

curve such as that in Fig. 2 is dependent upon the rapidity with which the measurements are carried out in the case of crystals doped with divalent cations.

The behavior of the "pure" crystal showed that both n_T^0 and n_T^0 were very low. This result agrees with that of Kawamura¹⁵ who observed very little bleaching and consequently practically no *M*-center formation with specially purified colored KBr.

All measurements on these crystals were repeated upon adjacent pieces after one year. Considerable decrease in sensitivity occurred in the "pure" crystal, which may be ascribed either to inhomogeneity of the crystal or to aging. In the others there was no appreciable change. It does not appear that sensitivity decreases with time at room temperature, as previously reported,² as a usual occurrence, provided storage and handling are in total darkness.

(e) Additional Observations

An interesting observation was made during the course of this study, which merits remark and further experimentation. The sensitivity of a given crystal was higher if measured immediately after depolarization (illumination with zero field) than if the crystal remained in the dark for a minute or so before measure-

ment. There seems to be a decay time associated with the presence of shallow traps which, during illumination, contain electrons in equilibrium with the conduction electrons. The half-time for attainment of equilibrium, or emptying of the traps, was found to be about 40 seconds. Polarization entirely obscures the effect of such shallow traps upon the rise-time of photoconductivity, when dc measurements are made; the effect should be apparent when an ac method is used, but does not seem to have been previously noted in pure alkali halides containing *F* centers. MacDonald,¹⁶ however, using ac of frequency 20 sec⁻¹ observed an even slower photocurrent decay in KBr containing both *F* and *U* centers, which he attributed to the presence of shallow traps, possibly interstitial hydrogen atoms.

In order to eliminate the effects of shallow traps on the sensitivity reported, all measurements were made after a 20-second dark interval following depolarization. This standardized procedure rendered successive measurements reproducible.

ACKNOWLEDGMENT

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¹⁵ H. Kawamura, *J. Phys. Chem. Solids* **8**, 161 (1959).

¹⁶ J. R. MacDonald, *J. Chem. Phys.* **23**, 275 (1955).

Interpretation of Relative Thermoelectric Phenomena at Low Temperatures with Special Consideration of the Effects of Cold-Work on Copper

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Formulas first derived by Kohler and more recently discussed by MacDonald are used to account for relative thermoelectric effects at low temperatures in pure metals, dilute alloys, and in cold-worked copper. Since calculations based on these formulas give diffusion thermoelectricity, phonon drag contributions to thermoelectricity should appear as differences between the calculated and measured curves of thermoelectric power as a function of temperature.

I. INTRODUCTION

THE thermoelectric behavior of relatively pure metals at low temperatures (say below $\theta/15$) is often puzzling since it is possible to obtain absolute thermoelectric powers from different samples which may differ not only in sign but by as much as two orders in magnitude, although residual resistivity measurements indicate that there is but little difference in the overall purity of the samples. Kohler¹ (see also Nordheim and Gorter²) first derived expressions from formal electron transport theory which have been deduced again more

recently by MacDonald directly from simple thermal circuit theory.³ These, as we shall show, can be applied to account for relative thermoelectric phenomena in pure metals and dilute alloys at low temperatures. The theorem which considers the influence of competing scattering mechanisms on the thermoelectricity of a homogeneous conductor containing only one type of charge carrier by treating them independently in series, can be expressed as follows

$$S = \sum W_i S_i / \sum W_i. \quad (1)$$

¹ M. Kohler, *Z. Physik* **126**, 481 (1949).

² L. Nordheim and C. J. Gorter, *Physica* **2**, 383 (1935).

³ A. V. Gold, D. K. C. MacDonald, W. B. Pearson, and I. M. Templeton, *Phil. Mag.* (to be published).

Where S is the observed thermoelectric power and $S_1, S_2 \dots$ and $W_1, W_2 \dots$ are, respectively, the characteristic thermoelectric contributions and thermal resistivities at a given temperature due to the various scattering mechanisms 1, 2... present in a metal. For Eq. (1) to be valid the characteristic thermoelectric powers, $S_1, S_2 \dots$ must be functions of temperature only, being independent of impurity concentration (i.e., the presence of impurity atoms must not effectively modify the electron density of states function of the solvent metal) and this is generally the case when only very dilute alloys are considered.

