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Low-Temperature Transport Properties of Copper and Its Dilute Alloys: Pure Copper, Annealed and Cold-Drawn

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Experimental results between 4° and 300°K are given for (1) the thermal conductivity, electrical resistivity, and thermoelectric force and power of two high-purity coppers, one annealed and one cold-drawn 26%; and (2) the electrical resistivity of a series of seven samples of high-purity copper cold-drawn between 0% and 20% elongation. The total electronic thermal resistivities each consist of *three* terms: the intrinsic resistivity, W_i; the imperfection resistivity, W_0; and a deviation term, W_{i0}, indicating the departure from strict additivity of W_i and W_0. The intrinsic thermal resistivity and intrinsic electrical resistivity vary as $T^{2.8}$ and $T^{4.5}$, respectively, contrary to the predictions of the usual transport theory using Bloch approximations and assumptions. The resistivity of pure copper is 1.545 μohm cm at 0°C. The increase in imperfection electrical resistivity is approximately linear with increase in cold-drawn elongation. However, the added resistivity is not independent of temperature (Matthiessen's rule), but about twice as great at the ice point as it is at 4°K. The change in thermoelectric power with drawing is positive at the lower temperatures, but negative above 38°K. The Lorenz number does not approach the Sommerfeld value at the lowest temperatures, but flattens out to a value considerably smaller. A qualitative discussion for each of the various effects is given.

I. INTRODUCTION

THE low-temperature transport properties of pure metals, thermal conductivity, electrical conductivity, and thermoelectric power have been measured often in the past. However, most of the measurements on copper were on samples that contained so many imperfections that the behavior of the "ideal" metal was overshadowed by the uncontrolled effects of chemical impurities and physical defects. Only in recent years have copper samples become available that contain a very low concentration of imperfections, either physical or chemical. Furthermore, precisely controlled, very dilute alloys of various elements in copper are now also available. For these reasons, it was decided at this laboratory to begin a research program on the low-temperature transport properties of high-purity copper and its dilute alloys. It was hoped that (1) results could be obtained of sufficient accuracy to provide a reliable guide for the advancement of the theories of conduction processes and (2) the samples would be of sufficient purity or controlled imperfection so that the "ideal" or intrinsic properties could be easily separated from the various effects caused by chemical or physical imperfections. The results presented here differ significantly in several details, both qualitatively and quantitatively, from previous experimental measurements or theoretical predictions.

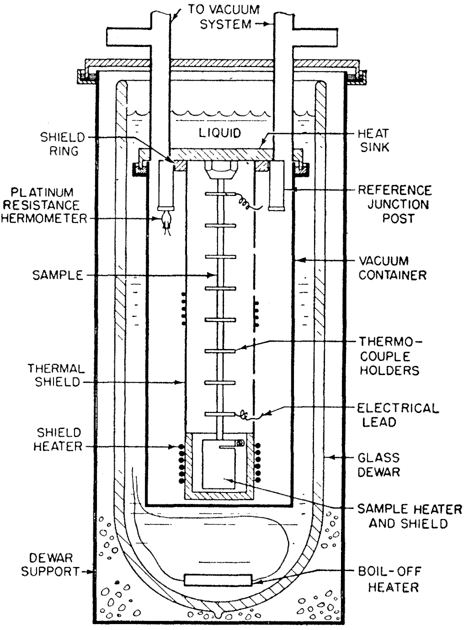

FIG. 1. Pictorial of conductivity apparatus.

II. APPARATUS

A detailed description of the apparatus and measurement techniques has been previously published.[1] The method of determining thermal conductivity by axial heat flow through a long cylindrical sample is used. A pictorial diagram of the apparatus is shown in Fig. 1. Since the previous publication the apparatus has been modified to allow simultaneous measurements of electrical resistance and thermal emf. Wires of commercial purity copper magnet wire are connected electrically to the top and bottom thermocouple holders, approximately 7 inches apart. Electrical current leads are connected to the ends of the sample. The thermoelectric force of the sample rod relative to the commercial purity copper is determined by measuring the potential difference between the two copper wires when no electrical current is flowing through the sample. The temperatures of the two contact points are determined by the gold-cobalt *vs* copper thermocouples that are connected thermally, but not

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[1] Powell, Rogers, and Coffin, J. Research Natl. Bur. Standards **59**, 349 (1957).

electrically, to the thermocouple holders. The electrical resistance of the sample is determined by measuring the potential drop across the same two wires when a measured current is flowing through the sample. The thermoelectric force is subtracted from the total potential drop to obtain the potential drop resulting from the electrical current. Both the readings of electrical resistance and thermoelectric force have a scatter of about 2%.

III. SAMPLES

Copper rods of 99.999% purity were supplied by the Central Research Laboratories of the American Smelting and Refining Company. The techniques of purification and preparation have been described by members of those laboratories.[2] The three sets of samples were obtained from adjacent segments of a rod of approximately $\frac{3}{8}$-in. diameter. Each sample was cleaned with a 1:1 solution of HCl and a 1:10 solution of HNO_3 before any fabrication. Sample 1 was swaged down to about 0.072 in., cleaned with the above acids, annealed in a vacuum for two hours at 400°C, drawn through tungsten carbide dies to 0.070 in., cleaned with acids, and then finally annealed again in a vacuum for two hours at 400°C. There was a slight unavoidable work-hardening of the sample during installation in the apparatus. Sample 2 was swaged down to about 0.0816 in., cleaned with acids, annealed in a vacuum for two hours at 400°C, and then drawn through tungsten carbide dies to 0.070 in. This sample was thus reduced in cross-sectional area by 26.4%, and *was not annealed after the reduction*. Sample 3 was treated the same as sample 1 down to the annealed 0.070-in. rod. After that it was cold-drawn through tungsten carbide dies without intermediate anneals. The percent reductions in area for each of the series were: (a) 0; (b) 2.22; (c) 4.97; (d) 7.70; (e) 10.40; (f) 13.05; and (g) 19.80.

The swaging of the samples was performed under the direction of Dr. R. H. Sherman of the Los Alamos Scientific Laboratory.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

A. Thermal Conductivity

Several articles were published recently that gave summaries of the experimental and theoretical developments of the thermal conductivity of metals.[3–6] Therefore, only a brief review is given here, enough to allow a discussion of the methods of analysis and separation of conductivity components.

