

## Thermoelectric Effects in Copper-Gold Alloys

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Measurements of the resistivity and thermoelectric power of the binary alloy CuAu and of CuAu alloys containing dilute amounts of Ni are analyzed using the thermoelectric power formula of Mott. At the transition temperature, anomalies in the thermoelectric power are observed. The scattering cross section and its derivative with respect to energy for Ni in CuAu are determined. The results are similar in value to these same parameters measured for dilute amounts of Ni in Cu.

### INTRODUCTION

ONE of the most studied alloys showing an order-disorder transition is the binary alloy CuAu.<sup>1</sup> The face-centered tetragonal ordered phase, CuAu I, has been found to change to an orthorhombic ordered phase, CuAu II, above 380°C. Above the critical temperature, about 410°C, the equilibrium structure is face-centered cubic, and no long-range order exists.

The relationship between electrical resistivity and long range order has been examined theoretically by Muto,<sup>2</sup> and used by Dienes<sup>3</sup> to study the ordering kinetics in CuAu. The relationship between thermoelectric power and order parameter has received little attention. Cooper, Schmed, and Webeler<sup>4</sup> have measured the thermoelectric power of CuAu alloys disordered by cold work.

In the absence of a good theoretical understanding of the electrical properties of these rather complicated systems, we have used the change in the electrical properties of CuAu caused by a third component to obtain some information about transport effects. Our results are analyzed using free electron theory.

### THEORY

Muto<sup>2</sup> has shown that the resistivity of an alloy whose state of order can be characterized by an order parameter  $S$  should depend on  $S$  in accordance with the relation

$$\rho = \rho' + \rho''S + \rho'''S^2, \quad (1)$$

where the three constants are functions of temperature and composition. Dienes<sup>3</sup> has evaluated these constants using the relations

$$\begin{aligned} \rho &= \rho_{\text{disordered}} & \text{at } S=0, \\ \rho &= \rho_{\text{ordered}} & \text{at } S=1, \\ d\rho/dS &= 0 & \text{at } S=0, \end{aligned}$$

<sup>1</sup> For recent reviews of order-disorder phenomena including many references to the CuAu system, see articles by T. Muto and Y. Takagi, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1955), Vol. 1, p. 193 and L. Guthman, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1956), Vol. 3, p. 145.

<sup>2</sup> T. Muto, Sci. Papers Inst. Phys. Chem. Research (Tokyo) **30**, 99 (1936).

<sup>3</sup> G. J. Dienes, J. Appl. Phys. **22**, 1020 (1951).

<sup>4</sup> Cooper, Schmed, and Webeler, J. Appl. Phys. **27**, 516 (1956).

the latter relation being justifiable experimentally. The resulting equation is

$$(\rho - \rho_{\text{ord}})/(\rho_{\text{dis}} - \rho_{\text{ord}}) = 1 - S^2, \quad (2)$$

where all resistivities are measured at the same temperature. If we define

$$\rho_{\Delta} = \rho_{\text{dis}} - \rho_{\text{ord}}, \quad (3)$$

we can write Eq. (2) as

$$\rho_{\text{CuAu}} = \rho_{\text{ord}} + \rho_{\Delta}(1 - S^2). \quad (4)$$

In this way, we can think of the resistivity of the partially disordered alloy as the sum of the resistivity of ordered alloy plus the additional resistivity  $(\rho - \rho_{\text{ord}})$ , of the disordered atoms acting as an impurity contribution.

If we dissolve small amounts of a third component in the alloy, we assume the resistivity (at least for well ordered material) to be given by

$$\rho = \rho_{\text{ord}} + \rho_{\Delta}(1 - S^2) + \rho_i, \quad (5)$$

where  $\rho_i$  is the additional resistivity of the added component. The added resistivity is assumed independent of temperature and, according to free electron theory, may be written as<sup>5</sup>

$$\rho_i = (3h^3/16\pi m e^2)(n_i \sigma_i/E_F), \quad (6)$$

where  $E_F$  is the Fermi energy,  $e$  and  $m$  are the electronic charge and mass,  $n_i$  is the number of impurity atoms per unit volume, and  $\sigma_i$  is the effective cross section for scattering.