In our discussion of the thermoelectricity of pure metals and dilute alloys which follows we shall consider only the diffusion thermoelectricity and ignore phonon drag, except when it is explicitly discussed, and we shall assume that the concentration of impurities is never large enough to cause any effective modification of the Fermi surface.

Equation (1) may be written in the form

$$S = \frac{W_1}{W_{\text{total}}} S_1 + \frac{W_2}{W_{\text{total}}} S_2 + \dots + \frac{W_{\text{th}}}{W_{\text{total}}} S_{\text{th}}, \quad (2)$$

where 1, 2... refer to scattering processes due to physical or chemical imperfections present in the metal and th refers to thermal scattering processes. If we consider only low temperatures where thermal scattering is negligible (i.e., in the Lorentz relationship, $L_0 = \rho/WT$, L_0 has a constant value of 2.45×10^{-8} volts²/deg²) then expression (1) can be written in the form

$$S = \frac{\rho_1}{\rho_{\text{total}}} S_1 + \frac{\rho_2}{\rho_{\text{total}}} S_2 + \dots, \quad (3)$$

where $\rho_1, \rho_2 \dots$ are the electrical resistivities due to the scattering mechanisms 1, 2..., $\rho_{\text{total}} = \sum \rho_i$, and $S_1, S_2 \dots$ are as before the characteristic thermoelectric powers due to 1, 2... at a given temperature. If we consider only two scattering mechanisms this reduces to

$$S = S_2 + \frac{\rho_1}{\rho_{\text{total}}} (S_1 - S_2). \quad (4)$$

II. THERMOELECTRICITY OF A PURE METAL AT LOW TEMPERATURES AND THE INFLUENCE OF PHYSICAL AND CHEMICAL IMPURITIES

Equations (1) and (2) emphasize that in terms of scattering phenomena, thermoelectricity is an "intensive" parameter in contrast to thermal and electrical resistances which are "extensive" parameters of the system. Thus the size of the thermoelectric effect depends on the relative amounts of the scattering due to the various chemical and physical imperfections present, whereas the normal thermal and electrical resistivities

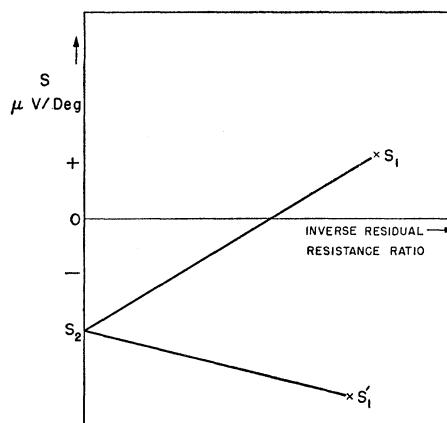


FIG. 1. Hypothetical plots of S against $1/\rho_{\text{total}}$ for Eq. (4) when solute 2 is added to a metal having (1) S_1, ρ_1 , and (2) S'_1, ρ'_1 as the thermoelectric and resistivity contributions from all residual chemical and physical impurities present in it.

depend only on the total amount. The important consequence of this is that the intrinsic thermoelectric power of a metal due to dominant thermal scattering at low temperatures cannot generally be determined from measurements on a single rather pure sample, especially if the characteristic thermoelectric power of one or more common impurities (solutes) is large in that particular metal. This is because the observed thermoelectricity due to an impurity with a large characteristic thermoelectric power can be as large when only 0.0001% is present as when, say 0.1% is present provided that this impurity gives rise to the dominant scattering mechanism in the metal.

Let us now in Eqs. (3) and (4) attribute S_2 and ρ_2 to a particular impurity which is to be alloyed with a pure metal in which S_1 and ρ_1 represent the thermoelectric and resistivity contributions due to all other physical and chemical impurities already present, these being held constant throughout the alloying processes. As Fig. 1 indicates, the change in the observed thermoelectric power of the "pure" metal on alloying with impurity 2 may be either positive or negative and it will depend on the initial value of S_1 due to the residual impurities in the metal, and on S_2 which is the value the thermoelectric power, S , of the metal must approach as the impurity 2 becomes the dominant scattering mechanism. Hence it can be seen that both the diffusion thermoelectric power of the "pure" metal, and its change on alloying with a specific impurity may adopt all kinds of values. This is particularly the case with copper (Gold et al.⁸) where one of the common impurities, iron, has a large characteristic thermoelectric power and most of the other impurities have small ones. The observed behavior on alloying then depends on the relative fraction of the total residual resistivity of the initial copper which is due to iron.