Separation of Components

Two principal mechanisms are responsible for the low-temperature transport of heat in a metal. The first is the lattice thermal conduction, the transport by directional cooperative quantized vibrations (phonons) of the interacting lattice ions. The second is the electronic thermal conduction, the transport of thermal energy by the motion of conduction electrons. For the pure coppers that were measured, the lattice thermal conductivity is expected to be much smaller than the electronic thermal conductivity, and therefore is neglected in the discussion and analyses of results.

There are two main scattering processes that limit the electronic thermal conductivity. The first is the scattering of conduction electrons by thermal vibrations of the lattice, as represented by the intrinsic or electron-phonon resistivity, W_i, a characteristic property for a given metal. This scattering is most important at intermediate and higher temperatures. The second process is the scattering of conduction electrons by imperfections (both impurity atoms and lattice defects), as represented by the imperfection or electron-defect resistivity, W_0. This scattering is most important at the lower temperatures. The total electronic thermal resistivity, W_e, defined as the reciprocal of the total electronic thermal conductivity, λ_e, is usually assumed to be the sum of the two resistivities W_i and W_0; that is, Matthiessen's rule for thermal resistivity is obeyed:

$$1/\lambda_e \equiv W_e \cong W_i + W_0. \tag{1}$$

The absolute magnitudes and the temperature dependences of the two resistivity terms have been extensively studied both experimentally and theoretically. In his Handbuch article, Klemens[3] discussed the theoretical concepts of electronic thermal conduction based upon the treatment of Bloch[7] as developed and modified by Makinson,[8] Sondheimer,[9] Wilson,[10] Ziman,[11] Klemens,[3] and others. More recent developments were discussed at the Ottawa conference.[12] Klemens[3] also gave a critical evaluation and discussion of many selected experimental results. In 1954 a comprehensive review of the experimental results on metals and alloys was also published.[13]

Both theoretical and experimental research have led to expressions for the magnitudes and temperature de-

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[2] Smart, Smith, and Phillips, American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1289, 1941.

[3] P. G. Klemens, *Handbuch der Physik* (Springer-Verlag, Berlin, 1956), Vol. 14, pp. 198–281.

[4] J. L. Olsen and H. M. Rosenberg, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1953), Vol. 2, p. 28.

[5] J. M. Ziman, Suppl. Nuovo cimento **7**, 353 (1958).

[6] H. Jones, *Handbuch der Physik* (Springer-Verlag, Berlin, 1956), Vol. 19, pp. 227–315.

[7] F. Bloch, Z. Physik **52**, 555 (1928); **53**, 216 (1929); **59**, 208 (1930).

[8] R. E. B. Makinson, Proc. Cambridge Phil. Soc. **34**, 474 (1938).

[9] E. H. Sondheimer, Proc. Roy. Soc. (London) **A203**, 75 (1950).

[10] A. H. Wilson, *Theory of Metals* (Cambridge University Press, Cambridge, 1953), second edition.

[11] J. M. Ziman, Proc. Roy. Soc. (London) **A226**, 436 (1954).

[12] *Proceedings of the International Conference on Electron Transport in Metals and Solids*, edited by T. H. K. Barron and D. K. C. MacDonald [Can. J. Phys. **34**, 1071 (1956)].

[13] R. L. Powell and W. A. Blanpied, National Bureau of Standards Circular No. 556 (U. S. Government Printing Office, Washington, D. C., 1954).

pendences of the intrinsic and imperfection resistivities:

$$W_i = AT^n;\quad n \cong 2,\quad T < 40°K. \qquad W_0 = B/T. \tag{2}$$

The constant A in the intrinsic resistivity term is related to characteristic properties of the given metal; B in the imperfection resistivity term is related to the imperfections and residual electrical resistivity of the specific sample. Above 40°K the intrinsic resistivity approaches a constant value, often labelled W_∞.

Two standard methods have been utilized to separate the two thermal resistivity terms from the total thermal resistivity. *Both methods require the assumption that the two resistivities are strictly additive as given in Eq. (1).* The first depends upon the insertion of Eq. (2) into Eq. (1) followed by a graphical analysis of a specialized plot of thermal resistivity values. The revised equation is

$$W_eT = W_iT + W_0T = AT^{n+1} + B;\quad n \cong 2,\quad T < 40°\text{K}. \tag{3}$$

If W_eT values are plotted as a function of T^{n+1}, then the constant, B, is obtained from the straight line extrapolation to the ordinate and A is obtained from the slope of the resultant straight line. This method was discussed by Hulm.[14] However, a fundamental deficiency has been evident in this method since it was first used by Hulm. Even for pure metals and dilute alloys, the plotted values of WT *vs* T^{n+1} do not always lie on a straight line in the temperature range where the approximations are most valid, 2° to 20°K. It is then difficult to obtain a consistent value for either the intercept B or the slope A. Deviations from the ideal behavior may sometimes have important physical significance.[15,16]

The second standard method for separating the two thermal resistivity terms depends upon the simultaneous measurement of the electrical and thermal resistivities. The thermal imperfection resistivity may then be obtained from the electrical residual resistivity by means of the Wiedemann-Franz-Lorenz law

$$\rho_0 = LW_0T, \tag{4}$$

where ρ_0 is the residual electrical resistivity, and L is the Lorenz number, assumed to be the Sommerfeld value 2.45×10^{-8} watt ohm/deg^2. This method also has its deficiencies. First, the Lorenz law is not obeyed for all metals and dilute alloys to within the accuracy of experimental measurements. Second, it is difficult to have a sample with the proper size and form factor that allows accurate measurements of both the thermal and electrical resistivities over a large temperature range.

Previous research reports on the thermal and electrical conductivities of pure copper and its dilute alloys have utilized one or the other of the two above methods for analyses of data.[17–21] The data on the coppers reported in this paper were first analyzed by using a modification of the first of the above methods where the value of the exponent n was obtained by successive approximations.

