negligible effect on the results.[23] In addition, the reproducibility of the work function of the iron suggests that a single-crystal plane is probably exposed by cleavage.

The exact agreement between the results reported here and those of Riviere[10] must be considered fortuitous. The exposed planes on a film evaporated on a cold glass substrate cannot be expected to be the same as those on a cleaved surface.

[23] Even if the work function of 5% of the surface differed by 0.5 electron volt from the rest of the surface, it would change the measured work function by only 0.03 electron volt. For further discussion of the patch effect see C. Herring and M. H. Nichols, Revs. Modern Phys. **21**, 185 (1949).

## ACKNOWLEDGMENTS

The author wishes to thank Professor Robert L. Sproull for his guidance throughout the course of this work. The assistance of J. Gilvey, L. Hinman, and S. Jacobs in the construction of the apparatus and M. Moss in the photomicrography and x-ray studies of the crystals is gratefully acknowledged.

PHYSICAL REVIEW VOLUME 116, NUMBER 3 NOVEMBER 1, 1959

# Thermoelectric Power of Cold-Rolled Pure Copper*

R. H. KROPSCHOT† AND F. J. BLATT
*Physics Department, Michigan State University, East Lansing, Michigan*
(Received June 15, 1959)

The difference between the thermoelectric power of severely cold-rolled and well annealed pure copper has been measured between about 8°K and 320°K. The absolute thermoelectric power of our annealed and cold-worked samples were determined over the same temperature range by measuring the thermoelectric power of a thermocouple formed from annealed pure copper and pure lead. The thermoelectric power of cold-rolled copper is positive relative to annealed pure copper over the entire temperature range, and the effect of cold work is largest at very low temperatures where the thermoelectric power of annealed copper displays a pronounced minimum. Our results are in fair agreement with recent work by Powell and by van Ooijen.

## INTRODUCTION

WE report here the result of measurements of the thermoelectric power (TEP) of severely cold-rolled pure copper between about 8°K and 320°K. The investigation of the TEP of cold-worked metals is a natural sequel to the studies of the resistivity due to cold work.[1] Indeed, the change in the TEP due to cold work has already been studied experimentally[2] and theoretically.[3] The experimental work of the past was carried out using relatively impure copper (99.98% and 99.97% pure). Studies of very dilute copper alloys have shown conclusively that minute amounts of certain impurities can change the TEP of copper by orders of magnitude at low temperatures.[4] Recently Powell has reexamined the TEP of cold-worked pure copper, using material of the highest purity available, and has obtained good agreement with previous work.[5]

## EXPERIMENTAL PROCEDURE

Our samples were prepared from nominally 99.999% pure copper supplied by the American Smelting and Refining Company. The metal, in the form of cylindrical billets of about 5-mm diameter, was cold-rolled at room temperature into strips about 5 mils thick. Some of these strips were then annealed for three hours in vacuum (pressure less than $10^{-5}$ mm Hg) at 950°C. A thermocouple was formed using an annealed and an unannealed strip, and the thermal emf's were measured with a Leeds and Northrup microvolt amplifier. The temperature difference between the cold junction (in liquid He, liquid air, or ice bath) and the hot junction was measured by means of calibrated gold-2.1% cobalt *versus* copper and copper *versus* constantan thermocouples.[6]

We estimate that our errors are ±1.5% of the measured thermoelectric emf and ±0.1°K for the temperature measurements. We have also carried

* Supported in part by the Office of Ordnance Research, U. S. Army and by an All-University Research Grant, Michigan State University, East Lansing, Michigan.
† Present address: National Bureau of Standards, Cryogenics Laboratory, Boulder, Colorado.
[1] C. W. Berghout, Acta Met. **4**, 212 (1956); H. G. van Bueren, Acta Met. **3**, 524 (1955); H. G. van Bueren, thesis, University of Leiden, 1956 (unpublished).
[2] D. J. van Ooijen, thesis, University of Delft, 1956 (unpublished); see also references to earlier work contained therein.
[3] A. W. Saenz, Phys. Rev. **91**, 1142 (1953); H. Bross and A. Seeger, J. Phys. Chem. Solids **4**, 161 (1958).
[4] D. K. C. MacDonald and W. B. Pearson, Acta Met. **3**, 392, 403 (1955); Phil. Mag. **45**, 491 (1954); Physica **19**, 841 (1953).
[5] R. L. Powell (to be published).
[6] We are grateful to R. L. Powell and M. D. Bunch of the National Bureau of Standards for providing us with some calibrated copper constantan and copper and gold-cobalt thermocouple wires.