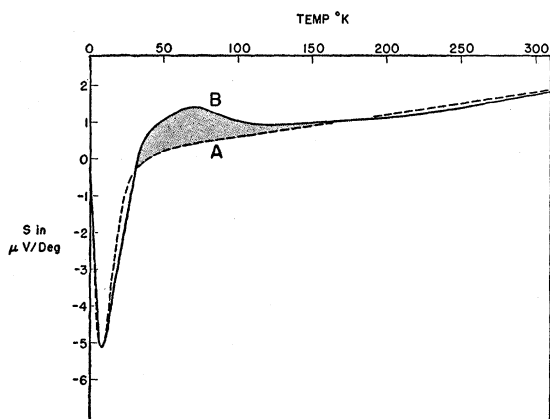


FIG. 2. *B*. Observed thermoelectric power of an annealed sample of American Smelting and Refining Company copper as a function of temperature. *A*. Diffusion thermoelectric power calculated from Eq. (2) using thermal conductivity data from Powell et al. (see text). His data referred to a sample of lower resistivity than that giving Curve *B*, hence the deviation of *A* and *B* in the region from 15° to 30°K.

III. THE EFFECTS OF THERMAL SCATTERING AT RELATIVELY LOW TEMPERATURES

The theorem of Kohler and MacDonald can be used to account for the variation of the diffusion thermoelectric power with temperature, reproducing particularly the change when thermal vibrations become the dominant scattering mechanism. We shall give but one example from the work of Gold et al.³ A particular copper sample which gave a residual resistance ratio $[R_{4.2^\circ\text{K}}/(R_{296^\circ\text{K}} - R_{4.2^\circ\text{K}})]$ of 1.1×10^{-3} was found by chemical analysis to contain about 0.0001 at. % Fe equivalent in scattering power to about half of the total residual resistivity. As we have already noted, iron has a very large characteristic thermoelectric power when dissolved in copper, whereas most other common impurities have very small characteristic thermoelectric powers, so that we may assume that $S_1 \sim 0$ at the temperature considered. The value of S_{th} at any temperature is determined from the observed variation of S with T for copper at room temperature. Putting then the appropriate data into Eq. (2) where W_2, S_2 refer to iron in copper and W_1, S_1 refer to the remaining impurities, and taking $W_1 \sim W_2, S_1 \sim 0$, the curve *A* (Fig. 2) is calculated for S in fair agreement with the observed curve *B*. Such a calculation also indicates very clearly what we believe to be the contribution of phonon drag to the thermoelectricity of pure copper, since it appears in Fig. 2 as the difference between the calculated diffusion thermoelectricity and the observed thermoelectricity (shaded area).

IV. THERMOELECTRICITY OF COLD-WORKED COPPER AT LOW TEMPERATURES

We wish to devote the main portion of this paper to a discussion of the effects of cold-work on the thermo-

electricity of pure copper at low temperatures. Pearson⁴ first showed that the thermoelectric power of cold-worked copper was positive relative to annealed copper below 20°K. van Ooijen⁵ then confirmed this result and showed that at somewhat higher temperatures (say above 40°K) the thermoelectric power of cold-worked copper became negative relative to annealed copper. Recently Powell et al.⁶ obtained results similar to those of van Ooijen but stated that their results were in "sharp disagreement" with those quoted above, principally because of the different magnitude of the effects, especially for the positive ΔS found at low temperatures. It is easy to show in the light of the Kohler-MacDonald formula and the work of Gold et al.³ that there is no real disagreement. From the work of Pearson⁴ and the results given below it can be ascertained that the characteristic thermoelectric power due to imperfections introduced into copper by cold-work is a rather small positive quantity at a temperature of 8°K. Hence the essential effect of cold-work on the thermoelectricity of copper at low temperatures is to introduce a dominant excess of scattering centers which cause a very small characteristic thermoelectric power in much the same way as thermal vibrations (see also van Ooijen⁵).