Deviations from Additivity

Although the intrinsic resistivity is supposedly a characteristic property of the given metal, previous measurements on coppers[19,21] showed that the apparent intrinsic resistivity obtained by using Eqs. (1) and (2) varied with changes in the imperfection resistivity and thus was not really characteristic of the given metal, but was different for each sample. Those results indicated that the resistivities were not additive. The intrinsic resistivities for samples 1 and 2, as calculated by the method outlined above, were found to have a similar behavior. The apparent intrinsic resistivity not only varied between samples but also did not have a constant temperature dependence below 40°K, even for one sample. Both of these deviations from ideality strongly indicated that *an additional term,* W_{i0}, *is necessary in the total resistivity.*

Deviations from additivity for electronic transport properties have been studied theoretically by Sondheimer,[9] Kohler,[22] and Wilson.[10] Kohler proved that the deviations were in general positive and gave some simplified expressions for the electrical resistivity terms. In general the deviations can be significant only when the intrinsic and imperfection resistivities are of the same order of magnitude.

We have assumed that the total thermal resistivity is given by

$$W_e = W_i + W_0 + W_{i0}, \tag{5}$$

where W_{i0} is the deviation from additivity and is given by an expression of the form

$$W_{i0} = \alpha W_iW_0/(W_i + W_0). \tag{6}$$

The constant α should be of order 1 and can be determined experimentally. (It is $\frac{1}{2}$ for the coppers that we have measured.) The term W_{i0} is similar to a deviation term, Δ, suggested by Kohler[22] for electrical resistivity.

If W_i and W_0 are given by Eq. (2), the term W_{i0} will have a maximum where $T^{n+1} = nB/A$. The terms W_i and W_0 are equal where $T^{n+1} = B/A$. For $n = 2.76$, the value used in this analysis, the temperature where W_{i0} is a maximum is about 1.3 times the temperature where W_i and W_0 are equal.

The final detailed analysis is carried out as follows:

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[14] J. K. Hulm, Proc. Roy. Soc. (London) **A204**, 98 (1950).

[15] See reference 3, pp. 246–7.

[16] H. M. Rosenberg, Phil. Mag. **2**, 541 (1957).

[17] R. Berman and D. K. C. MacDonald, Proc. Roy. Soc. (London) **A211**, 122 (1952).

[18] K. Mendelssohn and H. M. Rosenberg, Proc. Phys. Soc. (London) **A65**, 385 (1952).

[19] G. K. White, Australian J. Phys. **6**, 397 (1953).

[20] H. M. Rosenberg, Trans. Roy. Soc. (London) **A247**, 441 (1955).

[21] Powell, Roder, and Rogers, J. Appl. Phys. **28**, 1282 (1957).

[22] M. Kohler, Z. Physik **126**, 495 (1949).

TABLE I. Thermal conductivities of pure coppers.[a,b]

		Sample 1—annealed						Sample 2—drawn			
Temp. (°K)	λ (w/cm°K)	W_0	W_i	W_{i0}	W_T(calc)	W_T(exp)	λ (w/cm°K)	W_0	W_{i0}	W_T(calc)	W_T(exp)
		(All W's in units of 10^{-3} cm °K/watt)						(All W's in units of 10^{-3} cm °K/watt)			
4	66.9	14.75	0.09	0.04	14.88	14.95	6.37	153.7	0.0	153.8	157.0
6	96.7	9.83	0.27	0.13	10.23	10.34	9.45	102.5	0.1	102.9	105.8
8	119.9	7.38	0.59	0.27	8.24	8.34	12.5	76.88	0.29	77.76	80.00
10	133.3	5.90	1.09	0.46	7.45	7.50	15.57	61.50	0.54	63.13	64.23
12	134.5	4.92	1.81	0.66	7.39	7.43	18.4	51.25	0.87	53.93	54.35
14	127.5	4.21	2.77	0.84	7.82	7.84	20.85	43.93	1.30	48.00	47.96
16	115.7	3.69	4.00	0.96	8.65	8.64	22.8	38.44	1.81	44.25	43.86
18	102.7	3.28	5.53	1.03	9.84	9.74	23.9	34.17	2.38	42.08	41.84
20	88.0	2.95	7.40	1.05	11.40	11.36	24.41	30.75	2.98	41.13	40.97
22	75.0	2.68	9.63	1.05	13.36	13.33	24.44	27.95	3.58	41.16	40.92
24	63.5	2.46	12.24	1.02	15.72	15.75	24.00	25.62	4.14	42.00	41.67
26	53.5	2.27	15.26	0.99	18.52	18.69	23.09	23.65	4.64	43.55	43.31
28	45.25	2.11	18.73	0.95	21.79	22.10	21.87	21.96	5.05	45.74	45.72
30	38.50	1.97	22.65	0.91	25.53	25.97	20.45	20.50	5.38	48.53	48.90
32	33.10	1.84	27.07	0.86	29.77	30.21	19.08	19.22	5.62	51.91	52.41
34	28.60	1.74	32.00	0.83	34.57	34.97	17.69	18.09	5.78	55.87	56.53
36	24.90	1.64	37.46	0.79	39.89	40.16	16.32	17.08	5.87	60.41	61.27
38	21.75	1.55	43.49	0.75	45.79	45.98	15.03	16.18	5.90	65.57	66.53
40	19.20	1.47	50.10	0.71	52.28	52.08	13.88	15.37	5.88	71.35	72.05
45							11.4	13.7			87.72
65	7.04	0.91	140.5	0.45		142	6.4	9.5	4.5	154.5	156
75	5.7	0.79	173.7	0.48		175	5.36	8.2	3.9	185.8	187
85	5.1	0.69	195.0	0.34		196	4.85	7.2	3.5	206	206
95	4.7	0.62	212	0.30		213	4.55	6.5	3.1	222	220
105	4.4	0.56	226	0.28		227	4.3	5.8	2.8	235	233

[a] $W_i = AT^n$; $A = 1.903 \times 10^{-6}$, B(annealed) $= 0.059 \pm 0.0005$, $n = 2.759$, B(drawn) $= 0.615 \pm 0.005$. The A and n values are applicable below 40°K. Above 40°K the intrinsic resistivity is estimated from sample 1, not calculated.

[b] The number of significant digits do not necessarily indicate the accuracy, but are carried for computational convenience.

The value for the imperfection constant, B, is obtained by successive approximations from WT *vs* T^{n+1} graphs as outlined above. The imperfection resistivity, W_0, is calculated from this value of B. The imperfection resistivity is then subtracted from the total resistivity in order to give $(W_i + W_{i0})$. The constants A and n in the low temperature (4°–40°K) intrinsic resistivity and α in the deviation term are obtained by successive iterations.