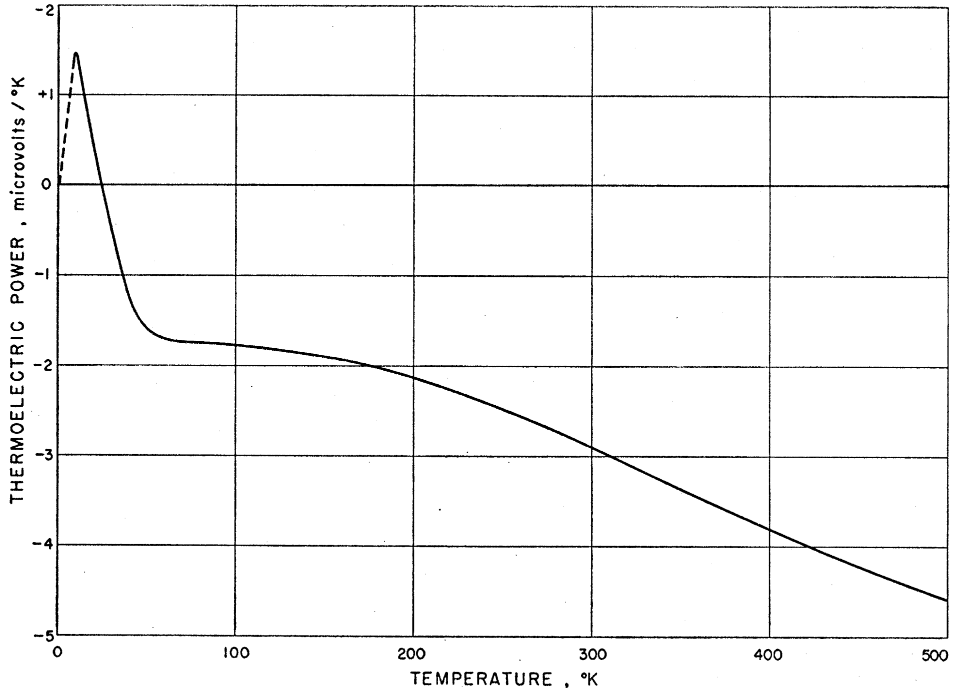



FIG. 1. The thermoelectric power of a pure annealed copper *versus* lead thermocouple.

through a least square analysis for the annealed *versus* unannealed pure copper thermocouple data. The standard deviation in the range 4.2°K to 80°K is 0.1 microvolt; in the range 80°K to 320°K it is 0.05 $\mu$v.

The absolute TEP of our pure annealed copper was determined by the same technique using a copper *versus* lead thermocouple. The absolute TEP of lead has recently been remeasured at Ottawa.[7]

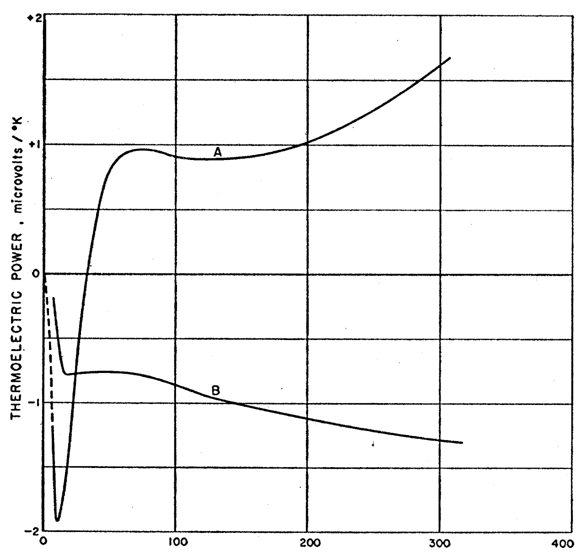



FIG. 2. A. The absolute thermoelectric power of pure annealed copper. B. The absolute thermoelectric power of pure annealed lead.

