may be estimated from the magnitude of the photoconductive signal on the basis of unity quantum efficiency.[14] The result of such a calculation applied to the largest response observed at 85°K (sample *C*-20) yields a value for τ of 250 μsec (for 4 μ radiation). As yet no theoretical expression for the photoconductive threshold has been derived; the situation here is as unsatisfactory as for the absorption edge. It has been customary in recent years to use a criterion formulated by Moss[15] for the correlation of the energy gap with the cutoff of the photoresponse. According to this rule the energy gap is determined by that wavelength for which the response has fallen to one-half of its maximum value. Indeed, this rule has been applied with reasonable success to several elements and compounds. Loferski,[16] however, has shown that this criterion leads to significant disagreement in the case of tellurium; extrapolating to absolute zero, one finds the photoconductive threshold of tellurium at 0.30 ev, while electrical measurements indicate a value for E_0 of 0.34 ev. According to Loferski the energy gap is more closely connected with the maximum of the spectral distribution.

Identifying the width of the energy gap with either the maximum or the "break" of the photoconductive response, we find values of E as indicated in the last two columns of Table I. These figures are somewhat lower than the results from electrical and transmission data.

CONCLUSIONS

The compound Mg_2Sn appears to be a semiconductor, which obeys the "simple" theory rather well. Hall effect and conductivity data, as well as optical absorption data, indicate an energy gap of about 0.33 ev at absolute zero. The value deduced from the photoconductive threshold (4.2 μ) is, however, about 0.03 ev lower. An explanation of this discrepancy will probably have to await a better understanding of the correlation between optical transitions and band structure. The magnitude of the photoresponse is quite sizable at low temperatures.

The authors are greatly indebted to Mr. D. E. Roberts for preparing most of the crystals used.

[14] A. Rose, *Photoconductivity* (John Wiley and Sons, Inc., New York, to be published).
[15] T. S. Moss, *Photoconductivity in the Elements* (Butterworth Scientific Publications, London, 1952).
[16] J. J. Loferski, Phys. Rev. **93**, 707 (1954).

PHYSICAL REVIEW VOLUME 100, NUMBER 2 OCTOBER 15, 1955

Effect of Point Imperfections on the Electrical Properties of Copper. II. Thermoelectric Power*

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(Received June 24, 1955)

The changes in the thermoelectric power of copper due to the presence of interstitials and vacancies have been calculated in the free electron approximation. It is found that the changes for concentrations of defects encountered in experiments on radiation damage due to massive charged particles are, at liquid nitrogen temperature, of the same magnitude as the absolute thermoelectric power of pure copper. Both interstitials and vacancies tend to reduce the absolute thermoelectric power of copper, and this effect should be readily observable in a suitably designed experiment. It is suggested that the effect may also be used to throw additional light on the processes which occur in the annealing of an irradiated sample.

The calculated changes in the thermoelectric property of copper due to Frenkel defects are also of such magnitude as to make adequate precautionary measures necessary whenever the thermocouple, which is used to measure the temperature of the specimen, is also in the beam of the massive charged particles. Unless the thermocouple is suitably screened from the beam, unreliable temperature measurement is likely to result. Curves showing the predicted temperature and concentration dependence of the thermoelectric power change due to Frenkel defects are presented.

The effect of small concentrations of arsenic in solid solution in copper on the thermoelectric power of copper has also been calculated by the same procedure. The calculated results are in satisfactory agreement with experiment, indicating that the results for interstitials and vacancies are probably of the correct magnitude.

I. INTRODUCTION

IT has been known for many years that impurities exert a considerable influence on the thermoelectric properties of metals. For example, Norbury[1] found that almost all dilute binary alloys of the noble metals are thermoelectrically negative compared to the pure metal. There have been attempts to formulate empirical rules relating the thermoelectric power of a dilute alloy to that of the pure metal; but these, apart from their failure to be satisfying from a fundamental point of view, are not universally applicable. For example, Kohler[2] is able to account for most of Norbury's results, but copper-manganese alloys form a notable exception to his additivity rules.

In the case of copper, at any rate, the change of

* Supported by the Office of Naval Research.
[1] A. L. Norbury, Phil. Mag. **2**, 1188 (1926).
[2] M. Kohler, Z. Physik **126**, 481 (1949).

thermopower with addition of impurities is most pronounced at very low temperatures, where changes in sign and in orders of magnitude have been observed.[3] For example, at 10°K the addition of 0.0026 atomic percent of Sn changes the absolute thermoelectric power from its value of about 0.3 μvolt/degree to -60 μvolt/degree. Other impurities give rise to similar astonishingly large effects. At these temperatures the anomalously large changes in thermoelectricity appear to be intimately related to the appearance of a resistance minimum, a phenomenon which has yet to be explained satisfactorily. In what follows, we shall not concern ourselves with this very low temperature region but restrict our discussion to that range of temperature in which the free electron approximation may, perhaps, be employed with more confidence, although even there a certain skepticism is justified in view of the many discrepancies between theoretically predicted and experimentally observed thermoelectric forces.