Our description of the absolute thermoelectric power of the alloys uses the relation first presented by Mott and Jones.<sup>6</sup>

$$Q = (\pi^2 k^2 T/3|e|) \left[ \frac{d \ln \rho(E)}{dE} \right]_{E=E_F}. \quad (7)$$

From Eqs. (5) and (7) we obtain

$$Q = (\rho_{\text{ord}}/\rho)Q_{\text{ord}} + (AT/\rho)[\lambda_{\Delta}\rho_{\Delta}(1 - S^2) + \lambda_i\rho_i], \quad (8)$$

where  $A = \pi^2 k^2/3|e| = 0.0243$  (electron volt) (microvolt/degree),  $Q_{\text{ord}}$  represents the absolute thermo-

<sup>5</sup> C. A. Domenicali, Phys. Rev. **112**, 1863 (1958).

<sup>6</sup> N. F. Mott and H. Jones, *Theory of the Properties of Metals and Alloys* (Oxford University Press, London, 1936).

electric power of the ordered alloy at  $T^\circ\text{K}$ , and  $\lambda_i$  and  $\lambda_\Delta$  are scattering parameters<sup>5</sup> defined as

$$\lambda_i = \left[ \frac{d \ln \sigma_i(E)}{dE} \right]_{E=E_F} - \frac{1}{E_F} = \left[ \frac{1}{\rho_i} \frac{d\rho_i}{dE} \right]_{E=E_F}, \quad (9)$$

$$\lambda_\Delta = \left[ \frac{d \ln \sigma_\Delta(E)}{dE} \right]_{E=E_F} - \frac{1}{E_F} = \left[ \frac{1}{\rho_\Delta} \frac{d\rho_\Delta}{dE} \right]_{E=E_F}.$$

For slightly disordered CuAu at any temperature we can write Eq. (8) as

$$\rho_{\text{CuAu}} Q_{\text{CuAu}} = \rho_{\text{ord}} Q_{\text{ord}} + AT \rho_\Delta \lambda_\Delta (1 - S^2). \quad (10)$$

For alloys of CuAu containing nickel as a third component we can write using Eqs. (8) and (10)

$$\rho Q = \rho_{\text{CuAu}} Q_{\text{CuAu}} + AT \rho_{\text{Ni}} \lambda_{\text{Ni}}, \quad (11)$$

where all values of resistivity and absolute thermoelectric power are measured at the same temperature  $T$ .

In the preceding equations, the ordered binary alloy is considered to have an absolute thermoelectric power,  $Q_{\text{ord}}$ , at  $T^\circ\text{K}$  which is altered with a decrease in long-range order. The quantity  $Q_{\text{ord}}$  is not derived, but is expected to be small and of the order of the absolute thermoelectric power of pure copper. We find by extrapolation that  $Q_{\text{ord}} = -0.6 \mu\text{volt}/^\circ\text{C}$  at  $25^\circ\text{C}$ . Similarly, the quantity  $\lambda_\Delta$ , the derivative with respect to energy of  $(\rho_{\text{dis}} - \rho_{\text{ord}})$ , is a measure of the energy dependence of the scattering of electrons by regions between out of phase domains or by localized fluctuations in short range order.

The use of free electron theory (spherical energy surfaces, effective mass near unity) may be more suitable for CuAu alloys than for either Cu or Au individually, as the Fermi surface of the CuAu system may actually become spherical at some concentration.<sup>7</sup> Our treatment of impurity scattering by Eq. (6) assumes that impurities are sufficiently dilute to be essentially noninteracting. The resulting equations will be restricted to order parameters near unity and nickel concentrations of a few atomic percent.

### EXPERIMENTAL

Three alloys were prepared for this investigation. For all alloys, the 50-50 copper-to-gold atom ratio was accurate to better than 0.04% as determined by weighing. In addition, nickel was added to two of the alloys to the extent of 1.44 and 2.44 atomic percent.

High-purity copper was obtained from American Smelting and Refining Company, and wire rolled from this material was used for all connections to the alloys. Gold was obtained from Baker and Company and the nickel was obtained from Johnson-Matthey.

The alloys were prepared by sealing the constituents in evacuated quartz tubes and melting in an electric

furnace. The alloys were held above their melting point for two hours and periodically agitated to assist in attaining homogeneity. The alloys were then removed from the furnace, allowed to freeze, and water quenched. The resulting ingots were cold rolled to produce wires of square cross section about  $75 \times 10^{-3}$  cm on a side.

