

Transport properties of copper and silver

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Investigations were made of the electrical resistivity ρ , thermal resistivity $W \equiv 1/K$, and thermoelectric power α of high-purity copper and silver single crystals ($\rho_{300\text{ K}}/\rho_{4.2\text{ K}} \approx 10\,000\text{--}30\,000$ for copper and ≈ 6500 for silver) at temperatures 1.2–17 K. In the absence of magnetic impurities the temperature dependence of the electrical resistivity measured at $T < 7$ K was governed primarily by the electron-electron scattering, the contribution of which was in satisfactory agreement with theoretical estimates. This scattering was manifested also in the temperature dependence of the thermal resistivity. The limiting values ($\rho_0 \rightarrow 0$) of the coefficient in front of the phonon part of the thermal resistivity determined for Cu and Ag were in good agreement with the results of calculations reported by I. M. Suslov [*Sov. Phys. JETP* **53**, 1288 (1981)]. The thermoelectric power of silver measured at $T > 9$ K, where it was governed by the phonon drag, exhibited a deviation from the familiar relationship $\alpha = aT + bT^3$ (cf. J. M. Ziman, *Electrons and Phonons*, Clarendon Press, Oxford, 1960), which may be associated with umklapp processes in the phonon system.

Studies of the transport properties of electrons in metals are complicated by the fact that the experimental results can be compared with self-consistent theoretical calculations only for a limited class of substances. For example, in the case of metals, which are easiest to investigate experimentally (Sn, In, Tl, Al, etc.) the Fermi surface of electrons is so complex that reliable theoretical calculations are impossible, whereas metals with simple Fermi surfaces (Li, Na, K) are difficult to study experimentally. Clearly, the noble metals (Cu, Ag, Au) are the most convenient materials for such investigations. The Fermi surfaces of metals belonging to this group have been investigated thoroughly and are sufficiently simple for a rigorous theoretical analysis of the transport effects^{1,3,4}; the Fermi surfaces of each of these metals are spheres linked by necks in the [111] directions.

There have been many experimental investigations of the transport properties of electrons in noble metals (mainly concerned with the electrical resistivity ρ and the thermal resistivity W , for which information can be found in Refs. 1, 3, and 5). However, although investigations of samples of sufficiently high purity have been reported recently, the treatment of the results obtained has been largely arbitrary. This has been due to the fact that the authors usually employ empirical relationships of the $\rho = \rho_0 + AT^n$ (Ref. 6) or $\rho = \rho_0 + NT^n + AT^5$ (Ref. 7) and similar type to describe, for example, the electrical resistivity and these relationships cannot be compared directly with theoretical representations. On the other hand, it follows from the theory^{2,8} that at low temperatures ($T \ll \theta$) the electrical resistivity $\rho(T)$ is governed mainly by the scattering of electrons on static defects, electrons, and lattice vibrations:

$$\rho(T) = \rho_0 + CT^2 + AT^5, \quad (1)$$

where ρ_0 is the residual resistivity due to the scattering of electrons by static defects; CT^2 and AT^5 are the resistivities associated with the electron-electron and electron-phonon

scattering processes, respectively.

The electron scattering mechanisms can of course be separated if the investigated material is sufficiently pure. This applies particularly to the electron-electron scattering, which is observed clearly only in the case of samples of extreme purity. Therefore, only recently it has become possible to determine the contribution of the electron-electron scattering to the electrical resistivity of aluminum⁹ and copper¹⁰ but not the contribution CT^2 in the case of silver.^{6,10} The electron-electron scattering should be manifested also in the thermal resistivity, but in the earlier experimental studies this has not even been attempted. The interest in the determination of the electron-electron scattering has recently increased because of theoretical representations¹¹ indicating a possible change in this parameter of a metal depending on details of the scattering of electrons by static defects.

In contrast to the majority of earlier studies, we investigated simultaneously all the transport coefficients of copper and silver, namely the electrical resistivity ρ , the thermal resistivity W , and the thermoelectric power α . This has made it possible to identify the range of temperatures where the dependence $\rho(T)$ is not distorted by the presence of magnetic impurities in a sample. The measurements indicate that the electron-electron scattering in high-purity samples is the main process at sufficiently low temperatures. The observed dependence of the electron-electron scattering on the orientation of a sample has been successfully interpreted, at least in the qualitative sense, on the basis of the representations put forward in Ref. 11.

We investigated samples deformed by bending at 300 K. According to Ref. 12, one would expect considerable (even severalfold) deviations from the Wiedemann-Franz law. This prediction of Ref. 12 was not confirmed by our results.

All the transport coefficients were determined employing a superconducting quantum interference device (SQUID¹³), which enabled us to measure ρ and W with errors not exceeding 0.15 and 0.4% (random error).