Now the copper examined by Pearson⁴ had virtually no iron in solid solution; its value of S at 8°K was about $-0.04 \mu\text{V}/\text{deg}$, hence the effect of cold work on the observed thermoelectric power was very small as reported in 4. Although Powell et al.⁶ do not give a curve for the variation of thermoelectric power of their annealed copper with temperature, the copper was said to have come from the American Smelting and Refining Company. Such copper (see Gold et al.) generally contains a small but dominant quantity of iron in solid solution and thus shows a rather large negative thermoelectric power at low temperatures. The large change of thermoelectric power found by Powell et al. on cold-working the copper is mainly the consequence of the reduction of the contribution due to scattering by iron through the introduction of a large excess of scattering centers as shown above. Indeed we have deduced the thermoelectric power of Powell's annealed copper at 8°K from the data in our Figs. 5 and 7 and we have used Powell's thermal resistivity data and thermoelectric data from Gold et al. to calculate from Eq. (2) the change of thermoelectric power due to cold work for Powell's sample which was reduced 26.2% in cross-sectional area. The agreement below 40°K of the calculated ΔS curve with the observed ΔS curve given by Powell is striking (see Fig. 3).

Above about 40°K Powell and van Ooijen both find that the thermoelectric power of cold-worked copper relative to annealed copper is negative in sign. This is

⁴ W. B. Pearson, Phys. Rev. **97**, 666 (1955).

⁵ D. J. van Ooijen, thesis, Tech. Hogeschool, Delft, 1957 Excelsior, 'S-Gravenhage.

⁶ R. L. Powell, H. M. Roder, and W. J. Hall, Phys. Rev. **115**, 314 (1959).

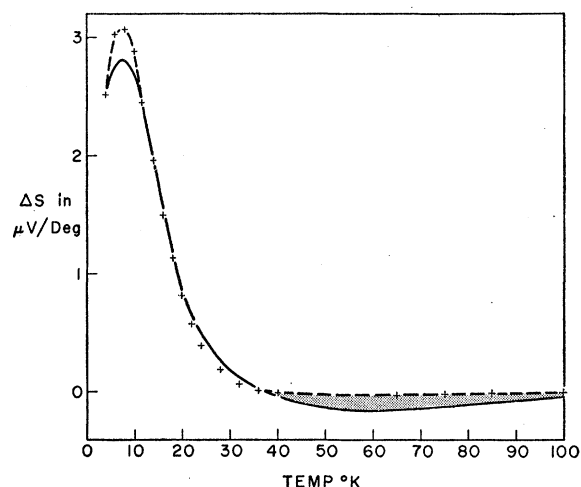


FIG. 3. Full line: Measurements of Powell et al. of the thermoelectric power of cold-worked copper (reduced 26.2% in cross-sectional area) relative to annealed copper, ΔS , plotted as a function of temperature. +---+---+ Calculated curve for ΔS (diffusion thermoelectricity only: see text).

very interesting since it is exactly what would be expected if there was an appreciable positive phonon drag contribution to the thermoelectricity of copper in this region. The work of Gold et al. suggests that this is the case, and the maximum contribution from phonon drag occurs at 60° to 70°K. In cold-worked copper we argue that the large number of defects introduced causes appreciable phonon scattering thus reducing the fraction of momentum transferred to the conduction electrons (see e.g., MacDonald⁷) and hence the magnitude

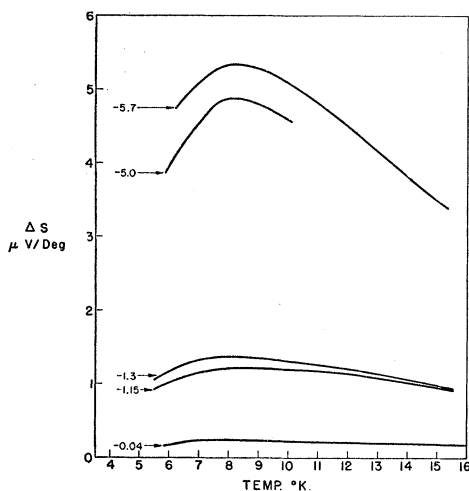


FIG. 4. Thermoelectric power of cold-worked copper (reduced 96% in cross-sectional area at room temperature) relative to the same sample in the annealed state before drawing, ΔS , plotted as a function of temperature.

