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 polykrystallinem AsJ$_3$ und SbJ$_3$ fest. Ihre Ergebnisse 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 $C\overline{3}$ 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 Wellenzahlniedrigung beobachtet. Eine Ausnahme bilden hierbei die entarteten Deformationsschwingungen ($v_6$ und $v_8$).

Ich danke Herrn J. BRANDMÜLLER für sein Interesse bei der Durchführung dieser Arbeit, sowie für die Be-
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The main idea of the present attempt, inspired from unpublished work by BANYAI\(^4\), is to take exactly into account the electric field, by using the eigenfunctions of free electrons in an external field.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 \(\Omega\), 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:

\[
\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_E + \mathbf{V}
\]  

(2.1)

where \(\mathcal{H}_0\) is the Hamiltonian of free electrons without field, \(\mathcal{H}_E\) is the interaction with the electric field and \(\mathbf{V}\) 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

\[
\mathcal{H}_E' = \begin{cases} 0 & \text{at } t \leq 0, \\ \mathcal{H}_E = eE \mathbf{r} & \text{at } t > 0. \end{cases}
\]  

(2.2)

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

\[
\langle I_i \rangle = N \text{Tr} \{ \varrho_{st} \mathbf{j}_i \} 
\]  

(2.3)

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

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

(2.4)

\(^4\) L. BANYAI, unpublished.

\[
\varrho(0) = \varrho_0 (\mathcal{H}_0 + \mathbf{V}) = Z^{-1} e^{-\beta (\mathcal{H}_0 + \mathbf{V})}, \\
Z = \text{Tr} \{ e^{-\beta \mathcal{H}_0} \}
\]  

and \(\beta = T^{-1}\).

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:

\[
\varrho(t) = \varrho_0 + \frac{1}{i} \lim_{s \rightarrow +0} \int_0^t dt' e^{-st'} e^{-\beta \mathbf{H}} [\mathcal{H}, \varrho_0] e^{\beta \mathbf{H}}
\]  

(2.5)

so that the current is

\[
\langle I_i \rangle = N \text{Tr} \left\{ \frac{1}{i} \lim_{s \rightarrow +0} \int_0^\infty dt [\mathcal{H}, \varrho_0] \mathbf{j}_i(t) e^{-st} \right\}
\]  

(2.6)

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

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

(i) The interaction term \(\mathbf{V}\) 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 \(\mathcal{H}_0 + \mathcal{H}_E\) also, of the scattering by means of a relaxation time matrix \(\tau\) which can be calculated from the quantum theory of perturbations.

The first assumption will allow us to make the approximation

\[
\varrho_0 (\mathcal{H}_0 + \mathbf{V}) \approx \varrho_0 (\mathcal{H}_0)
\]  

(2.7)

and therefore

\[
[\mathcal{H}, \varrho_0 (\mathcal{H}_0 + \mathbf{V})] = [\mathcal{H}_E, \varrho_0 (\mathcal{H}_0 + \mathbf{V})] \\
\approx [\mathcal{H}_E, \varrho_0 (\mathcal{H}_0)]
\]  

(2.8)

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

\[
\mathbf{J}_i(s) = \int_0^\infty dt \, e^{-st} \mathbf{j}_i(t)
\]  

(2.9)

between the eigenfunctions of \(\mathcal{H}_0 + \mathcal{H}_E\), with eigenvalues \(\mathcal{W}_\alpha\), we can write

\[
\lim_{s \rightarrow i \omega} \langle \mathbf{J}_i(s) \rangle_{\alpha \beta} = \frac{i (\mathbf{j}_i)_{\alpha \beta}}{\mathcal{W}_\alpha - \mathcal{W}_\beta - i \omega + i \tau_{\alpha \beta}(\omega)}
\]  

(2.10)

\(^5\) M. LAX, Phys. Rev. 109, 1921 [1958].
Hence, the expression of the current (2.6) becomes
\[ \langle I_1 \rangle = N \sum_{\alpha \beta} \frac{(W_\alpha - W_\beta)}{W_\beta - W_\alpha + i \tau_{\beta \alpha}} \langle \varphi_0 \rangle_{\alpha} \langle j_\beta \rangle_{\beta}. \] (2.11)