The thermoelectric power of alloys was analyzed recently by Domenicali and Otter,[4] in whose paper a good review of the experimental situation is also presented. Their analysis involves consideration of the change in the Fermi energy due to alloying as well as the details of scattering of conduction electrons by the impurity atoms. The energy dependence of the cross section for momentum transfer is expressed in terms of two parameters, α_1 and α_2, which are determined by fitting their expressions for the change in thermoelectric power to experimental observation. As they and Friedel[5] have pointed out, these parameters may also be derived theoretically from Mott's expression for the resistivity due to small impurity concentrations.[6] In this connection, however, it is well to bear in mind that Mott's formula is based on the use of the Born approximation; but, as shown by Fujiwara[7] and others, a more exact partial wave analysis leads to very different numerical results.

In the present discussion, we shall be concerned primarily with the effect of Frenkel defects on the thermoelectric power of copper. We shall also briefly consider the influence of arsenic in copper so as to be able to compare calculated with measured thermoelectric power changes and thereby obtain at least a rough estimate of the validity of our results for vacancies and interstitials.

The influence of Frenkel defects on the thermoelectric properties of metals is of interest for several reasons. In experiments on the effects of cyclotron or pile irradiation on solids the temperature of the sample is generally measured by means of a thermocouple attached to the specimen. The thermocouple, however, is calibrated prior to irradiation; since a portion of the couple is generally also in the flux of the high-energy particles, the reliability of the temperature measurement is suspect if the thermoelectric properties of the couple are substantially altered by the presence of vacancies and interstitials. Of course, it is only that arm of the couple, such as the copper arm of a copper-constantan thermocouple, which is a pure metal that is likely to have its properties significantly altered; since the residual resistance of the alloy is already quite high, it is rather unlikely that a concentration of about 0.2 atomic percent of Frenkel defects, encountered in the strongest cyclotron irradiation used at this time, would influence its thermoelectric behavior very much.

Changes in thermoelectricity due to the presence of vacancies and interstitials might also present themselves as yet another tool for investigating the annealing spectrum of an irradiated specimen. On the basis of previous results,[8] it is probable that both types of imperfections contribute almost equally to the resistivity of copper, and it is, therefore, practically impossible to distinguish annealing of interstitials from that of vacancies on the grounds of observed resistivity changes alone. On the other hand, as the following results indicate, interstitials probably exert a significantly larger influence on the thermoelectric power than do vacancies, so that simultaneous resistance and thermoelectric power measurements on an irradiated copper sample could lead to results which may throw additional light on the annealing of radiation damage in copper.

Finally, thermoelectricity is more sensitive than resistivity to the details of the scattering process of conduction electrons in metals. For the latter, all that matters is the total cross section for momentum transfer, while the former is related to the dependence of this cross section on the electron energy. Calculated thermoelectric power changes are, then, also more sensitive, generally, to the model which one chooses to represent the impurity, and comparison with experiment may permit the elimination of inferior models.

In calculating $\Delta S/S$, the relative change of the absolute thermoelectric power of copper due to the presence of imperfections, we shall assume that the Fermi level of the conduction electrons of copper remains unaffected by concentrations of imperfections of the order of magnitude encountered in radiation damage, that is 0.2 atomic percent or less. This assumption is justified for two reasons. First, at these small concentrations each imperfection finds itself in an environment of the pure metal, and the overlap of screening charge around the imperfections is negligible. Under these conditions, as shown by Friedel,[7] the Fermi level remains unchanged. Furthermore, even for slightly larger concentrations, for which a small change in the Fermi level might be expected, the correction which

[3] D. K. C. MacDonald, Physica **19**, 841 (1953).
[4] C. A. Domenicali and F. A. Otter, Phys. Rev. **95**, 1134 (1954).
[5] J. Friedel, J. phys. radium **14**, 561 (1953).
[6] N. F. Mott, Proc. Cambridge Phil. Soc. **32**, 281 (1936).
[7] H. Fujiwara, J. Phys. Soc. Japan **10**, 339 (1955). J. Friedel, Advances in Phys. **3**, 446 (1954).
[8] F. J. Blatt, Phys. Rev. **99**, 1708 (1955). Hereafter referred to as I.