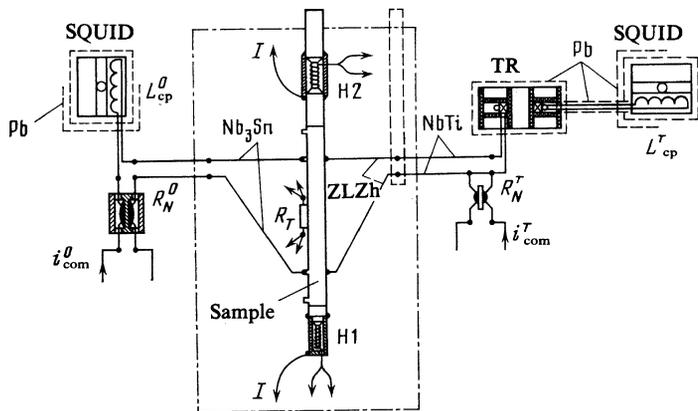


FIG. 1. Schematic diagram of the apparatus: $H1$ and $H2$ are 1000- Ω heaters ($H1$ is used to create a temperature gradient and $H2$ to alter the average temperature of a sample); R_T is a carbon thermometer; $R_N^0 = 2.76 \times 10^{-8} \Omega$ is the normal resistance in the circuit used to compensate the voltage across a sample (technical-grade copper wire 10 mm in diameter, $d \sim 1$ mm) placed inside a temperature-stabilizing copper screen; $R_N^T = 1.143 \times 10^{-4} \Omega$ is the normal resistance in the circuit for compensating the voltage on a thermocouple (Manganin diameter 2.5 mm, $d \sim 1$ mm); T_R is a flux transformer; Pb are lead screens; i_{com}^0 and i_{com}^T are the compensation currents (measured with an R363 potentiometer); I are the current leads used to measure the electrical resistivity of a sample ($i_s = 10$ mA); the chain line represents the vacuum chamber and the dashed line inside the chamber is a copper rod with bonded ZLZh-NbTi junctions.

EXPERIMENTAL INVESTIGATION

Measurements of ρ , W , and α carried out on copper and silver single crystals were made using apparatus similar to that described earlier.¹⁴ The difference between the potentials on a sample and on a thermocouple, which was used to find the temperature gradient, was measured by a compensation method using a SQUID as a null indicator.

The following two measures were taken in the determination of ΔT :

1) The junctions of a thermocouple made of ZLZh alloy (Au with 0.03% Fe) 0.1 mm in diameter and of a superconducting wire 0.07 mm in diameter were bonded to a sample alongside potential leads.

2) Leads made of ZLZh were soldered at two points to a sample (Fig. 1). The other two ends of the leads were bonded together at a distance ~ 10 cm to a copper rod which was in contact with liquid helium. Superconducting wires were soldered to these ends of the ZLZh leads so that the ZLZh—superconductor junctions were kept very accurately at the same temperature (control measurements indicated that the temperature difference between these junctions of the thermocouple did not exceed 10^{-7} K). This method made it possible to determine the temperature gradient at temperatures above T_c of the superconducting component of the thermocouple (in our experiments this was done in the interval 1.2–17 K).

The balancing circuit of the thermocouple included a flux transformer (Fig. 1). Its primary winding consisted of 200 turns made of NbTi and the secondary winding had one turn of the same wire. The transformer was enclosed in a lead screen, together with leads from the secondary winding to a coupling coil of inductance L_{cp}^T . The temperature difference measured using this transformer was accurate to within 3×10^{-7} K (the error in the absence of the transformer¹⁴ was 5×10^{-6} K). The error in ΔT was governed by the precision of calibration of the thermocouple and did not exceed 0.4%. The calibration was carried out several times during measurements in the same system and this was done as follows (The majority of the measurements were made employing the same thermocouple). The ZLZh-NbTi junction was kept at a constant temperature of 4.2 K or 1.2 K. Variation of the temperature of the ZLZh-Nb₃N (superconductor) thermo-

couple by a heater $H2$ was used to find the dependence of the emf at the ends of ZLZh on the temperature of this thermocouple in steps of 0.1 K within the intervals 4.2–17 K and 1.3–5 K (Fig. 1). This dependence was then used to find the thermoelectric power $\alpha_{ZLZh} = \Delta U / \Delta T$.

We used copper and silver single crystals of length 5–6 cm and 0.1–0.15 cm² cross section, prepared at the Institute of Solid State Physics, Academy of Sciences of the USSR. The starting material from which copper samples were formed was of OSCh-11-4 purity and it was subjected to electrolysis in a sulfate electrolyte followed by subsequent melting in vacuum ($p = 10^{-5}$ Torr) during which a temperature of 1200 °C was maintained for about 2 h. An ingot obtained in this way was then used to grow single crystals in a hydrogen atmosphere by the Czochralski method. The finished samples were annealed in oxygen at a pressure of 10^{-4} Torr and a temperature of 1050–1070 °C applied for 3 days. The temperature was then lowered at a rate of 30 °C/h. Before annealing the residual resistance ratio was $\sim 10^3$ and after annealing it was $\sim (10-30) \times 10^3$. The results of a mass spectroscopic analysis carried out before annealing indicated the presence of the following impurities: magnetic impurities—iron $\sim 3 \times 10^{-5}$, chromium $\sim 10^{-6}$, cobalt $< 2 \times 10^{-6}$, manganese $< 2 \times 10^{-6}$; the other impurities $< 10^{-5}$ wt. %.

Silver samples were prepared from a solution of silver nitrate (of analytic purity grade) which was purified by employing a sorbent in the form of oxidized carbon; this was followed by drying and zone melting. Silver nitrate purified in this way was converted into the chloride by precipitation with hydrochloric acid. The freshly precipitated silver chloride was reduced at 400–450 °C in a stream of purified hydrogen and melted into ingots at 1000 °C. Single-crystal ingots were prepared by directional crystallization in a hydrogen atmosphere. The impurity concentrations in these ingots were as follows: magnetic impurities—chromium $< 3 \times 10^{-6}$, nickel $< 6 \times 10^{-6}$, iron $< 6 \times 10^{-7}$, manganese $< 5 \times 10^{-7}$; the other impurities $< 6 \times 10^{-6}$ wt. %. The samples used in the measurements were cut by spark machining. After etching the samples were annealed for 8 h in a hydrogen atmosphere at 600–650 °C.