Making use of the expressions for the matrix elements from the appendix (A.7—10) one obtains for the current densities
\[ \langle J_2 \rangle = \langle J_y \rangle = 0, \]
\[ \langle J_z \rangle = \frac{N e^2 E}{m \Omega} \sum_{\mathbf{k}_\perp} \langle \varphi_0 \rangle \mathbf{e} \mathbf{k}_\perp \tau_{\mathbf{k}_\perp} \] (2.12)
\[ = \frac{n e}{2 \pi m^2 T L_z} \int d\mathbf{e} \int d\mathbf{K}_\perp \exp \left\{ -K_\perp^2 / 2mT \right\} \tau_{\mathbf{k}_\perp} \] (2.13)
and hence the electrical conductivity is
\[ \sigma_{ij} = \delta_{ij} \frac{e^2 n}{m} \sum_{\mathbf{k}_\perp} \langle \varphi_0 \rangle \mathbf{e} \mathbf{k}_\perp \tau_{\mathbf{k}_\perp}. \] (2.14)

For abridgement we noted the diagonal elements by a simple index [e. g. \( \langle \varphi_0 \rangle_{\mathbf{k}_\perp} \equiv \langle \varphi_0 \rangle_{\mathbf{k}_\perp}. \)]

If \( \tau \) is constant, then Eq. (2.13) reduces to
\[ \langle J_z \rangle = \frac{n e \tau}{m L_z} \int d\mathbf{e} \]

which for a domain of integration \(-eEL_z/2 \leq \varepsilon \leq eEL_z/2\) gives the well known expression for the ohmic range
\[ \langle J_2 \rangle = n e^2 \tau E/m. \] (2.15)

It would also be possible, instead of the above form of Liouville's Eq. (2.4), to introduce directly for the current densities 
\[ \langle J_2 \rangle = \langle J_y \rangle = 0, \]
\[ \langle J_z \rangle = \frac{N e^2 E}{m \Omega} \sum_{\mathbf{k}_\perp} \langle \varphi_0 \rangle \mathbf{e} \mathbf{k}_\perp \tau_{\mathbf{k}_\perp} \] (2.12)
\[ = \frac{n e}{2 \pi m^2 T L_z} \int d\mathbf{e} \int d\mathbf{K}_\perp \exp \left\{ -K_\perp^2 / 2mT \right\} \tau_{\mathbf{k}_\perp} \] (2.13)
and hence the electrical conductivity is
\[ \sigma_{ij} = \delta_{ij} \frac{e^2 n}{m} \sum_{\mathbf{k}_\perp} \langle \varphi_0 \rangle \mathbf{e} \mathbf{k}_\perp \tau_{\mathbf{k}_\perp}. \] (2.14)

3. The Current Fluctuations Spectral Density

The Wiener-Khintchine theorem for the fluctuation of the current operator \( \delta \mathbf{I}_i(t) = \mathbf{I}_i(t) - \langle \mathbf{I}_i \rangle \) may be written as:
\[ S_{lk}(v) = \int_0^\infty e^{-i\omega t} \left[ \langle \delta \mathbf{I}_l(t + T) \delta \mathbf{I}_k(t) \rangle + \langle \delta \mathbf{I}_k(t) \delta \mathbf{I}_l(t + T) \rangle \right] dT \] (3.1)
\[ = \int_0^\infty e^{-i\omega T} \left[ \langle \delta \mathbf{I}_l(t + T) \delta \mathbf{I}_k(t) \rangle + \langle \delta \mathbf{I}_k(t) \delta \mathbf{I}_l(t + T) \rangle \right] dT \]
\[ + \int_0^\infty e^{-i\omega T} \left[ \langle \delta \mathbf{I}_l(t) \delta \mathbf{I}_k(t + T) \rangle + \langle \delta \mathbf{I}_k(t + T) \delta \mathbf{I}_l(t) \rangle \right] dT \]
\[ = S_{lk}^I(v) + S_{lk}^{II}(v) + S_{lk}^{III}(v) + S_{lk}^{IV}(v). \] (3.2)