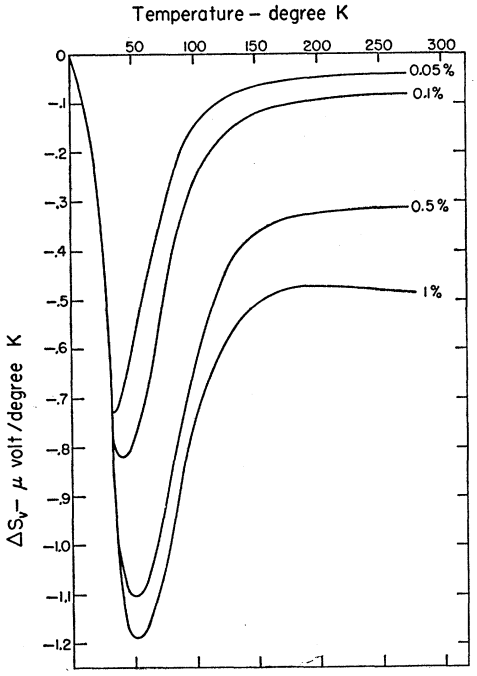

FIG. 1. ΔS_v, the changes of the absolute thermoelectric power of copper resulting from concentrations of 1.0, 0.5, 0.1, and 0.05 atomic percent of vacancies, as functions of temperature.

this introduces into the expression for $\Delta S/S$ is quite small.

In the free electron approximation the expression for the absolute thermoelectric power is

$$S=(\pi^2k_0^2T/3e)(d\log\rho(\epsilon)/d\epsilon)_{\epsilon_0}, \tag{1}$$

where e is the electronic charge, k_0 Boltzmann's constant, T the absolute temperature, $\rho(\epsilon)$ the resistivity for electrons of energy ϵ, and the logarithmic derivative is to be evaluated at the Fermi energy ϵ_0.

When an imperfection is introduced, raising the resistivity of the metal to $\rho+\Delta\rho$, the accompanying change in the thermoelectric power is

$$\Delta S=\frac{\pi^2k_0^2T}{3e}\left[\frac{d\log(\rho+\Delta\rho)}{d\epsilon}-\frac{d\log\rho}{d\epsilon}\right]_{\epsilon_0} \tag{2}$$

and the fractional change, $\Delta S/S$, is given by

$$\Delta S/S=\frac{-(1-\Delta x/x)}{(1+\rho/\Delta\rho)}, \tag{3}$$

where

$$x=\epsilon_0\left(\frac{d\log\rho}{d\epsilon}\right)_{\epsilon_0}, \quad \Delta x=\epsilon_0\left(\frac{d\log\Delta\rho}{d\epsilon}\right)_{\epsilon_0}. \tag{4}$$

The quantity x is simply related to the absolute thermoelectric power of the pure metal and is determined from experimental observation. The change in resistivity due to the addition of imperfections is also known from observation in many instances, or, in the case of vacancies and interstitials, has been calculated recently by the present author and others.[8,9] The only unknown quantity in Eq. (3) is Δx, and it has the virtue of being, for a given metal, a function only of the type of imperfection present and does not depend on the concentration or temperature. Thus, once this last quantity has been evaluated, the concentration and temperature dependence of $\Delta S/S$ can be ascertained without further calculation.

II. RESULTS

We make the same assumptions as in I, namely, (1) The free electron approximation is valid. (2) The scattering potential associated with the imperfection has spherical symmetry. (3) Matthiessen's rule is valid. (4) The effect of relaxation of the lattice about the imperfection is negligible.

We make use of the additional assumption, discussed earlier, that the Fermi level of the free electron gas remains unchanged.

The resistivities $\Delta\rho_i$ and $\Delta\rho_v$ due to interstitials and vacancies, respectively, have been calculated in I and are

$$\Delta\rho_i=1.4\ \mu\text{ohm-cm/atomic percent},$$
$$\Delta\rho_v=1.3\ \mu\text{ohm-cm/atomic percent}.$$

There remains the problem of determining Δx in each case. This was done by evaluating the resistivities $\Delta\rho_i$ and $\Delta\rho_v$ at energies $\epsilon_0+\delta\epsilon$ and $\epsilon_0-\delta\epsilon$, where $\delta\epsilon$ was

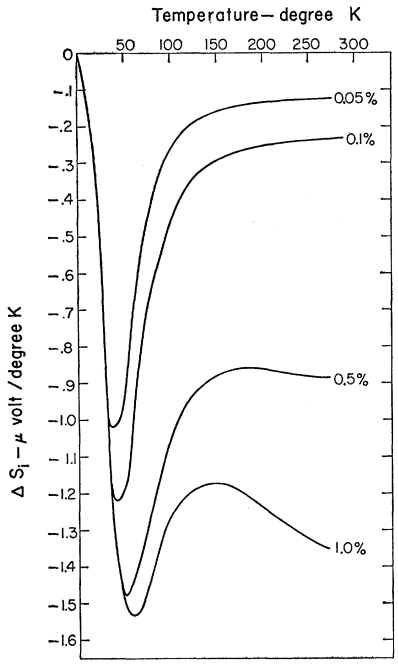

FIG. 2. ΔS_i, the changes of the absolute thermoelectric power of copper resulting from concentrations of 1.0, 0.5, 0.1, and 0.05 atomic percent of interstitials, as functions of temperature.