The figures to the left of the curves are the values of the greatest negative absolute thermoelectric power of the annealed samples (i.e., values at about 8°K).

⁷ D. K. C. MacDonald, *Physica* **20**, 996 (1954); *Science* **129**, 943 (1959).

of the phonon drag thermoelectric power. The thermoelectric power of cold-worked copper is thus expected to become negative relative to annealed copper in the region between about 40° and say 150°K where phonon drag appears to be important. It is interesting first to see that the maximum negative deviation found by both Powell et al. and van Ooijen occurs indeed at about 60° to 70°K where the phonon drag contribution to the thermoelectric power of pure annealed copper appears to be greatest. And secondly, that the calculated curve in Fig 3 which gives the diffusion thermoelectricity only, departs significantly from the observed ΔS curve above 40°K and does not reproduce the substantial negative values, suggesting further that they may be due to changes in the phonon drag component of the thermoelectricity.

In order to confirm further the correctness of our interpretation we give in Figs. 4 to 7 new data on the thermoelectric power of copper cold-worked at room temperature which we have collected using the approximate methods of MacDonald and Pearson⁸ and Pearson⁴ and checked by more precise experiments at the lowest temperatures.⁹ Figure 4 shows how the change of thermoelectric power of cold-worked copper relative to annealed copper, ΔS , depends on the greatest negative value of the absolute thermoelectric power of the pure

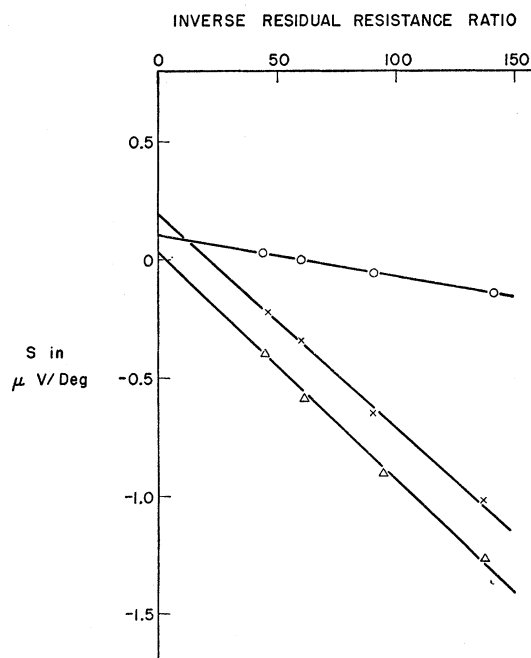


FIG. 5. Plots of S at 8°K against $1/\rho_{\text{total}}$ [see Eq. (4)] for three different copper samples which have been cold-worked for various amounts corresponding to between 20 and 96% reduction in cross-sectional area.

⁸ D. K. C. MacDonald and W. B. Pearson, *Proc. Roy. Soc. (London)* **A219**, 373 (1953).

⁹ Cf. D. K. C. MacDonald, W. B. Pearson, and I. M. Templeton, *Proc. Roy. Soc. (London)* (in press, 1960).

copper. This in turn depends on the relative scattering importance of traces of iron present in the copper. In Figs. 5 and 6 we show plots of S_{observed} at 8°K and 15°K against the inverse residual resistivity (see Sec. II). Each of the lines shows results obtained for various degrees of cold-work on a copper sample of a particular purity. The plots represent the equation,

$$S_{\text{obs.}} = S_{\text{cold worked}}$$

$$+ \frac{\rho_{\text{other impurities}}}{\rho_{\text{total}}} (S_{\text{cold worked}} - S_{\text{other impurities}}),$$

the intercept on the ordinate giving $S_{\text{cold worked}}$, the characteristic value of the thermoelectric power due to imperfections introduced by cold-work in copper at the temperature considered. The extrapolated values of $S_{\text{cold worked}}$ at 8°K for samples of copper of various purities, which lie within about 0.1 μv per deg of each other, suggest a small positive characteristic thermoelectric power of $\sim 0.1 \mu\text{v}$ per deg for imperfections at this temperature. We use the data in Figs. 4 to 7 only to demonstrate the principles involved in our discussion, since the absolute values of thermoelectric powers are not known too precisely. This is apparent in Figs. 5 and 6 where the extrapolated $S_{\text{cold worked}}$ values from differ-