In some of the experiments we used also plastically deformed copper and silver samples. The deformation was pro-

duced by bending against a template of 10 cm radius in the (110) plane at 300 K.

RESULTS AND DISCUSSION

1. Electrical resistivity and thermal resistivity

As already pointed out, it follows from theoretical considerations that the temperature dependence of the electrical resistivity can be described¹⁾ by Eq. (1). However, in analyzing the results obtained for noble metals it was essential to be sure that the sample was free of magnetic impurities which could change the dependence $\rho(T)$ because of the Kondo effect. The presence of magnetic impurities appeared clearly in the thermoelectric power of the samples because they indicated a considerable negative contribution to α (Ref. 15 and 16). The results of a determination of the thermoelectric power of copper and silver samples are plotted in Figs. 2 and 3. They show that all the silver samples and also copper samples Cu1 and Cu6 were affected negligibly by the influence of magnetic impurities at $T > 5$ K. Bearing this in mind, we used the results of our investigation of $\rho(T)$ of these samples to calculate the constants in Eq. (1), which are listed in Table I. It was subsequently found that the criterion in selection of the range of comparison of the experimental data with Eq. (1) was too stringent. It was found that in the case of these samples all the experimental values of $\rho(T)$ agreed with Eq. (1) down to 1.2 K and this was true within the experimental error of $\sim 0.2\%$ (Figs. 4–6). This was allowed for in the determination of the constants in Eq. (1) for other samples, also listed in Table I. The constants in Eq. (1) for samples Cu1 and Cu5 and all the silver samples were independent of the temperature interval within which they were determined (5.5

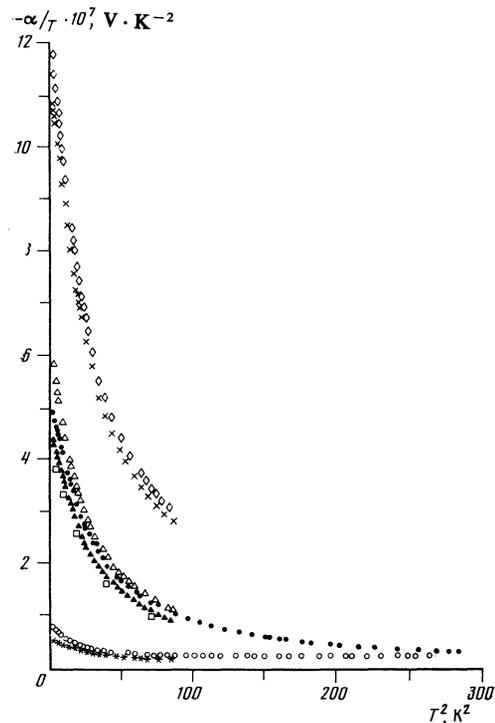


FIG. 2. Temperature dependence of the thermoelectric power of copper. The notation is explained in Table I.

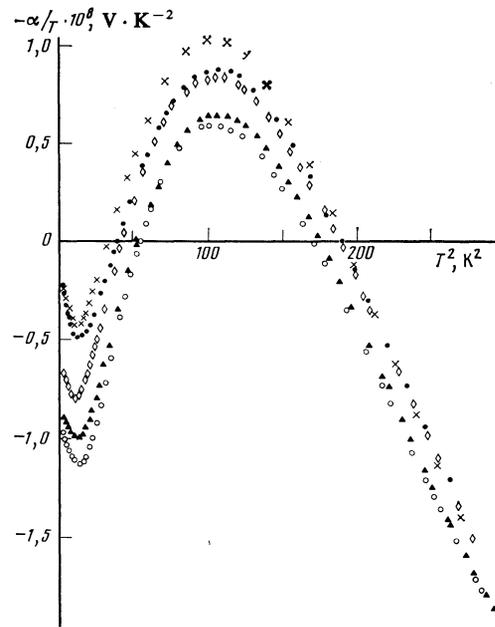


FIG. 3. Temperature dependence of the thermoelectric power of silver. The notation is explained in Table I.

$K < T < 10$ K or $5.5 < T < 17$ K). Table I gives also the results of recalculations of the data of Rumbo¹⁷ and those of Schroeder *et al.*,¹⁰ Ehrlich and Schriempf,¹⁸ and of Fenton *et al.*¹⁹ obtained for samples of unknown orientations.

It is clear from Table I that the value of A rises on increase in ρ_0 . The dependence of A on ρ_0 is known also for other metals, such as tin.¹⁴ The limiting value of A_0 corresponding to $\rho_0 = 0$ was obtained by extrapolation of $A(\rho_0)$ and amounted to $1.1 \times 10^{-16} \Omega \cdot \text{cm} \cdot \text{K}^{-5}$ for copper and $4.5 \times 10^{-16} \Omega \cdot \text{cm} \cdot \text{K}^{-5}$ for silver. These values were considerably smaller (by one and a half orders of magnitude) than those obtained by theoretical calculations of Lawrence.³ The experiments showed that at temperatures below ~ 7 K (corresponding to $CT^2 \approx AT^5$) the electron-electron scattering in copper and silver dominated the temperature dependence of the electrical resistivity.