[7] Christian, Jan, Pearson, and Templeton, Proc. Roy. Soc. (London) **A245**, 213 (1958).

As a partial check on the purity of our copper samples we measured the resistance ratios $p=R_{4.2}/(R_{273}-R_{4.2})$ of the annealed and the unannealed strips. For the annealed specimen we obtained $p_a=1.85\times10^{-3}$. This value compares favorably with the resistance ratios of $2.5\times10^{-3}$ quoted by Pearson and MacDonald,[4] and $7.1\times10^{-3}$ and $4.3\times10^{-3}$ quoted by van Ooijen for his nominally purer and less pure samples, respectively. From the measured value of the resistance ratio for the unannealed strip $p_u=5.4\times10^{-3}$, we conclude

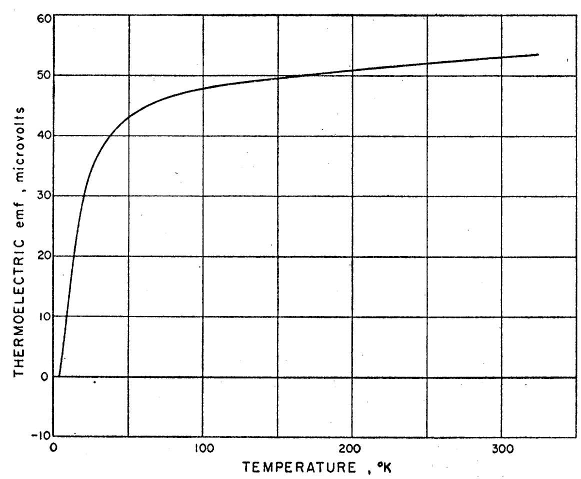
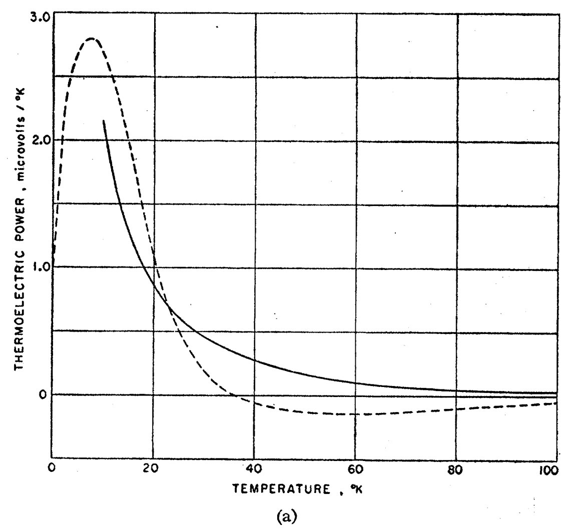
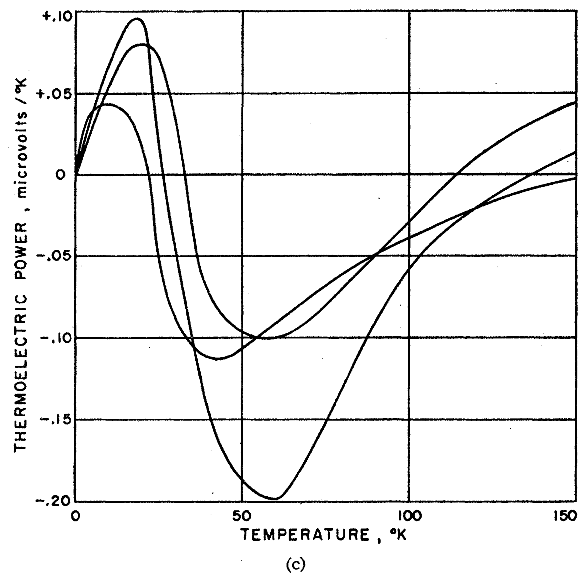



FIG. 3. The thermoelectric emf of a thermocouple formed from pure annealed and pure unannealed copper. The cold junction reference temperature is 4.2°K. The curve was extended to temperatures above 90°K by matching slopes of the measured data at 79°K, the cold junction temperature for the higher temperature measurements.