Once determined for the high-purity, well annealed sample, the same values of A, n, and α are used for all additional copper specimens. The imperfection resistivity and the deviation term are unambiguously determined experimentally for each additional specimen. This technique of analysis has been utilized on the two pure coppers reported in this paper and also on dilute alloys of copper studied more recently. It works equally well on samples containing appreciable physical imprefections and on dilute alloys containing chemical impurities ranging from about 10 ppm to 1000 ppm. *The intrinsic resistivity is then found to be a characteristic property of the metal, and does not change from specimen to specimen.*

Intrinsic Resistivity

The thermal conductivities of samples 1 and 2 are given in Fig. 2 and in Table I. The dashed parts of the curves indicate interpolated values. The calculated values for samples 1 and 2 of the imperfection resistivity, W_0, intrinsic resistivity, W_i, and deviation term, W_{i0}, are also given in Table I. Curves for the calculated deviation term, W_{i0}, and the equivalent experimental term, $(W_e - W_i - W_0)$, are given in Fig. 3.

The agreement between corresponding experimental and calculated quantities is seen to be good, considering that the deviation term, W_{i0}, is itself small compared to the total thermal resistivity. The experimental and calculated values agree within about 2% over the

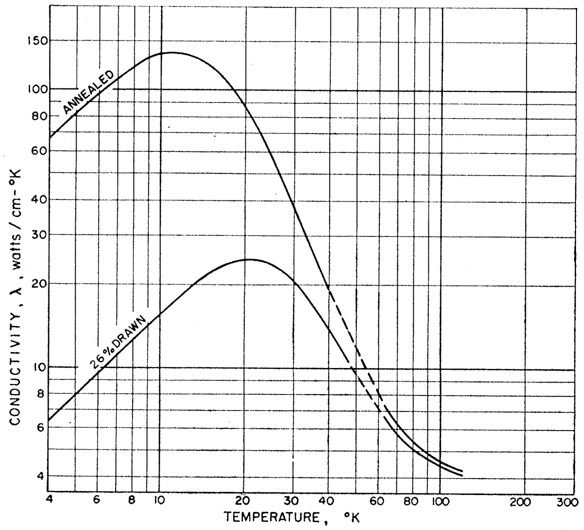

FIG. 2. Thermal conductivity of high-purity copper. The cold-drawn sample is reduced 26.4% in area. The dashed parts of the curves indicate interpolated regions.

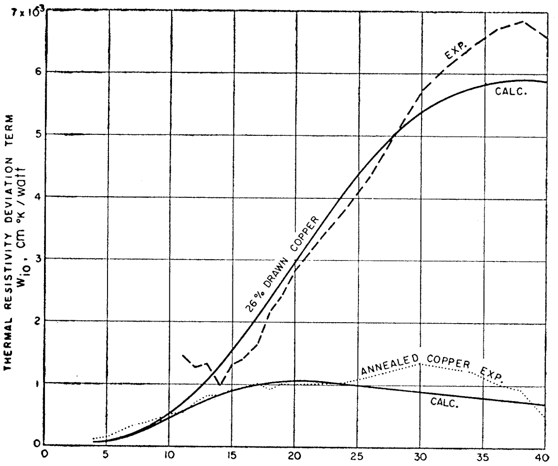

FIG. 3. Thermal resistivity deviation term W_{i0} for annealed sample 1 and cold-drawn sample 2. The broken curves represent the experimental value $(W_e-W_0-W_i)$, equivalent to the calculated W_{i0}.

entire temperature range. Below about 40°K the intrinsic resistivity, W_i, for copper has a coefficient, A, of 1.90×10^{-6} and an exponent, n, of 2.76. Both of these constants are somewhat arbitrary and may be varied while still giving a reasonable fit to the experimental data. In particular, the exponent has an uncertainty of about 0.3. Both of these two constants differ considerably from the theoretical predictions as outlined by Klemens.[3]

The temperature exponent, n, and the constant A for the intrinsic resistivity were derived by Makinson,[8] Sondheimer,[9] and others. Their theories lead to a value of 2 for n, in disagreement both with the results on copper presented in this paper and with previous results as reported by White[19] and reviewed by Klemens.[23] Since the intrinsic thermal resistivity of copper does not even appear to follow a T^2 dependence, discussion of the disagreement between theoretical and experimental values for the intrinsic constant, A, is probably not fruitful. The theories, developed using the Bloch method, utilized many simplifying assumptions, several of which are known to be incorrect in their details.[11] Two of the assumptions appear to be very important for electronic conduction in copper and are discussed next.

The first critical assumption for the usual conduction theory is that the metal has a single electronic band with spherical energy contours in the electronic momentum space, that is, there is a single spherical Fermi surface. In the last several years, the shape of the Fermi surface has been discussed by several authors using indirect experimental evidence. Klemens[24] discussed the relation between electrical and thermal conduction; Jones,[25] the thermoelectric power of monovalent metals; Chambers,[26] the magnetoresistance; and Cohen,[27] the relation between optical constants and specific heats. These authors concluded that the Fermi surface for copper either is not spherical or approaches closely the Brillouin zone boundaries. More direct experimental measurements were made on the Fermi surface in copper by Pippard[28] using a technique involving the anomalous skin resistance of plane surfaces of a single crystal. He concluded from his extensive analysis that there is contact over small areas between the Fermi surface and the Brillouin zone boundaries in the (111) direction.

A second critical assumption is that the scattering cross section does not vary strongly with the angle of scatter. Ziman[11] studied the scattering functions different than the one assumed in the usual Bloch theory developments. The exact form of the scattering function is extremely critical in the conduction process if the Fermi surface is either nonspherical or approaches the Brillouin zone boundaries. Since the Fermi surface for copper probably fulfills those provisions, the exact form of the scattering function is important. No quantitative calculations have yet been made for the scattering function for copper based on Pippard's model for the Fermi surface. However, general qualitative arguments by Ziman[29] suggest that reasonable scattering functions may be found that will give the proper temperature dependence for the intrinsic thermal resistivity of copper.