The averaging is done over the stationary state, so that
\[ \langle \delta \mathbf{I}_l(t + T) \delta \mathbf{I}_k(t) \rangle = \text{Tr} \left\{ \varphi_{\alpha \beta} e^{i\mathbf{H}T} \delta \mathbf{I}_l e^{-i\mathbf{H}T} \delta \mathbf{I}_k \right\} \] (3.3)
and use was made of the relation \( \langle \delta \mathbf{I}_l(t - T) \delta \mathbf{I}_k(t) \rangle = \langle \delta \mathbf{I}_l(t) \delta \mathbf{I}_k(t + T) \rangle. \) The terms in Eq. (3.2) obviously obey the relations
\[ S_{lk}^{IV}(v) = S_{kl}^{IV}(-v) \quad \text{and} \quad S_{lk}^{III}(v) = S_{kl}^{III}(-v). \] (3.4)

In the same sense as in the preceding 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. \( \langle \delta \mathbf{I}_l(t + T) \delta \mathbf{I}_k(t) \rangle = N \langle \delta \mathbf{f}_l(t + T) \delta \mathbf{f}_k(t) \rangle \)] we obtain
\[ S_{lk}^I(v) = \lim_{\varepsilon \to +0} N \int e^{-s_1 T} \text{Tr} \left\{ \varphi_{\alpha \beta} \delta \mathbf{J}_l^{(s_1)}(T) \delta \mathbf{J}_k^{(s_1)} \right\} dT \]
\[ = \lim_{\varepsilon \to +0} N \text{Tr} \left\{ \varphi_{\alpha \beta} \delta \mathbf{J}_l(s_1) \delta \mathbf{J}_k(s_1) \right\} \]
\[ + \frac{1}{i} \lim_{\varepsilon \to +0} N \text{Tr} \left\{ \mathbf{H}_l \varphi_{\alpha \beta} \int_0^\infty e^{-s_1 t} e^{i\mathbf{H}t} \delta \mathbf{J}_l(s_1) \delta \mathbf{J}_k e^{-i\mathbf{H}t} \right\}. \] (3.5)
Similarly to Eq. (2.10) we have for the Laplace transform of the current fluctuations
\[ \lim_{s \to \infty} \delta f_{\alpha\beta}(s) = i \left( \frac{\delta f_{\alpha\beta}}{W_{\alpha} - W_{\beta} - \omega + i \tau_{\alpha\beta}(\omega)} \right) \]
and
\[ \lim_{t \to +0} \int e^{-st} \left[ e^{\beta H} \delta f_{\alpha\beta} e^{-\beta H} \right]_a \beta = i \left[ \frac{\delta f_{\alpha\beta}}{W_{\alpha} - W_{\beta} + i \tau_{\alpha\beta}(0)} \right] \]
respectively. Introducing again the approximations (2.7) and (2.8) we can write finally
\[ S_{ik}(v) = -N \sum_{a \neq \gamma} \frac{\tau_{\alpha\beta}^{-1}(0) (\varphi_{\alpha})_{\alpha\beta} (\delta j_{\gamma})_{\gamma}}{W_{\gamma} - W_{\alpha} - \omega + i \tau_{\gamma\gamma}(\omega)} \]
and in the same way
\[ S_{ik}(v) = -N \sum_{a \neq \gamma} \frac{\tau_{\alpha\beta}^{-1}(0) (\varphi_{\alpha})_{\alpha\beta} (\delta j_{\gamma})_{\gamma}}{W_{\gamma} - W_{\alpha} + \omega + i \tau_{\gamma\gamma}(\omega)} \]
Summing now the four terms from Eq. (3.2) with the aid of Eq. (3.4) we obtain
\[ S_{ik}(v) = \frac{1}{2N} \sum_{a \neq \gamma} \frac{\tau_{\alpha\beta}^{-1}(0) (\varphi_{\alpha})_{\alpha\beta} (\delta j_{\gamma})_{\gamma}}{W_{\gamma} - W_{\alpha} - \omega + i \tau_{\gamma\gamma}(\omega)} \]
Taking into account the definition of fluctuation
\[ c_{\alpha\beta}(\omega) = (\delta f_{\alpha\beta}(0))_{\alpha\beta} - \frac{1}{N} \langle I \rangle \delta_{\alpha\beta} \]
and the symmetry \( S_{ik}(v) = S_{ki}(v) \), the current noise spectral density takes the form
\[ S_{ik}(v) = \frac{1}{N} \sum_{a \neq \gamma} \frac{\tau_{\alpha\beta}^{-1}(0) (\varphi_{\alpha})_{\alpha\beta} (\delta j_{\gamma})_{\gamma}}{W_{\gamma} - W_{\alpha} - \omega + i \tau_{\gamma\gamma}(\omega)} \]
In a large domain of frequencies, the relaxation time does practically not depend on frequency, i.e. \( \tau_{\alpha\beta}(\omega) \approx \tau_{\alpha\beta}(0) = \tau_{\alpha\beta} \) and the above expression becomes considerably simpler. However, this limitation in frequency will exclude the appearance of any quantum correction factor.