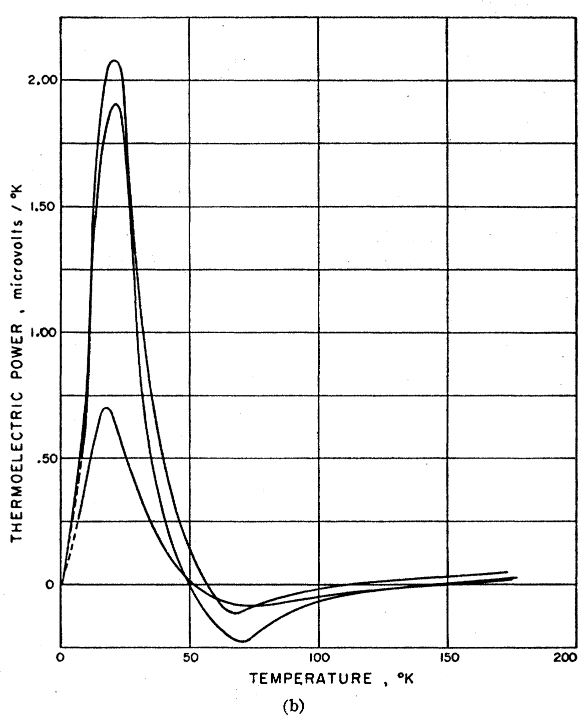




FIG. 4. (a) The thermoelectric power of the pure annelaed copper *versus* pure unannealed copper thermocouple, solid line. The dashed line shows the corresponding results obtained by Powell; we would like to thank Mr. Powell for making his results available to us prior to their publication. (b) The thermoelectric power of unannealed *versus* annealed copper, 99.98% pure, for several amounts of cold work, as determined by van Ooijen, reference 2. (c) The thermoelectric power of unannealed *versus* annealed copper, 99.97% pure, for several amounts of cold work, as determined by van Ooijen, reference 2.

that the increase in residual resistivity due to cold-rolling was $5.5\times10^{-3}$ $\mu$ohm-cm, a value consistent with results reported from other laboratories.[1]

## RESULTS AND DISCUSSION

Our results are shown in Figs. 1–5. Figure 1 shows the TEP of the pure annealed copper *versus* lead thermocouple. The absolute TEP of pure annealed copper obtained therefrom and from the currently accepted values of the absolute TEP of lead[7] is shown in Fig. 2. Of particular interest is the sign reversal of the absolute TEP of copper at about 40°K and the pronounced minimum at about 10°K. At that temperature the TEP of copper is orders of magnitude larger in absolute value than the free electron theory would predict even under the most favorable assumptions. In this respect pure copper appears to behave similarly to pure silver and gold which also show sign reversals in their absolute TEP at low temperatures and a TEP at very low temperatures which is anomalously large.[8] Moreover, a negative absolute TEP in pure copper appears to have been observed also by MacDonald and co-workers.[9] There remains the possibility

[8] MacDonald, Pearson, and Templeton, Phil. Mag. **3**, 657 (1958).

[9] MacDonald, Mooser, Pearson, Templeton, and Woods, Phil. Mag. **4**, 433 (1959).

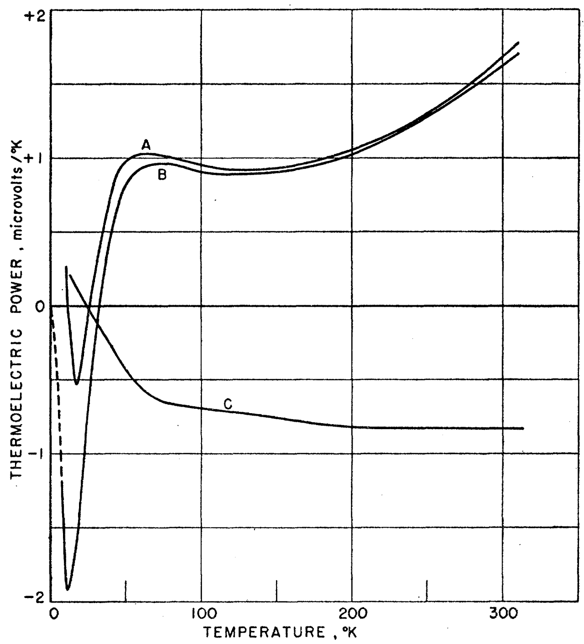



FIG. 5. The absolute thermoelectric power of cold-rolled pure copper, curve *A*. We also show here, for comparison, the absolute thermoelectric power of pure annealed copper, curve *B*, and the absolute thermoelectric power of a one atomic percent CuSb alloy, also well annealed, curve *C*.