For measurement of the thermoelectric power of the wires near room temperature, thermocouples were prepared using a sample wire and pure copper wire. One end of the thermocouple was held at  $0^\circ\text{C}$  as the other end was heated slowly to about  $150^\circ\text{C}$ . During heating, the temperature difference and thermoelectric voltage were automatically recorded on a Brown Instrument X-Y plotter, and the relative thermoelectric power against copper was obtained by graphically differentiating this curve. The absolute thermoelectric power of the sample was then obtained by adding the absolute thermoelectric power of pure copper given by Cusack and Kendall<sup>8</sup> to the relative thermoelectric power.

At higher temperatures, where the order-disorder effects change the electrical properties of the wires, a differential method was used to measure thermoelectric power. The alloy wires and a constantan wire were placed parallel to each other in a ceramic holder, 20 cm long, and copper leads were welded to each wire. When the ends of the ceramic holder were maintained at slightly different temperatures, the potential difference of the specimens could be measured and referred to the potential difference of the constantan wire. The thermoelectric power of our constantan wire (prepared in the laboratory) was measured separately.

The entire assembly was enclosed in a continuously pumped quartz tube and inserted within a one-inch wall stainless steel tube. The tube was within the center core of an electric furnace, and contained end heaters to control the size and direction of the temperature gradient.

The potential difference of the sample wires was plotted against the potential difference of the constantan wire for 5 to 10 different temperature gradients at a chosen mean temperature. From the slope of the straight lines thus obtained, the thermoelectric voltage of the wires against constantan could be determined.

The usual maximum differential temperature was  $\pm 4^\circ\text{C}$ . Thermoelectric voltages were measured with a Rubicon thermofree two-channel potentiometer. Below the transition temperature, the wires were allowed about 24 hours to come to equilibrium before each thermoelectric power determination.

Resistance was determined as a function of temperature for these alloys by automatically recording the voltage drop across the sample wires and a standard resistor as the wires were heated and cooled. The

<sup>7</sup> M. H. Cohen and V. Heine, *Phil. Mag.* **7**, 395 (1958).

<sup>8</sup> N. Cusack and P. Kendall, *Proc. Phys. Soc. (London)* **72**, 898 (1958).

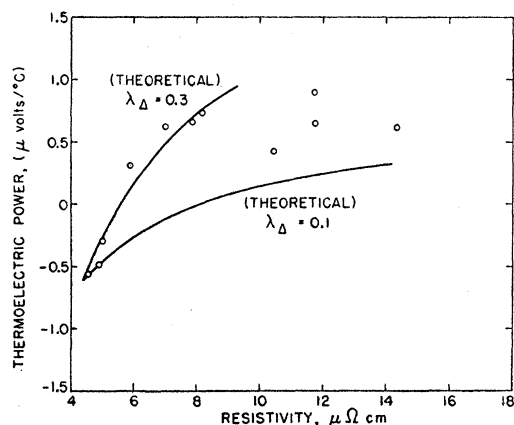


FIG. 1. Variation of absolute thermoelectric power with resistivity at 25°C for quenched CuAu wires.

wires (20 cm long) were wrapped inside ceramic tubes inserted within a solid copper block (10 cm long). The copper block was within a continuously pumped quartz tube. The sample temperature was raised and lowered in an electric furnace controlled by a cam actuated controller. The temperature was changed in a stepwise manner. In this way, the alloys were allowed to attain near-equilibrium conditions before a change in temperature occurred. The entire run from room temperature to 700°C and back took three days.