Since the electronic interactions in copper apparently do not agree with two of the critical assumptions utilized in the Bloch method for development of conduction theory, it is not unexpected that the experimental electronic transport properties also do not agree with the theoretical predictions based on that method. The standard theoretical values for both the absolute magnitude and the temperature dependence of the intrinsic thermal resistivity are in substantial error. Agreement between experimental results and theoretical predictions will probably await detailed quantitative calculations utilizing the techniques and scattering function approximations suggested by Ziman.[11]

Imperfection Resistivity

The imperfection resistivities, W_0 and imperfection constants, B, for samples 1 and 2 are given in Table I. The exact source of the imperfection resistivity in the high conductivity annealed copper sample 1 is unknown. As little as a few parts per million of chemical impurities or physical imperfections could cause the observed thermal imperfection resistivity. For the extremely pure and annealed sample, even the distribution of isotopes in copper may be significant as a scattering

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[23] See reference 3, Chap. 15, pp. 238–244.

[24] P. G. Klemens, Australian J. Phys. **7**, 70 (1954).

[25] H. Jones, Proc. Phys. Soc. (London) **A68**, 1191 (1955).

[26] R. G. Chambers, Proc. Roy. Soc. (London) **A238**, 344 (1956).

[27] M. H. Cohen, Phil. Mag. **3**, 762 (1958).

[28] A. B. Pippard, Phil. Trans. Roy. Soc. (London) **A250**, 325 (1957).

[29] J. M. Ziman (private discussion).

mechanism since the concentration of Cu^{65} (31%) is very much greater than the concentration of other imperfections. The additional imperfection resistivity observed in the cold-drawn sample 2 is undoubtedly caused by the increase in physical imperfections since there were no intermediate anneals or chemical treatments that might accidentally have introduced chemical impurities. However, the specific physical imperfections responsible for the additional resistivity of cold-drawn sample 2 are uncertain because the proportions of each type in cold-drawn copper are not known. Furthermore, the effects of each type of imperfection on the imperfection thermal resistivity are also not precisely known. Preliminary investigations of the effects of stacking faults have been carried out by Klemens[30] and Ziman.[5] It appears that the most important defect in our sample number 2 may be the stacking fault surface imperfection. The effects of dislocations are probably much less important.

B. Electrical Conductivity

Several lengthy review articles or books on the subject have been published in recent years,[31,32,6,10] so only very brief comments are given here.

A discussion of the separation of components and scattering mechanisms for electrical conductivity would follow almost exactly the discussion given in part *A* on the electronic thermal conductivity. The references on the development of the theory are also the same.[7–12] The total electrical resistivity, ρ, is assumed to be the sum of two separate resistivities, the residual or imperfection resistivity, ρ_0, and the intrinsic resistivity, ρ_i; that is, Matthiessen's rule for electrical resistivity is obeyed:

$$\rho=\rho_i+\rho_0. \tag{7}$$

The expressions for the magnitudes and temperatures dependence of the intrinsic and residual resistivities have been found to be given approximately by

$$\begin{aligned}&\rho_i=\alpha T^n;\quad n\cong 5,\quad T<40°\text{K},\\&\rho_0=a\text{ constant.}\end{aligned}\tag{8}$$

However, there are significant discrepancies.

Deviations from additivity for electrical resistivity, Eq. (7), have been observed experimentally for copper and its dilute alloys by Grüneisen,[33] van den Berg,[34] Linde,[35] and others more recently, including White.[19] The electrical resistivity of dilute copper alloys is further complicated by the existence of a minimum near 10°K for many alloy systems. MacDonald[31] discussed the latter effect in detail.

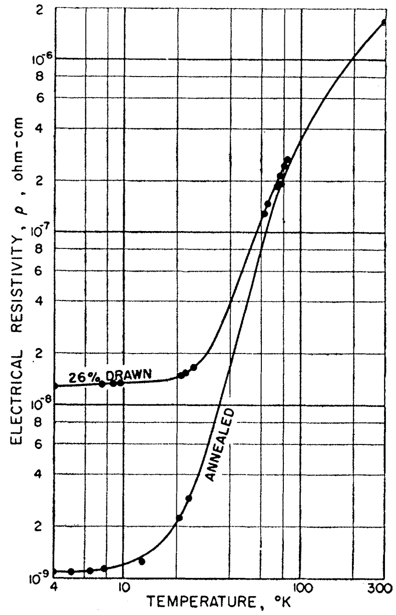

FIG. 4. Electrical resistivity of high-purity copper. The cold-drawn sample is reduced 26.4% in area.

The electrical resistivities of samples 1 and 2 are given in Fig. 4. As expected, no resistivity minimum is observed for the two samples since they do not contain any significant amount of metal impurities. The deviations from additivity could not be determined for the electrical resistivity because the experimental measurements were not of sufficient accuracy in the proper temperature ranges. The intrinsic resistivity between 20°K and 50°K was found to vary with the temperature as the 4.5±0.5 power. A comparative value (4.5±0.3) may be obtained from an analysis of the results between 19°K and 35°K published by Dauphinee and Preston-Thomas.[36] Other more extensive measurements in this laboratory on pure copper and very dilute copper alloys have given similar results. However, the value of 5 has been obtained by many others, including White[19] and Berman and MacDonald.[17] If the deviation from the predicted value of 5 is real, then the effect can probably be explained by the same modifications in theoretical assumptions that were discussed previously for the thermal intrinsic resistivity.

Experiments were also carried out on the effect of cold drawing on the electrical resistivity of pure copper. The measurements were made using another apparatus utilizing a simple four-lead potentiometer circuit. The residual resistivities, ρ_4, and residual resistivity ratio, ρ_{273}/ρ_4, for several of the samples are given in Fig. 5.

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[30] P. G. Klemens, Can. J. Phys. **35**, 441 (1957).

[31] D. K. C. MacDonald, *Handbuch der Physik* (Springer-Verlag, Berlin, 1956), Vol. 14, pp. 137–197.

[32] A. N. Gerritsen, *Handbuch der Physik* (Springer-Verlag, Berlin, 1956), Vol. 19, pp. 137–226.

[33] E. Grüneisen, Ann. Physik **16**, 530 (1933).

[34] G. J. van den Berg, thesis, Leiden, 1938.

[35] J. O. Linde, *Elektrische Widerstandseigenschaften der verdünnten Legierungen des Kupfers, Silbers und Goldes* (Gleerupska University Bökhandeln, Lund, 1939).

[36] J. M. Dauphinee and H. Preston-Thomas, Rev. Sci. Instr. **25**, 884 (1954).