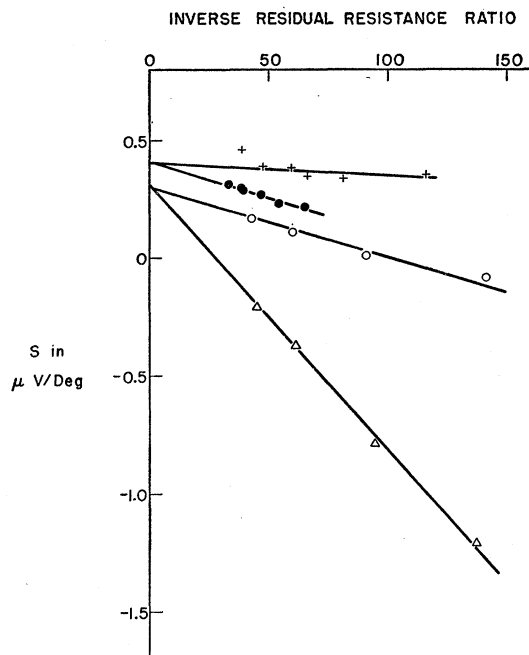


FIG. 6. Plots of S at 15°K against $1/\rho_{\text{total}}$ [see Eq. (4)] for four different copper samples which have been cold-worked for various amounts corresponding to between 20 and 96% reduction in cross-sectional area.

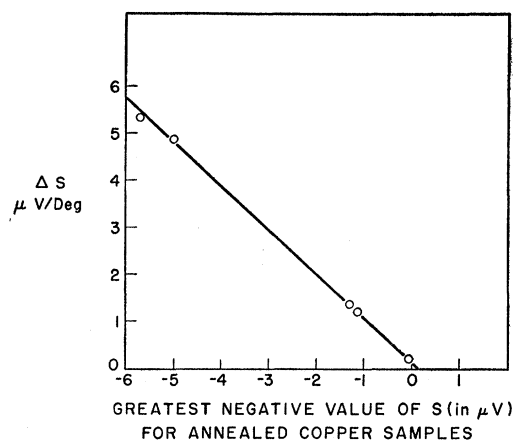


FIG. 7. Plot of the maximum values of ΔS from the curves in Fig. 4 against the values of the greatest negative absolute thermoelectric power of the annealed samples. These are given to the left of the curves in Fig. 4.

ent copper samples agree only to $\pm 0.1 \mu\text{v}$ per deg. (comparison of absolute values of thermoelectric power), although the points obtained for various degrees of cold-work on a particular sample are closely collinear (comparison of relative values of thermoelectric power).

It is interesting to use the data of Fig. 4 and plot the maximum value of $\Delta S_{\text{cold worked}}$ due to 96% reduction in cross-sectional area against the greatest negative value of the thermoelectric power of the corresponding annealed copper (see, e.g., Fig. 2) both of which occur at about 8°K. A linear relationship is obtained which extrapolates to $+0.15 \mu\text{v}$ per deg for a value of $\Delta S = 0$ agreeing, as it should approximately, with the value of the characteristic thermoelectric power of imperfections due to cold-work in copper at 8°K (Fig. 7).

IV. CONCLUSION

We have demonstrated how relative thermoelectric effects as a function of composition or temperature in pure metals, dilute alloys and cold-worked metals can be accounted for by the use of formulas first derived by Kohler. The application of Kohler's formulas, often overlooked in recent years, can contribute much to our understanding of thermoelectric phenomena in metals at relatively low temperatures, and to our recognition of phonon drag thermoelectricity at rather higher temperatures. The magnitude of the various thermoelectric effects still remains to be understood in detail.

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