For an electric field directed along the z-axis, substituting the matrix elements of \( \mathbf{q} \) and \( \mathbf{f_i} \) from the appendix, after some algebra we obtain the following formulae for the fluctuation spectrum matrix:
\[ S_{xx}(v) = \frac{4e^2 N}{m^2 L^2 E} \sum_{m} \frac{(\varphi_{\alpha})_{K_\perp} \tau_{K_\perp}}{1 + \omega^2 \tau_{K_\perp}^2} \]
\[ = \frac{2e N}{\pi m^2 T L^2 E} \int d\mathbf{q} \int dK_\perp K^2 \exp(-K^2/2mT) \frac{\tau_{K_\perp}}{1 + \omega^2 \tau_{K_\perp}^2} \]

(3.11)

(3.11')
\[ S_{yy}(v) = \frac{4 e^2 N}{m^2 L_y^2} \sum \frac{(\varrho_0)_{\mathbf{K}} \tau_{\mathbf{K}}}{1 + \omega^2 \tau^2_{\mathbf{K}}} K_y^2 \]  
(3.12)

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

\[ S_{zz}(v) = S_{xx}(v) = S_{yy}(v) = 0, \]  
(3.13)

\[ S_{zz}(v) = \frac{4 N e^2 T}{m L_z^2} \sum \frac{(\varrho_0)_{\mathbf{K}} \tau_{\mathbf{K}}}{1 + \omega^2 \tau^2_{\mathbf{K}}} \left[ \frac{2}{1 + \omega^2 \tau^2_{\mathbf{K}_\perp}} \right] + \frac{4 N \langle I_z \rangle^2}{m L_z} \sum \frac{(\varrho_0)_{\mathbf{K}} \tau_{\mathbf{K}}}{1 + \omega^2 \tau^2_{\mathbf{K}_\perp}} \left[ \frac{2}{1 + \omega^2 \tau^2_{\mathbf{K}_\perp}} \right], \]  
(3.14)

or, turning the sums into integrals,

\[ S_{zz}(v) = -\frac{2 N}{\pi m T} \frac{1}{e E L_z} \left\{ \int \frac{\omega}{d \mathbf{K}_\perp} \exp\left\{ -K_{\mathbf{K}_\perp}^2 / 2 m T \right\} \frac{\tau_{\mathbf{K}_\perp}}{1 + \omega^2 \tau^2_{\mathbf{K}_\perp}} \left[ \frac{2}{1 + \omega^2 \tau^2_{\mathbf{K}_\perp}} \right] \times \left( \frac{N e^2 E}{m L_z \langle I_z \rangle} \tau_{\mathbf{K}_\perp} - 1 \right) \right\}. \]

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 \(\tau_{\mathbf{K}_\perp}\) is a constant, leading, as we have seen in § 2 to the ohmic behaviour of the current, then

\[ L_z^2 S_{zz}(v) = L_z^2 S_{yy}(v) = \frac{4 N e^2 T \tau}{m (1 + \omega^2 \tau^2)} \]

and

\[ S_{zz}(v) = \frac{4 N e^2 T \tau}{m L_z^2 (1 + \omega^2 \tau^2)} + \frac{4 N \langle I_z \rangle^2}{m L_z} \frac{\tau}{1 + \omega^2 \tau^2} \]  
(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 \(S_{zz}(v)\) 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 probability of transition for the corresponding type of interaction. Unfortunately, due to the form of the interaction potential and 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:

\[ \tau_{\mathbf{K}_\perp} = \tau_1 \left( \epsilon - \epsilon_0 + K_{\mathbf{K}_\perp}^2 / 2 m \right)^{-1/2}. \]  
(4.1)