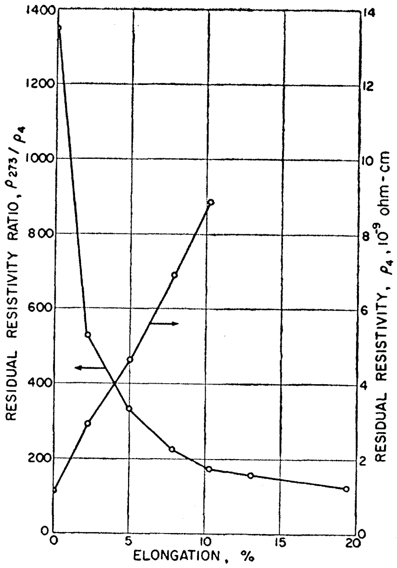

FIG. 5. Residual resistivities and residual resistivity ratios for a series of cold-drawn samples of high-purity copper.

The residual resistivities and ice-point resistivities for five samples are given in Table II. It is seen that the residual resistivity increase above the annealed value is approximately proportional to the elongation or reduction in area. The annealed sample has an ice-point resistivity of $(1.545\pm0.002)\times10^{-6}$ ohm cm and a helium boiling point resistivity of $(1.01\pm0.02)\times10^{-9}$ ohm cm.

As mentioned before, the specific physical imperfections responsible for the additional resistivity are uncertain. Recently a large amount of research has been carried out on the imperfection-producing processes in pure metals.[37] Apparently there are two regions or stages of hardening and elongation. Below about 1.5% elongation, the "linear" hardening stage, there is small dislocation movement, and therefore a relatively large dislocation generation for a given elongation. Above about 1.5% elongation, the "parabolic" hardening stage, there is greater dislocation movement, and therefore a smaller dislocation generation for a given elongation than in the previous stage.

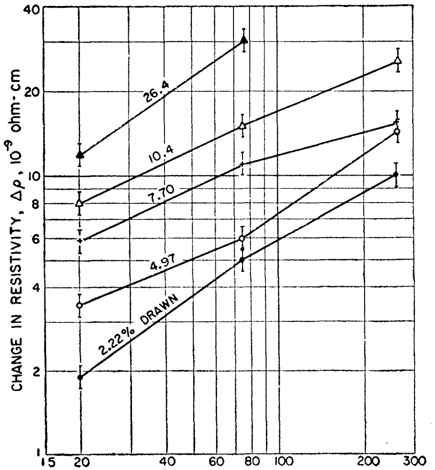

FIG. 6. Change in resistivity of cold-drawn samples with respect to annealed sample of high-purity copper. The vertical bars represent the estimated experimental error limits. The number by each line indicates the percent elongation by cold-drawing.

The increases in resistivity between the annealed sample and several of the drawn samples are given in Fig. 6. The resistivities were measured at four temperatures, 4°, 20°, 76°, and 273°K. The 4°K results are, however, included in Fig. 5. The added resistivities are clearly not constant with respect to temperature changes. There are two possible explanations: either the imperfection and intrinsic resistivities are not strictly additive, or the imperfection resistivity is temperature dependent. Our measurements cannot differentiate between the two possibilities. Others have also observed this apparent temperature dependence of the imperfection resistivity.[35,38] Gerritsen and van der Aa[38] found that the added resistivity caused by an increase in imperfections consisted of two parts, a large temperature-independent part and a relatively small temperature-dependent part. Our results gave the opposite effect: the added resistivity at the ice point was about four times as great as the added resistivity at the liquid-helium temperatures. However, it should be noted that our samples were much more pure than theirs and that their highest purity sample showed the greatest relative amount of temperature-dependent added resistivity.

C. Thermoelectromotive Force

There is comparatively very little literature on the thermoelectromotive forces for pure metals. Unfortunately there is no review article devoted to the subject in the recent *Handbuch der Physik*, and only relatively brief discussions in the book by Wilson.[10] Both the qualitative and quantitative predictions of the standard theory as outlined by Wilson are in serious error for pure copper. More recent discussions of the general theoretical concepts of thermoelectric power have been given by Domenicali,[39] Domenicali and Otter,[40] ter Haar and Neaves,[41] and Sondheimer.[42] Investigations on special aspects of the problem have been presented by Friedel[43] on chemical impurities, by

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[37] See for example *Dislocations and Mechanical Properties of Crystals*, edited by Fisher, Johnston, Thompson, and Vreeland (John Wiley & Sons, Inc., New York, 1956).

[38] A. N. Gerritsen and J. M. L. C. van der Aa, Appl. Sci. Research **A6**, 191 (1956).

[39] C. A. Domenicali, Revs. Modern Phys. **26**, 237 (1954).

[40] C. A. Domenicali and F. A. Otter, Phys. Rev. **95**, 1134 (1954).

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TABLE II. Electrical resistivities of annealed and cold-drawn pure coppers.

	Percent elongation by cold-drawing						
	0	2.22	4.97	7.70	10.40	13.05[a]	19.80[a]
Residual resistivity $\rho_4(10^{-9}$ ohm-cm)	1.01	2.92	4.61	6.92	8.86		
Ice-point resistivity $\rho_{273}(10^{-6}$ ohm-cm)	1.545	1.548	1.551	1.553	1.563		
Residual resistivity ratio ρ_{273}/ρ_4	1530.	531.	337.	224.	176.	161.	123.

[a] The absolute resistivities for the last two samples could not be determined because of an uncertainty in the form factor.

Abelés[44] on vacancies, and by Blatt[45] on interstitials and vacancies. Van Ooijen has given in his recent thesis[46] a discussion of various equations for the thermoelectric force of pure copper in the annealed and cold-worked states. In particular he discussed the interaction effects of chemical impurities and physical imperfections on the intrinsic thermoelectric force and power, and gave several expressions for changes in those quantities caused by physical imperfections. His work also included many experimental results describing the effects of cold-working on the thermoelectric force and power of moderately pure copper, silver, and gold.

The curves in Fig. 7 represent the difference in thermoelectric force and power between sample 1, annealed, and sample 2, 26% drawn. No direct comparison can be made with the general theories because measurements were not made on the absolute thermoelectric power, but only on the changes caused by a change in physical imperfection. However, it should be noted that the change in thermoelectric power below 30°K is of the same magnitude or greater than the absolute thermoelectric power of pure copper as determined by Borelius *et al.*[47] Because of the relatively large change at the lower temperatures in thermoelectric power caused by imperfections, a perturbation technique for discussing the change is probably not appropriate. Again, the specific physical imperfections responsible for the change in thermoelectric power are uncertain.