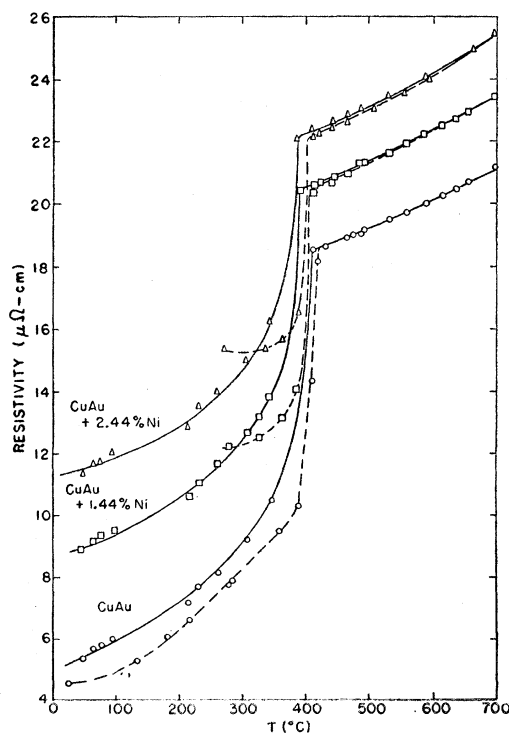


FIG. 2. Resistivities of CuAu-Ni alloys. The dashed and solid lines are the heating and cooling curves, respectively.

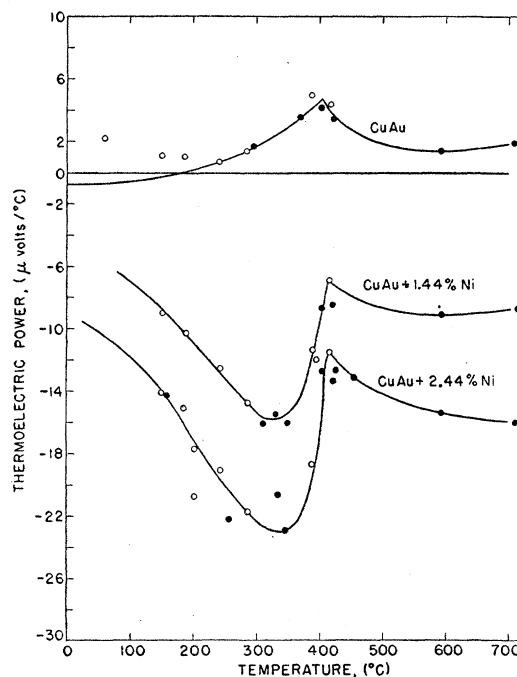


FIG. 3. Absolute thermoelectric power of CuAu-Ni alloys. The filled circles represent thermoelectric powers obtained during heating, the open circles during cooling.

## RESULTS

The results of some thermoelectric power and resistivity measurements on CuAu wires are shown in Fig. 1. Similar results were obtained by Cooper, Schmed, and Webeler.<sup>4</sup> The scatter of the data at higher resistivities is possibly due to difficulties in rapidly quenching the wires to obtain uniform resistivity values in a region where resistivity is very temperature dependent. The wires were sealed in

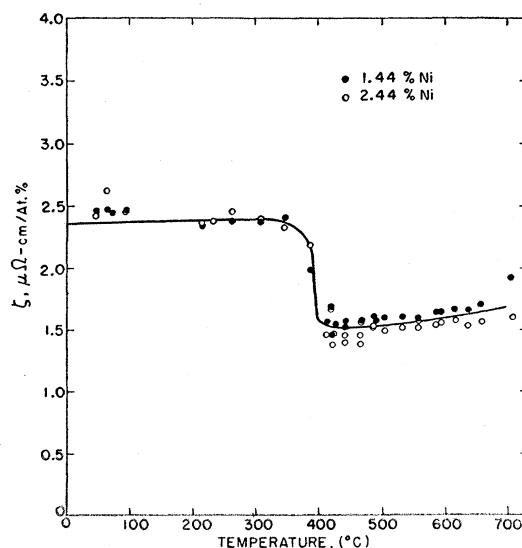


FIG. 4. Resistivity per atomic percent,  $\zeta$ , for CuAu-Ni alloys.

evacuated Pyrex tubes and heated to temperatures below 400°C in an electric furnace. A copper tube in the center of the furnace served to minimize variations in temperature. After 24 hours or more at temperature, the wire was pulled from the furnace and quenched by a quick plunge into water, simultaneously breaking the tube. Using values of  $\rho_{\text{ord}} = 4.4 \mu\text{ohm-cm}$  and  $\rho_{\text{dis}} = 14.2 \mu\text{ohm-cm}^3$ , the thermoelectric power described by Eq. (10) is shown for two values of the parameter  $\lambda_{\Delta}$ . For order parameters less than 0.9 (or resistivities above  $7 \mu\text{ohm-cm}$ ), the equation should no longer apply for the sources of "impurity" scattering should be sufficiently numerous to preclude their treatment as independent scatterers. A value of  $\lambda_{\Delta} = 0.3$  has about the correct slope and curvature to fit the data.