In the case of copper samples Cu2, Cu3, or Cu5 which contained magnetic impurities, as indicated by the thermoelectric power measurements, the dependence $\rho(T)$ deviated at $T < 5$ K considerably from $\rho_{\text{calc}} = \rho_0 + CT^2 + AT^5$ where the constants listed in Table I were substituted. This deviation was probably associated with the Kondo effect. The temperature dependence of $\Delta\rho = \rho(T) - \rho_{\text{calc}}$ was described satisfactorily by the theoretical dependence suggested by Suhl²⁰

$$\rho = \frac{\rho_{du}}{2} \left\{ 1 - \frac{\cos 2\delta_v \cdot \ln(T/T_K)}{(\ln^2(T/T_K) + \pi^2 S(S+1))^{1/2}} \right\} \quad (2)$$

in the case of scattering of electrons by magnetic impurities (δ_v is the phase shift, T_K is the Kondo temperature, and ρ_{du} is the limiting value of the resistivity during the scattering of electrons by the spins of magnetic impurities). The dashed curve in Fig. 5 represents $\Delta\rho$ calculated for Cu2 from Eq. (2) with $T_K = 2.2$ K and $S = 0.07$. The value of S corresponds to the smallest discrepancy between $\Delta\rho^{\text{exp}}$ and $\Delta\rho^{\text{theor}}$.

TABLE I

Sample	Notation	Orientation of sample	$\rho_0 \times 10^{10}, \Omega \cdot \text{cm}$	$C \times 10^{13}, \Omega \cdot \text{cm} \cdot \text{K}^{-2}$	$A \times 10^{16}, \Omega \cdot \text{cm} \cdot \text{K}^{-5}$	$W/T_{T=0} \times 10^3, \text{cm} \cdot \text{W}^{-1} \cdot \text{K}^2$	$D \times 10^5, \text{cm} \cdot \text{W}^{-1}$	$B \times 10^5, \text{cm} \cdot \text{W}^{-1} \cdot \text{K}^{-1}$	Remarks
1	2	3	4	5	6	7	8	9	10
Cu1	○	[111]	0,622	0,68	1,54	2,548	1,16	1,34	—
Cu2	△ (0)	$\theta=62^\circ, \varphi=45^\circ$	0,852	1,03	1,60	3,512	1,69	1,39	—
Cu2	▲ (1)	$\theta=62^\circ, \varphi=45^\circ$	1,153	1,06	1,71	4,741	1,73	1,46	*
Cu2	▲ (2)	$\theta=62^\circ, \varphi=45^\circ$	8,275	1,02	2,95	—	—	—	**
Cu2	▲ (3)	$\theta=62^\circ, \varphi=45^\circ$	30,05	1,00	4,33	—	—	—	**
Cu2	▽ (4)	$\theta=62^\circ, \varphi=45^\circ$	1,178	1,63	1,78	—	—	—	annealing
Cu3	□	[100]	1,063	1,81	1,82	4,327	2,74	1,45	500 °C, 5h
Cu4	◇	[100]	1,61	—	—	6,594	2,87	1,65	—
Cu5	●	[110]	1,445	1,71	1,98	5,874	2,77	1,54	—
Cu6	*	[110]	4,973	1,61	2,51	20,42	2,76	2,02	***
Cu7	×	$\theta=72^\circ, \varphi=45^\circ$	1,71	—	—	7,014	2,83	1,62	—
Cu8	┌	[100]	~20,0	—	~15,0	80,56	2,0	4,8	no annealing
Ag1	×	[210]	2,214	3,4	9,35	9,119	4,9	3,18	—
Ag2	●	[110]	2,445	3,1	9,58	9,964	4,4	3,23	—
Ag2	* (1)	[110]	2,846	2,9	9,70	11,61	3,9	3,29	*
Ag2	* (2)	[110]	8,052	3,2	14,1	32,90	4,8	3,74	**
Ag2	* (3)	[110]	13,45	3,3	19,5	54,71	4,5	4,35	**
Ag3	○	[111]	2,498	1,4	9,69	10,25	2,5	3,25	—
Ag4	◇	[113]	2,553	2,9	10,06	10,50	4,2	3,29	—
Ag5	▲	$\theta=62^\circ, \varphi=45^\circ$	2,769	1,8	10,62	11,28	3,0	3,33	—
Cu		[231]	1,131	1,14	1,58	—	—	1,3	[17]
Cu		[231]	2,101	1,02	1,34	—	—	1,5	[17]
Cu		[110]	1,759	0,8	1,98	—	—	—	[17]
Cu		—	1,33	0,65	—	—	—	—	[10]
Cu		—	5,8	—	—	—	—	2,1	[22]
Ag		[001]	4,53	4,29	11,5	—	—	3,4	[17]
Ag		[111]	5,31	1,94	16,3	—	—	3,9	[17]
Ag		—	1,46	—	7,64	—	—	2,96	[18]
Ag		—	7,99	—	16,0	—	—	4,3	[19]

*Single deformation by bending against a template of radius $R = 10$ cm at $T = 300$ K.

