(\varepsilon_n\,p_z - \frac{p_z^{\,3}}{6\,m}\right)\right]\delta_{\mathbf{K}_\perp,\boldsymbol{p}_\perp} \tag{A.6}$$

then $$(\varrho_0)_{12} = Z^{-1}\langle\varepsilon_1, \mathbf{K}_{\perp 1}|\,e^{-\beta \boldsymbol{H}_0}\,|\varepsilon_2, \mathbf{K}_{\perp 2}\rangle$$
$$= \frac{1}{Z\,e\,E\,L_z}\,[\eta(\varepsilon_1)\,\eta(\varepsilon_2)]^{-1/2}\sum_{K_z}\exp\left\{\frac{i}{e\,E}\,K_z(\varepsilon_1 - \varepsilon_2)\right\}\exp\left\{-\frac{\beta}{2\,m}\,(K_{\perp 1}^2 + K_z^{\,2})\right\}\delta_{\mathbf{K}_{\perp 1},\mathbf{K}_{\perp 2}} \tag{A.7}$$

$$Z = \mathrm{Tr}(e^{-\beta \boldsymbol{H}_0}) = \sum_{\boldsymbol{K}}\exp\{-\beta\,K^2/2\,m\} = \frac{\Omega}{(2\,\pi)^3}\,(2\,\pi\,m\,T)^{3/2}\,. \tag{A.8}$$

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[9] L. D. LANDAU and E. M. LIFSHITZ, Quantum Mechanics, Pergamon Press Inc., New York 1959, p. 70.

It is important to note that this value of the statistical sum is obtained either using the orthogonality and completitude relations for the wave functions, or integrating $(e^{-\beta H_0})_{\varepsilon \mathbf{K}_\perp, \varepsilon \mathbf{K}_\perp}$ in the variable ε, between the limits $(-e\,E\,L_z/2,\ +e\,E\,L_z/2)$ that is cutting the domain of integration in its upper part.

$$(j_i)_{12} = -\frac{e\,K_{i1}}{m\,L_i}\,\delta_{\varepsilon_1,\varepsilon_2}\,\delta_{\mathbf{K}_{\perp 1},\mathbf{K}_{\perp 2}} \approx -\frac{e\,K_{i1}}{m\,L_i}\,[\eta(\varepsilon_1)\,\eta(\varepsilon_2)]^{-1/2}\,\delta(\varepsilon_1-\varepsilon_2)\,\delta_{\mathbf{K}_{\perp 1},\mathbf{K}_{\perp 2}}\ (i=x,y) \tag{A.9}$$

$$\begin{aligned}(j_z)_{12} &= -\frac{1}{m\,E\,L_z^2}\,[\eta(\varepsilon_1)\,\eta(\varepsilon_2)]^{-1/2}\sum_{K_z} K_z \exp\left\{\frac{i}{e\,E}\,K_z(\varepsilon_1-\varepsilon_2)\right\}\delta_{\mathbf{K}_{\perp 1},\mathbf{K}_{\perp 2}}\\ &\approx -\frac{e^2\,E}{i\,m\,L_z}\,[\eta(\varepsilon_1)\,\eta(\varepsilon_2)]^{-1/2}\,\frac{\mathrm{d}}{\mathrm{d}\varepsilon_1}\,\delta(\varepsilon_1-\varepsilon_2)\,\delta_{\mathbf{K}_{\perp 1},\mathbf{K}_{\perp 2}}\,.\end{aligned} \tag{A.10}$$

Thermal Expansion of Alkali Sulphate Mixtures

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The linear thermal expansivities of polycrystalline samples of mixtures of Li_2SO_4 with K_2SO_4 and with Na_2SO_4 have been measured with a "Fused-Quarz Tube" apparatus [1]. Phase transitions are accompanied by changes in the expansion coefficient and also by volume changes. The observed expansion coefficient is constant over wide temperature intervals. Simple crystal structures show higher expansivities than more complex structures. The "pre-melting" phenomenon in Li_2SO_4 does not measurably influence the thermal expansion.

A method has been devised to correct the observations for the plastic flow of the crystals close to the melting points.

The present investigation of the thermal expansion of alkali sulphate mixtures is a part of a program in this laboratory for an extensive study of the rheology of these mixtures. Since lithium sulphate is a purely cationic conductor a study of the electrical conductivity primarily gives information about the cations. Information of the same kind is obtained from diffusion studies since D_{Li^+} (and the interdiffusion coefficients of other monovalent cations) is of the order of $10^{-5}\ \mathrm{cm}^2\ \mathrm{s}^{-1}$ while $D_{\mathrm{SO}_4^{--}}$ is several magnitudes smaller (about $10^{-10}\ \mathrm{cm}^2\ \mathrm{s}^{-1}$ at 800 °C) [2, 3]. Thus anion diffusion studies are much more difficult to perform accurately than cation diffusion studies and they are only able to give a qualitative information of the transport parameters. The difference in magnitudes of the cation and anion diffusion coefficients is due to the fact that a Li_2SO_4 crystal consists of a rigid anion lattice in which the cations are able to move very freely. Studies of the mechanical properties of these crystals are, however, comparatively easy to perform and they will give direct information about the anion lattice. Semiquantitative preliminary studies of the rheology of solid lithium sulphate have been performed in this laboratory, plastic flow investigations by AUGUSTSSON and LUNDÉN [4] and thermal expansion investigations by AUGUSTSSON and EKHED [5]. The present work is a quantitative investigation of the linear thermal expansivity of pure lithium sulphate and of mixtures of lithium sulphate with potassium and sodium sulphates.

Experimental

Reagent grade lithium sulphate was obtained from Mallinckrodt Chemical Works, New York, USA, and potassium and sodium sulphates from E. Merck AG., Darmstadt, Germany. After drying in a drying oven for over 50 hours at 120 °C the salts were melted and mixed in a quartz crucible and then cast

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[1] P. HIDNERT and W. SOUDER, Nat. Bur. Standards (US) Circ. 486 [1950].

[2] A. KVIST and U. TROLLE, Z. Naturforsch. **22 a**, 213 [1967].

[3] A. BENGTZELIUS, private communication.

[4] B. AUGUSTSSON and A. LUNDÉN, Z. Naturforsch. **21 a**, 1860 [1966].

[5] B. AUGUSTSSON and A. EKHED, Z. Naturforsch. **23 a**, 1259 [1968].