that the behavior of our copper at low temperatures is associated with the appearance of a resistivity minimum, and is the result of small amounts of impurities. Although we cannot say so with certainty, we do not believe that the copper we used contained impurities necessary to give rise to such an anomaly. In particular, the measured resistance ratio is one which is normally ascribed to very pure copper.

Figure 3 shows the thermoelectric force of the thermocouple formed from unannealed and annealed pure copper. In Fig. 4(a) we show the TEP of the annealed copper *versus* unannealed copper thermocouple. In addition to our data we reproduce here the curve obtained by Powell[5]; in Figs. 4(b) and 4(c) we show the results of van Ooijen. It is apparent that our results are in fair agreement with those of Powell and also of van Ooijen (for his nominally purer samples). The main difference is that we do not observe the slight minimum found by Powell and van Ooijen near 60°K.

The absolute TEP of our cold-rolled copper is shown in Fig. 5. For ease of comparison we have reproduced here the absolute TEP of annealed copper, Fig. 2. It appears from these curves that the effect of cold-rolling on the TEP of copper is most significant at low temperatures, particularly in the region where the absolute TEP of the pure annealed copper suffers a sign reversal and exhibits its pronounced minimum. The major effect of cold work appears to be the nearly complete suppression of that minimum, leaving the TEP very nearly unaffected above about 40°K. The minimum in the TEP of copper apparently arises only if the specimen is relatively free of imperfections, specifically dislocations. However, it is interesting to note that dilute (approx. 1 atomic %) copper alloys show the same qualitative behavior at low temperatures as does cold-rolled copper.[10] The absolute TEP of a one atomic percent CuSb alloy is shown also in Fig. 5. These results suggest that at low temperatures impurities have much the same effect on the TEP as do dislocations, namely, that of suppressing the minimum in the TEP of pure copper. It would seem, then, that the pronounced change in the TEP of pure copper due to cold work is not so much a characteristic of cold work as such, but is rather a phenomenon which should perhaps be associated with a lack of crystal perfection per se. These suggestions are also in agreement with the results obtained by MacDonald and co-workers,[11] who have found that the TEP of their metallic samples is largest in magnitude the purer the sample, or at any rate the lower the residual resistivity. It is tempting to suggest that the minimum in pure annealed copper may be the result of a phonon drag mechanism, normal[12] or Umklapp,[13] which becomes inoperative when the phonon mean free path is substantially reduced by the presence of crystal imperfections, be they impurities, dislocations or other defects. At low temperatures especially, dislocations should be very effective in reducing a phonon drag TEP, if one exists, since at low temperatures the thermal resistivity due to phonon scattering by dislocations goes as $1/T^2$.[14]

There is one practical aspect of our results, as well as those of Powell and of van Ooijen which, though surely known already, is worth reiteration. It must be concluded that thermocouples which employ pure copper as one arm of the couple should not be used above about 200°C. Above that temperature the cold-worked copper wire will begin to anneal, and if the thermocouple is used subsequently in low temperature measurements, particularly in the region near 10°K, the readings may well be unreliable.

### ACKNOWLEDGMENT

We would like to take this opportunity to thank Dr. M. Garber for his valuable assistance.

[10] F. J. Blatt and R. H. Kropschot (to be published).
[11] MacDonald, Pearson, and Templeton, Phil. Mag. 4, 380 (1959).
[12] I. I. Hanna and E. H. Sondheimer, Proc. Roy. Soc. (London) **A239**, 247 (1957).
[13] M. Bailyn, Phys. Rev. **112**, 1587 (1958); J. M. Ziman, Phil. Mag. 4, 371 (1959).
[14] P. G. Klemens, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. 7, p. 1.