**Repeated deformation by bending and unbending at $T = 300$ K.

***Sample obtained from authors of Ref. 12.

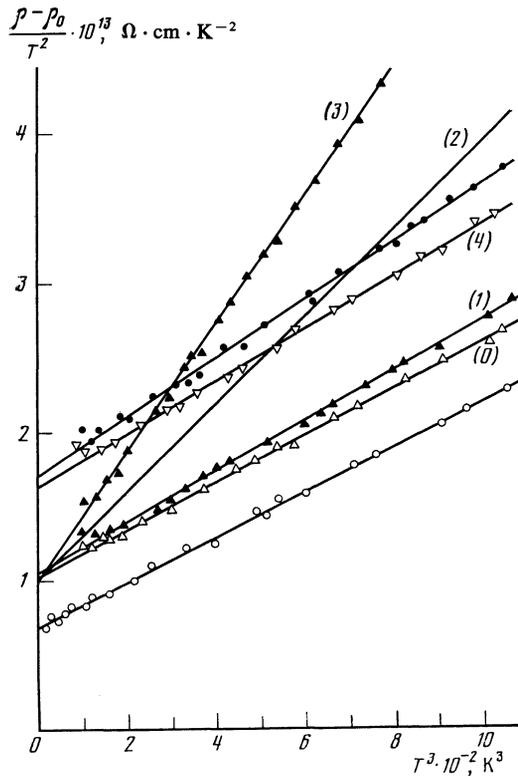


FIG. 4. Temperature dependence of the electrical resistivity of copper. The notation is explained in Table I; the experimental curves for sample Cu2 are labeled with numbers.

The thermal resistivity $W \equiv 1/K$ is governed at low temperatures mainly by the scattering of electrons on static defects, the scattering of electrons on phonons,² and at sufficiently low temperatures also by the scattering of electrons on other electrons²¹:

$$WT = \rho_0/L + DT^2 + BT^3, \quad (3)$$

where ρ_0 is the residual electrical resistivity in Eq. (1), $L = 2.445 \times 10^{-8} \text{ W} \cdot \Omega \cdot \text{K}^{-2}$ is the Lorenz constant; DT is

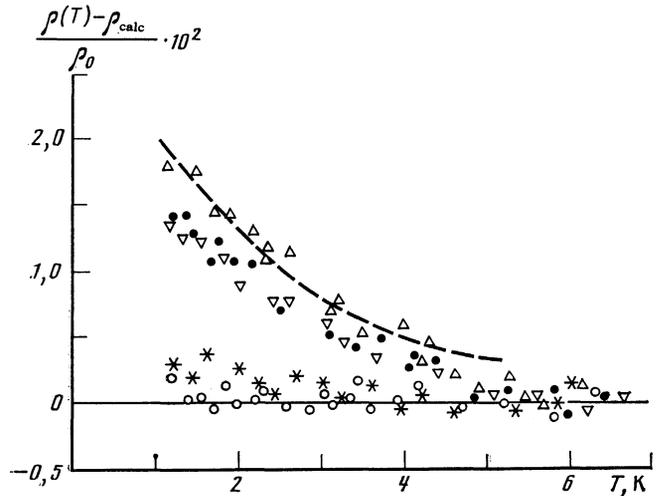


FIG. 5. Deviation of the electrical resistivity of copper from Eq. (5) at $T < 5$ K. The dashed curve is calculated from the theoretical dependence (2) of Ref. 20 for Cu2 sample.

$$\frac{\rho - \rho_0}{T^2} \cdot 10^{13}, \Omega \cdot \text{cm} \cdot \text{K}^{-2}$$

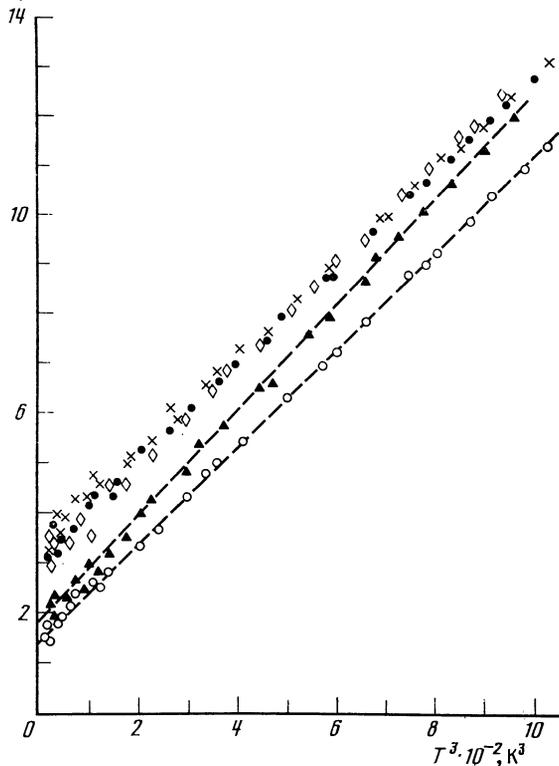


FIG. 6. Temperature dependence of the electrical resistivity of silver. The notation is explained in Table I.

the thermal resistivity associated with the scattering of electrons by other electrons; BT^2 is the resistivity due to the scattering of electrons by phonons.

The experimental data for all the investigated copper and silver samples were indeed described satisfactorily by Eq. (3), as shown in Figs. 7 and 8. The values of $(WT)_{T=0}$ were identical with ρ_0/L to within $\sim 0.7\%$ (Table I), representing the error in the determination of the geometric dimensions in the measurement of ρ and W . The coefficients D and B are listed in Table I. The reliability of the determination of the contribution of the electron-electron scattering was in this case low and the possible error in the coefficient D could reach 20%.