Making use of the approximate integration formula

\[ \int d\mathbf{K}_\perp f(\mathbf{K}_\perp) \exp\{ -K_{\mathbf{K}_\perp}^2 / 2 m T \} \approx 2 \pi m T \int f(\mathbf{K}_\perp) |\mathbf{K}_\perp|^2 = 2 m T \]  
(4.2)

the result of integrations in Eq. (2.13) for the current density on the intervals \(\epsilon_0 = -e E L_d / 2 \leq \epsilon \leq \epsilon_0', 0 \leq |\mathbf{K}_\perp| < \infty\) is

\[ \langle J_z \rangle \approx \frac{2 n e \tau_1}{m L_z} \left[ (\epsilon_0 - \epsilon_0' + T)^{1/2} - T^{1/2} \right]. \]  
(4.3)

If the integration in \(\epsilon\) were done over the whole spectrum, i.e. \(\epsilon_0'\) were infinite, then the result would
be divergent, which is obviously wrong. However, if we perform a cut-off at $e_{0}' = eE_{Lz}/2$, that is if the domain of variation of $e$ 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:

\[
\langle \xi \rangle \sim \begin{cases} 
\frac{2n e \tau_{1}}{m L_{z}^{3}} (eE)^{\nu_{1}^{2}} & \text{for } E \gg T L_{z}^{-1} \\
\frac{n e^{2} \tau_{1} E}{m T^{\nu_{1}}} & \text{for } E \ll T L_{z}^{-1} 
\end{cases} \quad (4.4)
\]

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, the proportionality factor must be written as

\[
\tau_{1} = \tau_{0} (eE_{Lz}/4 + T)^{\nu_{1}} (T/T_{0})^{\nu_{1}} \quad (4.5)
\]

where the relaxation time for ohmic conduction $\tau_{0} = 4/3 \pi m^{3/2} (2\pi T)^{-1/2}$, $l$ is the mean free path for scattering by acoustic phonons.

The electron temperature $T_{e}$ is given by

\[
T_{e} = \begin{cases} 
1 & \text{for } E \gg m u_{i} \tau_{0}^{-1} \\
\frac{\pi^{3/4}}{2} \frac{(mT)^{1/4}}{(eE)^{\nu_{1}/4}} & \text{for } E \ll m u_{i} \tau_{0}^{-1},
\end{cases} \quad (4.6)
\]

\[u_{i} \text{ is the longitudinal sound velocity.}\]

Thus, from Eq. (4.4 - 6) we get

- in the low field limit

\[\langle \xi \rangle = \frac{4}{3} \frac{n e^{2} l E}{m T^{\nu_{1}}} \quad \text{(4.7)}\]

- in the high field limit

\[\langle \xi \rangle = \frac{(2\pi)^{\nu_{1}}}{T^{\nu_{1}}(3/4)} \frac{e n (eE u_{i})^{\nu_{1}}}{m T^{\nu_{1}}}.\]

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

\[L_{x}^{2} S_{xx}(v) = L_{y}^{2} S_{yy}(v) \approx \frac{8 N e T}{m E_{Lz}} \tau_{1} \left[ (eE_{Lz} + T)^{\nu_{1}/2} - T^{\nu_{1}/2} - \omega \tau_{1} \right] \arctan \left( \frac{(eE_{Lz} + T)^{\nu_{1}}}{\omega \tau_{1}} \right) - \arctan \left( \frac{T^{\nu_{1}}}{\omega \tau_{1}} \right) \quad (4.8)\]

\[= \frac{8 N e T}{m E_{Lz}} \tau_{1}^{3} \left[ \frac{1}{\omega \tau_{1}} - 2 \omega \tau_{1} \left( (eE_{Lz} + T)^{\nu_{1}/2} - T^{\nu_{1}/2} \right)^{2} - 3 e E L_{z} \left( (eE_{Lz} + T)^{\nu_{1}/2} - T^{\nu_{1}/2} \right) \ln \left( (eE_{Lz} + T)^{\nu_{1}/2} + (\omega \tau_{1})^{2} \right) \right. \]