Results for the variation of resistivity and thermoelectric power with temperature for the three wires are shown in Figs. 2 and 3. From the original resistivity data, it could be seen that the addition of nickel to the CuAu lattice not only lowers the transition temperature but also decreases the rate of approach to equilibrium below the transition temperature. As a

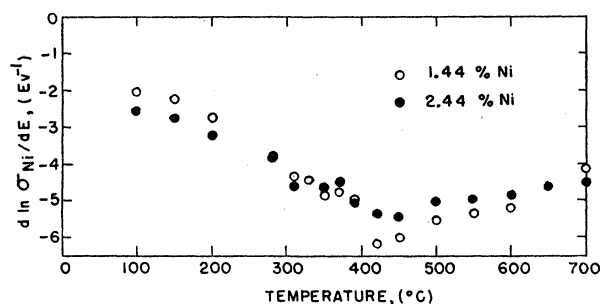


FIG. 5. Variation of  $(d \ln \sigma_{\text{Ni}} / dE)$  for Ni in CuAu.

result, we have extrapolated the thermoelectric power of the alloys containing nickel to obtain values at 100°C. For the CuAu alloy, the thermoelectric voltage against pure copper was measured below 150°C, using a well-ordered sample. The absolute thermoelectric voltage was determined from the slope of voltage against temperature, and joined to the curve determined by the differential method above 200°C.

The impurity resistivity per atomic percent,  $\zeta$ , [a measure of the  $\sigma_i$  of Eq. (6)] for Ni in the CuAu lattice is shown as a function of temperature in Fig. 4. The data of Figs. 2 and 4 were obtained during periods of constant temperature and stable resistance values. An apparent increase in  $\zeta$  near room temperature in Fig. 4 is due to incomplete ordering in the wires containing nickel. For  $\zeta$  we get 1.5 and  $2.4 \mu\text{ohm-cm}$  per atomic percent, respectively, above and below the transition temperature. These values are accurate to better than 10%, as determined by the scatter of the data. For comparison, the resistivity increase for Ni in Cu is 1.2 microhm-cm per atomic percent.<sup>9</sup>

<sup>9</sup> J. O. Linde, Ann. Physik 15, 219 (1932).

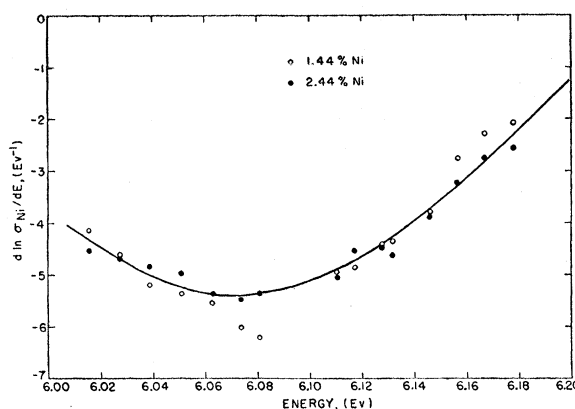


FIG. 6. Variation of  $(d \ln \sigma_{\text{Ni}} / dE)$  for Ni in CuAu.

The scattering parameter,  $\lambda_{\text{Ni}}$ , defined by Eq. (9), can be determined from the resistivity and thermoelectric power data by the use of Eq. (11). From the lattice constants of CuAu<sup>10</sup> and free electron theory we calculate the Fermi energy,  $E_F = 6.19 \text{ eV}$  for CuAu at 25°C. The values of  $E_F$  for Cu and Au are 7.04 eV and 5.54 eV, respectively, at room temperature. From Eq. (9) the value of  $(d \ln \sigma_{\text{Ni}} / dE)_{E=E_F}$  can now be determined as a function of temperature. The results of this calculation are shown in Fig. 5.