The contributions made by the electron-electron scattering to the electrical resistivity and to the thermal resistivity are mutually related and the average value is $C/D = (0.64 \pm 0.13) \times 10^{-8} \text{ W} \cdot \Omega \cdot \text{K}^{-2}$, which was close to the theoretical estimate $(0.92 \times 10^{-8} \text{ W} \cdot \Omega \cdot \text{K}^{-2})$ obtained by Lawrence.²³

The contribution of the electron-phonon scattering [represented by the term BT^3 in Eq. (3)] depends on the value of ρ_0 . Extrapolation of the dependence $B(\rho_0)$ gave the limiting values of the coefficient B_0 for $\rho_0 = 0$, which were $1.15 \times 10^{-5} \text{ cm} \cdot \text{W}^{-1} \cdot \text{K}^{-1}$ for copper and $2.4 \times 10^{-5} \text{ cm} \cdot \text{W}^{-1} \cdot \text{K}^{-1}$ for silver. A theoretical calculation of these values carried out by Suslov¹ gave $1.3 \times 10^{-5} \text{ cm} \cdot \text{W}^{-1} \cdot \text{K}^{-1}$ for copper and $2.7 \times 10^{-5} \text{ cm} \cdot \text{W}^{-1} \cdot \text{K}^{-1}$ for silver, and agreed quite satisfactorily with the experimental results.

It is clear from Table I that the coefficient C varied from sample to sample and was within the range $(0.68-1.81) \times 10^{-12} \Omega \cdot \text{cm} \cdot \text{K}^{-1}$ for copper and $(1.4-3.4) \times 10^{-13} \Omega \cdot \text{cm} \cdot \text{K}^{-1}$ for silver. There was a correlation between the contribution of the electron-electron scattering (coefficients C and D) and the orientation of the investigated sample. The smallest values of C and D were obtained for the samples oriented along the [111] axis. This result was unexpected because the transport coefficients of metals with the cubic lattice should not have been anisotropic.

It is known that the electron-electron scattering appears when unklapp processes occur in the electron system. In the case of noble metals this process is most likely in the case of electrons with the wave vector direction \mathbf{k} close to the direction of necks of the Fermi surface. The correlation between the value of the coefficient C and the orientation of the sample could have been due to the selection of electrons in respect of the directions of \mathbf{k} in a sample carrying an electric current.

However, if a sample contains centers characterized by anisotropic scattering (such as dislocations), then the normal electron-electron scattering processes without umklapp can also contribute to the resistivity. This effect was considered theoretically in Ref. 11. A calculation²⁴ showed that in the case of copper we have

$$C = 0,27 [1 + 2/(1 + \rho_{\text{imp}}/\rho_{\text{dis}})^2] \cdot 10^{-13} \Omega \cdot \text{cm} \cdot \text{K}^{-2}, \quad (4)$$

where ρ_{imp} and ρ_{dis} are the electrical resistivity components associated with the scattering of electrons by isotropic and anisotropic centers, respectively. Therefore, depending on the relationship between ρ_{imp} and ρ_{dis} the coefficient C can vary from $0.3 \times 10^{-13} \Omega \cdot \text{cm} \cdot \text{K}^{-2}$ to $0.8 \times 10^{-13} \Omega \cdot \text{cm} \cdot \text{K}^{-2}$. It should be pointed out that in an earlier calculation Lawrence³ showed that $C = 0.76 \times 10^{-13} \Omega \cdot \text{cm} \cdot \text{K}^{-2}$ for copper and $C = 1.4 \times 10^{-13} \Omega \cdot \text{cm} \cdot \text{K}^{-2}$ for silver (only the unklapp scattering processes were allowed for).

It follows from the relationship (4) that if during the growth of samples along different crystallographic directions there is a change in the ratio between the number of isotropic and anisotropic scattering centers, there should be a correlation between the contribution of the electron-electron scattering to the resistivity and the orientation of a sample and the minimum value of C should correspond to the direction of growth of a crystal with the minimum number of anisotropic scattering centers (for example, dislocations). This explanation of the results appears highly plausible, because the direction [111] corresponds to the direction of the easiest growth of copper and silver single crystals.

At first sight it seems that this explanation is in conflict with the experimental results obtained for samples which were deformed by bending. It is clear from Table I that in the case of these samples there was no increase in C on increase in the density of linear dislocations that were formed as a result of bending. However, if the deformation created not only anisotropic scattering centers but also isotropic centers (for example, point lattice defects), so that the ratio $\rho_{\text{min}}/\rho_{\text{dis}}$ remained constant, then it follows from Eq. (4) that the value of C may be unaffected. This hypothesis was checked by