The curves are in sharp disagreement with the results reported on cold-worked copper by van Ooijen[46] and Pearson.[48] Our results show a large positive thermoelectric power at the lower temperatures and a small negative power above 80°K. Pearson found a small positive power at the lower temperatures and van Ooijen found a small positive power at the lower temperatures followed by a larger magnitude negative power at higher temperatures.[49] The differences between our work and the other two are probably caused primarily by the differences in purity of the annealed copper samples. Our annealed sample had a residual electrical resistivity about six times lower than the most pure copper sample used by van Ooijen and four times lower than the ones used by Pearson. However, results on silver by van Ooijen[46] had the same qualitative behavior as the results presented here on copper. The interaction effects of minor chemical impurities on the changes in thermoelectric power caused by physical imperfections are at present unknown and therefore the discrepancies between their work and ours cannot be explained rigorously.

Abelés[44] and Blatt[45] have found theoretically that vacancies or interstitials in the metal structure should decrease the total thermoelectric power of pure annealed copper, that is, the change in thermoelectric power should be negative. This is in qualitative agreement with our results above 70°K. However, in contrast we obtained a larger positive power below 38°K. A quantitative comparison of the theoretical and experimental results, even at the low temperatures, is not practical because the specific physical imperfections responsible for the changes in thermoelectric power are uncertain.

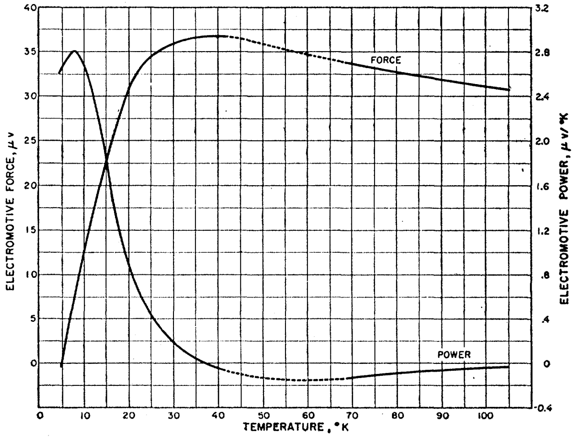

FIG. 7. Difference in thermoelectric power and force between a 26% cold-drawn sample and an annealed sample of high-purity copper for a reference junction at 5°K. The dashed parts of the curves indicate interpolated regions.

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[44] F. Abelés, Compt. rend. **237**, 796 (1953).

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[46] D. J. van Ooijen, thesis, Delft University, 1957.

[47] Borelius, Keesom, Johansson, and Linde, Commun. Kamerlingh Onnes Lab. Univ. Leiden No. 206a (1930).

[48] W. B. Pearson, Phys. Rev. **97**, 666 (1955).

[49] R. H. Kropschot, thesis, Michigan State University, 1959 (unpublished), obtains results similar to ours for the change in thermoelectric power of pure copper caused by cold-working. The purity and source of his copper were the same as ours.

D. Lorenz Number

The thermal resistivity may be compared to the electrical resistivity by means of the Wiedemann-Franz-Lorenz law

$$\rho = LWT, \tag{9}$$

where L is the Lorenz number, assumed to be a fundamental constant given by the Sommerfeld value, 2.45×10^{-8}. Kohler[50] showed that the Lorenz number should be constant *if the conduction electrons were scattered elastically.* That condition is approximately true at high temperatures and at very low temperatures where the residual resistivity is predominant. At intermediate temperatures the condition of elasticity no longer holds and the Lorenz number decreases considerably from the Sommerfeld value.

The experimental values for the Lorenz number of samples 1 and 2 are given in Fig. 8. The two curves are quite similar to the results published previously by others.[17,19] For the annealed sample the 0°K extrapolated value is not the Sommerfeld value, but is about $(1.9 \pm 0.1) \times 10^{-8}$, unless the curve changes its behavior again below about 4°K. At this laboratory measurements on the Lorenz number for very dilute copper alloys containing silver gave similar results. The curves either flatten out below 6°K, or bend over significantly so that the extrapolated values for 0°K do not approximate the Sommerfeld value. It has been observed here that the extrapolated values for the Lorenz number approach the Sommerfeld value more closely as the impurities increase and the residual resistivities increase. Only more careful experiments between 1°K and 10°K on the thermal and electrical resistivity of *very pure* copper can settle this question decisively.

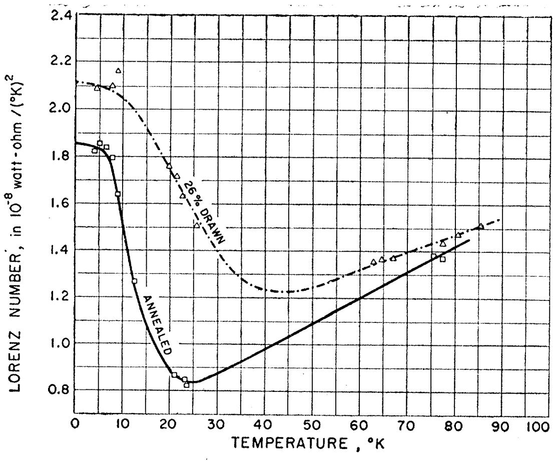

FIG. 8. Lorenz number of high-purity copper. The cold-drawn sample is reduced 26.4% in area.

V. SUMMARY

Our experimental results on the low-temperature transport properties of pure copper agree in general qualitatively with theoretical predictions and previous experimental work by others. However, for many significant details, there are deviations and discrepancies both in the qualitative and quantitative agreement. The results indicate the presence of a term in the thermal resistivity giving the deviation from strict additivity of the intrinsic and imperfection resistivities (Matthiessen's rule). It has a form similar to one proposed by Kohler[22] for the deviation term in electrical resistivities, the product of the two thermal resistivities divided by their sum. By using this method of analysis, it is found that the intrinsic thermal resistivity is a characteristic property of the metal (as it should be) and does not vary between samples of different imperfection resistivity, as was found by White.[19] The intrinsic thermal resistivity below 40°K varies as $T^{2.7}$. The exponent is considerably higher than the value, 2, predicted by theoreticians[3,10] using the usual Bloch approach and standard assumptions. The coefficient for the intrinsic thermal resistivity term is also quite different from the one predicted theoretically, and cannot be brought into agreement by any reasonable adjustment of the parameters, such as the number of free electrons or characteristic temperature, that enter into the theoretical expression. A resolution of the discrepancies between the theoretical predictions and the experimental results will probably await new calculations based upon the theories and suggestions of Ziman.[11] In particular, it seems that account must be taken of the nonspherical Fermi surface in copper and the dependence of the scattering cross section on the angle of electron scatter.