The rapid change of volume at the transition temperature in CuAu causes a lowering of the Fermi energy and is a possible explanation for the apparent change in slope at this point in Fig. 5. From the thermal expansion data of Kurnakow and Ageew<sup>11</sup> and the relation  $(1/E_F)(dE_F/dT) = -\frac{2}{3}(1/V_0)(dV_0/dT)$ , the variation of  $E_F$  with temperature can be determined. The data of Fig. 5 can now be plotted as a function of energy, and a discontinuity in slope is not required, as shown in Fig. 6. Using the curve of Fig. 6, a graphical integration gives the variation of  $\sigma/\sigma_0$  with energy (where  $\sigma_0$  represents the scattering cross section of Ni in a CuAu lattice at 0°C). In Fig. 7 our result for CuAu is compared with the scattering cross sections

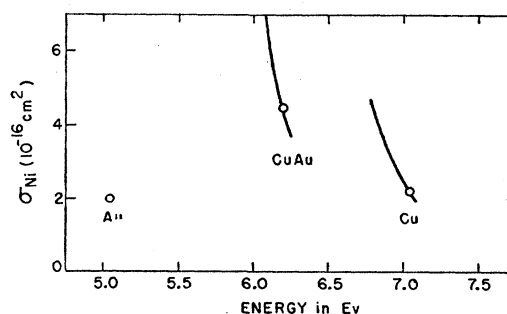


FIG. 7. Dependence of scattering cross section on electron energy as determined from thermoelectric power measurements.

<sup>10</sup> C. H. Johansson and J. O. Linde, Ann. Physik 25, 1 (1936).

<sup>11</sup> N. S. Kurnakow and N. W. Ageew, J. Inst. Metals 46, 481 (1931).

for Ni in Cu<sup>5</sup> and Ni in Au.<sup>12</sup> The circles represent the room temperature scattering cross section by resistivity measurements, and the curves give the variation of the cross section with energy as determined from thermoelectric power measurements.

### DISCUSSION

From Figs. 2 and 4, it can be seen that the variation of resistance with temperature for the alloys is largely independent of nickel concentration except near the transition temperature. The increase in resistance is proportional to the nickel concentration. Thus Matthiessen's rule as applied to dilute alloys is valid for the CuAu-Ni alloys.

Similarly, applying Mott's formula to the thermoelectric power of the CuAu-Ni alloys leads to a reasonable value for the scattering parameter of the added nickel. The effect of nickel additions on resistivity and thermoelectric power is not greatly dependent on the solvent metal as shown in Fig. 7 for the series Cu, CuAu, and Au. The smooth variation of  $(d \ln \sigma_i / dE)$  with energy in Fig. 6 is particularly interesting. This behavior is consistent with our interpretation of the  $\lambda_{Ni}$  of Eq. (11) as related to the scattering cross section. If this interpretation is valid, Fig. 6 shows, in addition, that the scattering of conduction electrons by the nickel atoms is little affected by the state of order of the surrounding lattice.

It is evident that Mott's formula fails to give a consistent relation between the scattering parameter

$\sigma_{Ni}$  and its derivative with respect to energy  $d\sigma_{Ni}/dE$ . Thus if we could reduce the Fermi level in a dilute alloy of nickel in copper, we should expect to obtain the cross section of nickel in CuAu when the Fermi level reaches 6.19 ev. As shown in Fig. 6, this will not be true. The explanation probably lies in the inadequacy of Mott's formula when the variation of scattering cross section with energy (or the variation of relaxation time with energy) is rapid.<sup>6</sup>

The change of  $\zeta$  at the transition temperature shown in Fig. 4 may be associated with a change in band structure. The variation of  $\zeta$  (or  $\sigma$ ) from resistivity measurements is not consistent with the variation of  $\sigma$  implied by thermoelectric measurements. Again Mott's formula may be inadequate for large values of  $\lambda$ , but near the transition temperature, a more detailed model is needed. Our treatment of transport properties based on the free electron model has ignored variations of band structure, number of conduction electrons, and shape of the Brillouin zone in the CuAu system. In this respect, the analysis is too naive. Sidorov<sup>13</sup> has reported variations in the Hall coefficient of CuAu, indicating the existence of changes in the effective electron concentration, at both the CuAu I-CuAu II transition and the order-disorder transition.

### ACKNOWLEDGMENTS

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<sup>12</sup> J. O. Linde, Ann. Physik **10**, 52 (1931).

<sup>13</sup> S. Sidorov, J. Exptl. Theoret. Phys. (U.S.S.R.) **16**, 503 (1946).