$$\frac{WT - (WT)_{T=0}}{T^2} = 10^5 \cdot W^{-1} \cdot \text{cm}$$

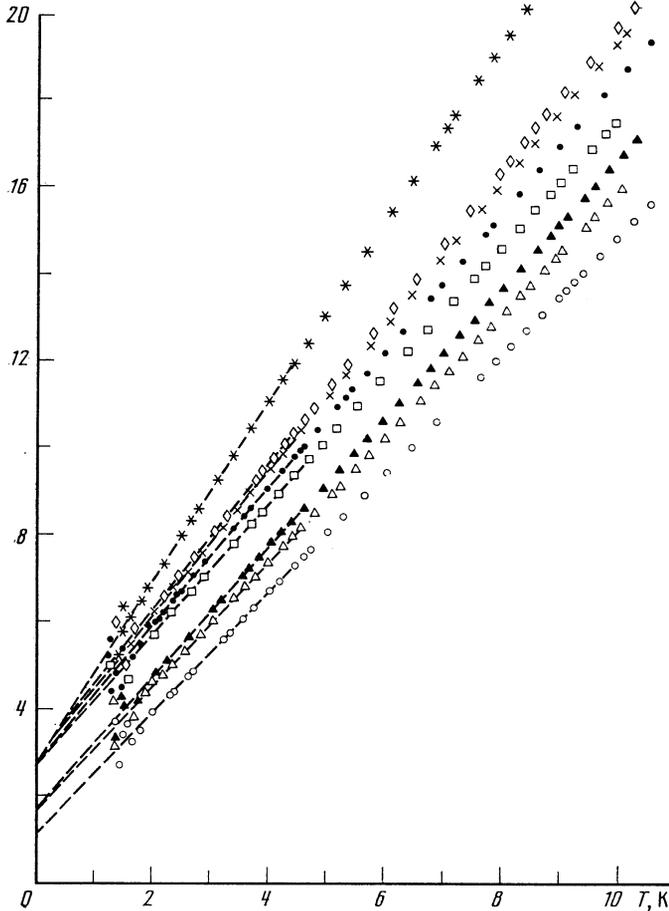


FIG. 7. Temperature dependence of the thermal resistivity of copper. The notation is explained in Table I.

subjecting the most strongly deformed sample Cu2 to annealing at 500 °C for 5 h at a pressure of $\sim 5 \times 10^{-4}$ Torr in an oxygen atmosphere, which resulted in healing of point defects.¹⁴ There was therefore a strong reduction in the value of ρ_0 and an increase in the coefficient C from $1.0 \times 10^{-13} \Omega \cdot \text{cm} \cdot \text{K}^{-2}$ to $1.63 \times 10^{-13} \Omega \cdot \text{cm} \cdot \text{K}^{-2}$, i.e., the value of C approached its maximum (see Table I).

This result was confirmed also by the experiments on sample Cu1 which was subjected to a cycle of successive deformations and annealing. The results of this experiment are presented in Table II. Clearly, the anisotropically scattering defects formed by bending (such as dislocations or twin boundaries) increased the coefficient C only when annealing suppressed point defects generated during deformation.

It follows from these results that the different values of the coefficient C of our copper and silver samples, like the apparent anisotropy of the electron-electron scattering, can be explained at least qualitatively using the theoretical representations given in Ref. 11. The minimum values of C for the electron-electron scattering correspond to this effect in ideal crystals. The experimental data do not differ significantly from theoretical estimates.^{3,24}

Plastic deformation was used as a method of altering

the residual electrical resistivity of the samples without introducing chemical impurities. The electrical and thermal resistivities of these samples were described satisfactorily by Eqs. (1) and (3). Some changes in the coefficients A and B (Table I) were clearly due to a change in the value of ρ_0 .

It should be pointed out that our deformed copper and silver samples showed no deviation from the Wiedemann-Franz law $K\rho = LT$ in the limit $T \rightarrow 0$, discussed in Ref. 12. This was true of copper sample Cu6 obtained from the authors of that paper and also of sample Ag2, on which a cycle of measurements with different degrees of deformation was carried out in order to determine whether the small strain was an exceptional feature, as postulated in Ref. 12. All our experiments indicated that at present there are no doubts that the Wiedemann-Franz law applies to bending-deformed samples in the limit $T \rightarrow 0$.

2. Thermoelectric power

The results of our determination of the thermoelectric power α of copper and silver are presented in Figs. 2 and 3. In the case of copper, in spite of the apparent high purity of the samples, the thermoelectric power was negative throughout the investigated temperature range, which was

$$\frac{WT - (WT)_{T=0}}{T^2} \cdot 10^5, \text{ W}^{-1} \cdot \text{cm}$$

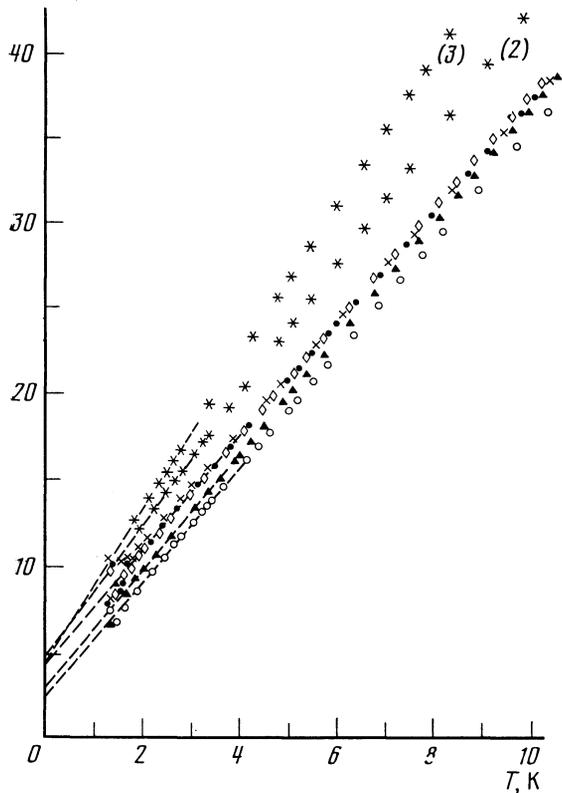


FIG. 8. Temperature dependence of the thermal resistivity of silver. The notation is explained in Table I.

typical of samples with magnetic impurities.¹⁵ Clearly, samples of copper with the thermoelectric power near the intrinsic value expected for this metal could be obtained by reducing the number of magnetic impurities by at least an order of magnitude. In the case of silver the contribution of magnetic impurities to the thermoelectric power was observed only at the lowest temperatures $T < 3$ K.