\[= \frac{1}{\omega \tau_{1}^{2}} \left[ (eE_{Lz} + T)^{\nu_{1}/2} \left( 16 T^{3} + 20 e E L_{z} T^{2} + 3(eE_{Lz})^{2} T \right) \right. \]

\[+ (eE_{Lz} + T)^{\nu_{1}/2} \left( 16 T^{3} + 28 e E L_{z} T^{2} + 11(eE_{Lz})^{2} T \right) \left. - (eE_{Lz})^{3} \right] \quad (4.9)\]

For low fields ($E \ll T L_{z}^{-1}$, $m u_{i} \tau_{0}^{-1}$), the above expressions can be put into more closed forms

\[L_{x}^{2} S_{xx}(v) = L_{y}^{2} S_{yy}(v) \approx \frac{8 N e^{2} T^{\nu_{1}}}{m T + (\omega \tau_{1})^{2}} \frac{\tau_{1}^{3}}{m} \frac{1 + o^{2} \tau_{0}^{2}}{1 + o^{2} \tau_{0}^{2}} \quad (4.10)\]

\[S_{zz}(v) \approx \frac{4 N e^{4} E^{2}}{m L_{z}^{2}} \frac{T^{\nu_{1}}}{1 + o^{2} \tau_{0}^{2}} \frac{\tau_{0}^{3}}{m L_{z}^{2}} \approx \frac{4 N e^{2} T}{m L_{z}^{2}} \frac{\tau_{0}^{3}}{1 + o^{2} \tau_{0}^{2}} + \frac{\tau_{0}^{3}}{1 + o^{2} \tau_{0}^{2}} \frac{4 L_{z}^{2}}{N}. \quad (4.11)\]

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

\[S_{ij}(v) = 4 T_{ij}^{N} \frac{Q}{L_{i} L_{j}} \text{Re } \sigma_{ij}(\omega)\]

can be then expressed in a simple manner:

\[T_{ij}^{N} = T \delta_{ij} + \frac{e^{2} E_{i} E_{j}}{m} \tau_{0}^{2}. \quad (4.12)\]

The noise temperature contains a convective term in addition to the lattice temperature, in agreement with Gurevich, Schlupe and Price. It does not depend on frequency, but probably this is a peculiarity of the parabolic bands.

In the high field limit \( eE \gg TL \), \( m \omega \tau_\rho^{-1} \)

\[
L_x^2 S_{xx}(\nu) = L_y^2 S_{yy}(\nu) \approx \frac{8N e^2 T}{mE L_z} \tau_1 (eE L_z)^{1/2} \left[ 1 - \omega \tau_1 (eE L_z)^{-1} \arctan \left( \frac{eE L_z}{\omega \tau_1} \right) \right],
\]

\[
S_{zz}(\nu) \approx S_{xx}(\nu) L_z^2 + \frac{8N e^2 \tau_1^2}{m^2 E L_z^4} (eE L_z)^{1/2} \left\{ 2 \frac{eE L_z - 2(\omega \tau_1)^2}{\omega \tau_1 (eE L_z)^{1/2}} - 3 \ln \left( \frac{T + (\omega \tau_1)^2}{eE L_z} \right) \right\} + \left( eE L_z \right)^{1/2} T \tau_1^2 \left[ 5 eE L_z - 13 (eE L_z T)^{1/2} + 4(\omega \tau_1)^4 \right] \right] eE L_z T + T^2 + (\omega \tau_1)^2 (eE L_z + 2T) + (\omega \tau_1)^4 .
\]