The intrinsic electrical resistivity below 40°K varies as $T^{4.5}$, a value in agreement with some previous research,[36] but in disagreement with others.[17,19] The theoretically predicted value is 5. The increase in imperfection resistivity is approximately linear with increase in elongation caused by cold-drawing. The additional resistivity caused by cold-drawing is temperature dependent, in violation of the usual Matthiessen's rule. This may be caused either by a deviation from additivity for the intrinsic and imperfection resistivities, or by a temperature-dependent imperfection resistivity, or possibly both. The discrepancies between theoretical and experimental results for electrical resistivity would probably be removed by the same improvements in basic conduction theory necessary for thermal resistivities.

The thermoelectric force and power of cold-drawn copper with respect to annealed copper are both positive at the lower temperatures. The relative thermoelectric power has a minimum of about +2.9 μv/°K at 8°K, is zero at about 38°K, and is slightly negative at higher temperatures. These results are not

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[50] M. Kohler, Ann. Physik **40**, 601 (1941).

explained, even qualitatively, by any current theory of thermoelectricity.

The Lorenz number for high-purity copper has approximately the same temperature behavior as has been observed by others previously.[17,19] However, the curve does not seem to extrapolate to the Sommerfeld value at 0°K, but rather flattens out to a considerably lower value. The same phenomenon has been observed in two very dilute copper alloys.

VI. ACKNOWLEDGMENTS

We would like to thank Dr. R. H. Sherman of the Los Alamos Scientific Laboratory for assistance in the preparation of the samples and Dr. A. J. Phillips and J. S. Smart, Jr., of the Central Research Laboratories of the American Smelting and Refining Company for supplying the original high-purity rods. We would also like to thank M. D. Bunch and M. Konecnik for assistance during many of the experimental runs.

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Crystal Structure of the Ferroelectric Phase of $(\text{Glycine})_3 \cdot H_2SO_4$†

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Ferroelectric $(\text{glycine})_3 \cdot H_2SO_4$ crystallizes at room temperature in the monoclinic system with $a=9.41_7$ A, $b=12.64_3$ A, $c=5.73_5$ A, $\beta=110° 23'$; the space group is $P2_1$, and the polar direction is along the two-fold screw axis. Above 47°C the spontaneous polarization disappears as the space group becomes $P2_1/m$. The crystal structure was determined from full three-dimensional x-ray diffraction data, using Cu $K\alpha$ radiation. Out of the three glycine molecules in the crystal, one has the usual zwitter-ion configuration, with the $-NH_3^+$ group out of the plane of the other atoms; the remaining two glycines are mono-protonated, and planar within experimental error, and are designated as glycinium ions. Thus the chemical formula is properly written as $(NH_3^+CH_2COO^-) \cdot (NH_3^+CH_2COOH)_2 \cdot SO_4^{--}$, and the compound is best described by the chemical name glycine diglycinium sulfate. One of the planar glycinium ions lies near but not in the plane $y=\frac{1}{4}$, which becomes the mirror plane in the high-temperature phase.

The nitrogen atoms form $N-H\cdot\cdot O$ hydrogen bonds of the usual strength, whereas a quite strong $O-H\cdot\cdot O$ hydrogen bond of a distance of 2.43_8 A is found between the oxygen atom of the carboxyl group of the zwitter-ion glycine and that of the planar glycinium ion which lies near the plane $y=\frac{1}{2}$.

Above the Curie point, at 47°C, mirror symmetry is attained by statistical arrangement of atoms around the mirror planes at $y=\frac{1}{4}$ and $\frac{3}{4}$. The disorder of the glycinium ions near the mirror planes, and the above-mentioned strong $O-H\cdot\cdot O$ bond, are of particular importance for the ferroelectric behavior of the crystal.

INTRODUCTION

MATTHIAS, Miller, and Remeika[1] discovered ferroelectric behavior at room temperature in the crystals $(\text{glycine})_3 \cdot H_2SO_4$ and isomorphous $(\text{glycine})_3$ H_2SeO_4. Pepinsky, Okaya, and Jona[2] later observed ferroelectricity in isomorphous $(\text{glycine})_3 \cdot H_2BeF_4$. Preliminary x-ray and morphological studies of these crystals[2,3] revealed that the crystals belong to the space group $P2_1$ in their ferroelectric phase, changing into $P2_1/m$ above the Curie points; the transition temperatures are 47°C, 22°C, and 70°C for the sulfate, selenate, and fluoberyllate, respectively. Since detailed dielectric and thermal studies of the crystals[4] showed that the ferroelectric transition in these substances is of second order, the deviation of the structure from the centrosymmetric space group $P2_1/m$ to the ferroelectric phase could be presumed to be slight. Complete crystal structure analyses of both the polar and nonpolar phases of $(\text{glycine})_3 \cdot H_2SO_4$, which is the most important ferroelectric among these isomorphs, are necessary in order to establish the nature of the hydrogen-bond system and also the configurations of the glycine and sulfate ions. Such a study is particularly important because discoveries within the last few years of a number of ferroelectric crystals suggest that hydrogen bonds in these crystals, and/or the presence of ions with particular symmetries—and especially those with tetrahedral, pyramidal, or planar configurations—play a dominant role in their dielectric behaviors.

These factors are suggested by a partial list of other newly-discovered ferroelectrics containing ammonium or substituted ammonium, glycine or guanidinium ions, and sulfate (or selenate or fluoberyllate), nitrate, or selenite ions. Included among these compounds are guanidinium$\cdot Al(SO_4)_2 \cdot 6H_2O$ and isomorphs,[5] $(NH_4)_2$-

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[4] Hoshino, Mitsui, Jona, and Pepinsky, Phys. Rev. **107**, 1255 (1957).

[5] Holden, Matthias, Merz, and Remeika, Phys. Rev. **98** 546, (1955).