The temperature dependence of the thermoelectric power of silver was complex. It could be interpreted as follows. At temperatures below 3 K all the samples exhibited a strong reduction in the value of α/T which was probably due to, as in the case of copper, the presence of magnetic impurities. At temperatures $3 \text{ K} < T < 9 \text{ K}$ the value of α/T depended linearly on T^2 (Ref. 2) and it was possible to distinguish the diffusion component $\alpha_e = aT$ and the phonon-drag component $\alpha_{ph} = bT^3$.

The coefficient a in the expression for the diffusion component is $+ (0.8-1.8) \times 10^{-8} \text{ V} \cdot \text{K}^{-2}$. This value agrees with $+ 0.5 \times 10^{-6} \text{ V} \cdot \text{K}^{-2}$ obtained by Pearson²⁵ by extra-

polation from the high-temperature range ($T \gtrsim \theta$). A theoretical calculation made by Abarenkov and Vedernikov²⁶ gave $a \approx + 0.7 \times 10^{-8} \text{ V} \cdot \text{K}^{-2}$.

The coefficient b in the expression for the phonon part α_{ph} of the thermoelectric power is $-(2.0-3.4) \times 10^{-10} \text{ V} \cdot \text{K}^{-4}$. An estimate of α_{ph} can be obtained also by measuring the acoustoelectric emf $v^A = E^A / \Gamma$ (E^A is the acoustoelectric field and Γ is the attenuation coefficient of sound),²⁷ which is also due to the drag of electrons by acoustic phonons. In the simplest case the coefficient b is related to the acoustoelectric voltage v^A by

$$b \approx \frac{e}{|e|} C_0 s v^A, \quad (5)$$

where C_0 is the coefficient of the lattice specific heat and s is the velocity of sound. Averaging the values of v^A in Ref. 27 over the angles, we find that $b_{ph} \approx -4 \times 10^{-10} \text{ V} \cdot \text{K}^{-4}$, in satisfactory agreement with direct measurements of α_{ph} . It should be pointed out that the frequency of sound used in the work reported in Ref. 27 corresponded to a phonon temperature of ~ 1.5 mK, which was three orders of magnitude less than the minimum temperature employed in the present study.

Above 9 K, where the main contribution to the thermoelectric power was due to the phonon drag, there was a deviation from the relationship

$$\alpha = \alpha_e + \alpha_{ph} = aT + bT^3. \quad (6)$$

As in the case of tin,¹⁴ this deviation could be due to umklapp processes in the phonon system. At low temperatures the interaction between phonons is negligibly weak and they are scattered mainly on conduction electrons. The energy momentum transferred by phonons to electrons is in the first approximation proportional to

$$\beta = \tau_{pe}^{-1} (\tau_{pe}^{-1} + \tau_p^{-1})^{-1}, \quad (7)$$

where τ_p is the characteristic time for the processes in the phonon system involving loss of momentum. If $\tau_{pe} \ll \tau_p$, then $\beta = 1$ and $\alpha_{ph} = b_0 T^3$. However, when temperature rises to $T \sim \theta/20$, phonon-phonon collisions with umklapp begin to appear in the phonon system and τ_p decreases strongly, which reduces β and, therefore, the phonon drag contribution. Measurements of the thermal conductivity of insulators²⁸ indicate that $\tau_p \propto C \exp(T^*/T)$. At temperatures where $\tau_p > \tau_{ep}$, we have

$$1 - \beta \approx \tau_{pe} / \tau_p \sim (\tau_{pe} / C) \exp(-T^*/T). \quad (8)$$

We shall consider the quantity

$$a + b_0 T^2 - \alpha(T)/T \equiv (1 - \beta) b_0 T^2. \quad (9)$$

An analysis shows that $\log(1 - \beta)$ does indeed vary proportionally to the reciprocal of temperature. The value of T^* is ~ 70 K, which is not in conflict with the value that can be

TABLE II

	Initial	Deformed	Annealed	Deformed	Annealed	Deformed	Annealed
$\rho_0 / \rho_0 \text{ init}$	1,0	1,94	1,04	25,9	1,14	62,6	1,53
$C \cdot 10^{13}$	0,68	0,63	0,74	0,61	0,97	0,66	1,46
$\Omega \cdot \text{cm} \cdot \text{K}^{-2}$							

deduced from the phonon spectrum of silver.²⁹ The proposed explanation naturally does not exclude the possibility that a reduction in the phonon drag is associated also with the electron umklapp processes near the necks of the Fermi surface when they are scattered by phonons.³⁰

Therefore, a comparison of the results of an experimental investigation of the transport coefficients of noble metals (copper and silver) with theoretical calculations demonstrates that the current theoretical models give the correct magnitude of the effect in the case of the electron-electron scattering, and of the contribution of the electron-phonon scattering to the thermoelectric power (phonon drag) and to the thermal resistivity.

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¹⁾ Obviously, the dependence $\rho(T)$ can be approximated also by a more complex expression, for example $\rho(T) = \rho_0 + C(n)T^n + AT^5$. An analysis of this relationship shows that a satisfactory agreement with experimental results can be obtained if $1.7 < n < 2.3$. The average value $n = 2$ was used in the present study, especially since it follows from a theoretical analysis.

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