These formulae become simpler for extreme frequencies

- For low frequencies \( [\omega \tau_0 \ll 2(T_0/T)^{1/2}] \)

\[
L_x^2 S_{xx}(\nu) = L_y^2 S_{yy}(\nu) \approx \frac{4N e^2 T}{m} \tau_0 (T/T_0)^{1/2},
\]

\[
S_{zz}(\nu) \approx \frac{4N e^2 T}{mL_2^2} \tau_0 (T/T_0)^{1/2} + \frac{2\pi N e^4 E^2}{m^2 L_2^4} \tau_0^2 \frac{T}{T_0} \frac{1}{\omega} = \frac{4N e^2 T}{mL_2^2} \tau_0 (T/T_0)^{1/2} + \frac{2\pi (I_2)^2}{N} \frac{1}{\omega} .
\]

- For high frequencies \( [\omega \tau_0 \gg 2(T_0/T)^{1/2}] \)

\[
L_x^2 S_{xx}(\nu) = L_y^2 S_{yy}(\nu) \approx \frac{16N e^2 T}{3m} \frac{1}{\omega^2 \tau_0} \left( \frac{T}{T_0} \right)^{1/2},
\]

\[
S_{zz}(\nu) = \frac{L_z^2}{L_z^2} S_{xx}(\nu) + \frac{16N e^4 E^2 \tau_0}{3mL_2^2} \frac{T}{T_0} = \frac{16N e^2 T}{3mL_2^2} \omega^2 \tau_0 \left( \frac{T}{T_0} \right)^{1/2} + \frac{16 (I_2)^2}{3N} \frac{1}{\omega^2 \tau_0} \left( \frac{T}{T_0} \right)^{1/2}.
\]

Denoting \( \tau_E = \tau_0 (T/T_0)^{1/2} \) we conclude that the pure Nyquist term looks like

\[
\frac{4N e^2 T}{mL_1^2} \frac{\tau_E}{1 + \omega^2 \tau_E^2} = \frac{4T \Omega}{L_1^2} \Re \sigma(\omega)
\]

in disagreement with Gurevich and Price who obtain \( T^N \approx T_0 \).

The convective part of the noise temperature \( T^N \) behaves quite normally at high frequencies \( (e^2 E_1 E_2 \tau_E^2/m) \) 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 explicitly 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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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 \( H_0 + H_E \) obey the equation

\[
\left( -\frac{1}{2m} \nabla^2 + eEz \right) \psi(r) = W \psi(r) \tag{A.1}
\]

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 \(^9\)

\[
\psi_{\epsilon_n K_z K_y}(r) \equiv \left| \epsilon_n K_\perp \right> = A_n \text{Ai}(\xi_n) \exp\left[i(K_z x + K_y y)\right]
\tag{A.2}
\]

where

\[
W = \epsilon_n + \frac{K_\perp^2}{2m} \quad \xi_n = \left(z - \frac{\epsilon_n}{eE}\right) \left(2m eE\right)^{1/4},
\]

\( K_\perp \) is the momentum perpendicular to the field direction, and the Airy function is defined by

\[
\text{Ai}(\xi) = \frac{1}{\sqrt{\pi}} \int_0^\infty \cos\left(\frac{u^3}{3} + u \xi\right) du . \tag{A.3}
\]

The constant \( A_n \) is gotten from the conditions of normalization on the volume \( \Omega = L_x L_y L_z \) \((-L_z/2 \leq z \leq L_z/2, \text{etc.}) \) and completeness on the discrete spectrum of \( \epsilon_n \).

\[
A_n = \left(\frac{2m}{\pi e E L_z^{1/4} L_x^{1/4} L_y^{1/4}}\right) \left[\eta(\epsilon_n)\right]^{-1/4}. \tag{A.4}
\]

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

\[
\eta(\epsilon_n) \approx \left(\frac{2m}{\pi e E L_z^{1/4}}\right) \left(\epsilon_n + \frac{eE L_z^{1/4}}{2}\right). \tag{A.5}
\]

The same condition gives the lower limit of the spectrum, \( \epsilon_0 = -eE L_z/2 \).

If the length of the box \( L_z \) is sufficiently great, \( L_z/(2m eE)^{1/4} \gg 1 \), and the spacing between levels \( \Delta\epsilon_n = [\eta(\epsilon_n)]^{-1} \) is small enough, then we can use a continuous density of states and integrate on the energy spectrum \( \epsilon_n \) instead of summing \( \sum \epsilon_n \eta(\epsilon_n) \ldots \). This corresponds to the semiclassical approximation when box normalized momentum eigenstates are used.

In order to calculate the matrix elements of \( \mathcal{Q} \) and \( \mathcal{J}_i \), we need the Fourier transform of \( \psi(r) \)

\[
\Phi_{\epsilon_n K_z}(p) = \frac{1}{Q^{1/4}} \int \exp\left(-ip \cdot r\right) \psi_{\epsilon_n K_z}(r) \, dr = \frac{1}{\left[eE L_z \eta(\epsilon_n)\right]^{1/4}} \exp\left[-\frac{i}{eE} \left(\frac{\epsilon_n p_2 - \frac{p_3^2}{6m}}{2m}\right)\right] \delta_{K_z P_z} \tag{A.6}
\]

then

\[
\langle \Phi_{\epsilon_1 K_z} \rangle_{12} = Z^{-1} \left\{ \frac{1}{eE L_z} \left[ \left(\eta(\epsilon_1) \eta(\epsilon_2)\right)^{1/4} \exp\left[-\frac{i}{eE} K_z (\epsilon_1 - \epsilon_2)\right] \right] \right\} \delta_{K_z, K_x} \tag{A.7}
\]

\[
Z = \text{Tr}(e^{-\beta H_z}) = \sum_K \exp\left(-\beta K_x^2/2m\right) = \frac{Q}{(2\pi)^3} \left(2\pi m T\right)^{1/4} . \tag{A.8}
\]

It is important to note that this value of the statistical sum is obtained either using the orthogonality and completeness relations for the wave functions, or integrating \( e^{-\beta H_0} \delta_{\bar{\epsilon}_1, \bar{\epsilon}_2} \) in the variable \( \epsilon \), between the limits \(-eEL/2, +eEL/2\) that is cutting the domain of integration in its upper part.

\[
(j_1)_{12} = -\frac{eK_{11}}{mL_1} \delta_{\bar{\epsilon}_1, \bar{\epsilon}_2} \delta_{\bar{\epsilon}_1, \bar{\epsilon}_2} \approx -\frac{eK_{11}}{mL_1} [\eta(\epsilon_1) \eta(\epsilon_2)]^{-1/2} \delta(\epsilon_1 - \epsilon_2) \delta_{\bar{\epsilon}_1, \bar{\epsilon}_2} \text{ (} i = x, y \text{)} \quad (A.9)
\]

\[
(j_2)_{12} = -\frac{eE_2}{mL_2} [\eta(\epsilon_1) \eta(\epsilon_2)]^{-1/2} \sum_{K_2} K_2 \exp \left\{ \frac{i}{eE} K_2 (\epsilon_1 - \epsilon_2) \right\} \delta_{\bar{\epsilon}_1, \bar{\epsilon}_2} \approx -\frac{eE_2}{i m L_2} [\eta(\epsilon_1) \eta(\epsilon_2)]^{-1/2} \frac{d}{d\epsilon_1} \delta(\epsilon_1 - \epsilon_2) \delta_{\bar{\epsilon}_1, \bar{\epsilon}_2} \text{.} \quad (A.10)
\]

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**Thermal Expansion of Alkali Sulphate Mixtures**

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The linear thermal expansivities of polycrystalline samples of mixtures of \( \text{Li}_2\text{SO}_4 \) with \( \text{K}_2\text{SO}_4 \) and with \( \text{Na}_2\text{SO}_4 \) have been measured with a “Fused-Quarz Tube” apparatus. 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 \( \text{Li}_2\text{SO}_4 \) 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 inter-diffusion coefficients of other monovalent cations) is of the order of \( 10^{-5} \text{cm}^2 \text{s}^{-1} \) while \( D_{SO_4^-} \) is several magnitudes smaller (about \( 10^{-10} \text{cm}^2 \text{s}^{-1} \) at 800 °C) \(^2\). 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 \( \text{Li}_2\text{SO}_4 \) 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. Semi-quantitative preliminary studies of the rheology of solid lithium sulphate have been performed in this laboratory, plastic flow investigations by AUGUSTSSON and LUNDEN \(^4\) and thermal expansion investigations by AUGUSTSSON and EKHELD \(^5\). 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


\(^3\) A. BENGTZELIUS, private communication.