[9] P. Jongenburger, Appl. Sci. Research **B3**, 237 (1953); Nature **175**, 545 (1955).

selected arbitrarily to be $\epsilon_0/20$, and approximating the derivative in Eq. (4) by the ratio of the differences, i.e.

$$\Delta x \simeq 10\{\log[\Delta\rho(\epsilon_0+\delta\epsilon)]-\log[\Delta\rho(\epsilon_0-\delta\epsilon)]\}. \quad (5)$$

The scattering potentials from which the resistivities were calculated were derived from the Hartree self-consistent potentials in the manner discussed in I.

The quantity x was obtained from the measured absolute thermoelectric power of copper,[10] and for the resistivity the values given by Meissner[11] were used. The results are shown in Figs. 1–4.

In order to gain some confidence in the numerical results, the effect of arsenic on the thermoelectric power of copper was also determined in a similar manner. Arsenic was chosen because of the impurities considered in I it is the only one for which the effect on thermoelectricity is known from experiment.[12]

Taking the same scattering potential as in I, Δx was found to be 2.1, which compares favorably with the value 2.0 deduced from observation. Abelès[13] has suggested the use of a square-well potential adjusted so as to satisfy the Friedel sum condition [see Eq. (5) of I], and this procedure was also carried out with the result $\Delta x=1.2$. Both procedures are thus seen to be satisfactory, leading to results of the correct magnitude, although, perhaps fortuitously, the former appears to be slightly better.

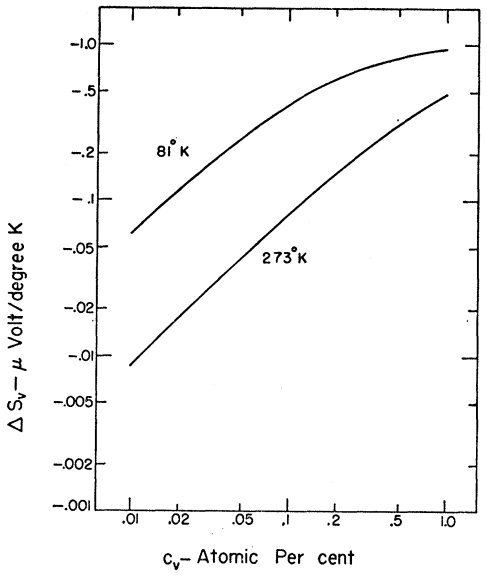

FIG. 3. ΔS_v, the change of the absolute thermoelectric power of copper resulting from vacancies, as a function of vacancy concentration, at 81°K and 273°K.

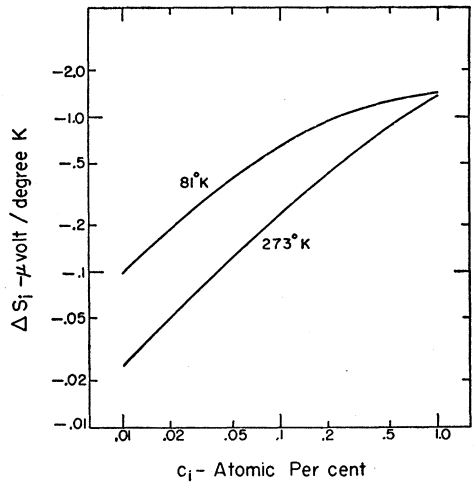

FIG. 4. ΔS_i, the change of the absolute thermoelectric power of copper resulting from interstitials, as a function of interstitial concentration, at 81°K and 273°K.

III. DISCUSSION

Figures 1 and 2 show a rather strong temperature dependence of the change in thermoelectric power due to Frenkel defects. This temperature variation arises first of all from the temperature variation of the denominator of Eq. (3) through the approximately linear dependence of ρ on T. In addition, there is the dependence of S on T which, ideally, should be linear so that the numerator of Eq. (3) should be independent of temperature. However, below about 150° K the thermoelectric power of copper deviates significantly from the linear temperature variation predicted by Eq. (1), and this departure from the predictions of the free electron theory leads to the pronounced minimum of ΔS.

Vacancies and interstitials both tend to decrease the thermoelectric power of copper, a circumstance which would make it more difficult to distinguish between these two imperfections on the basis of thermoelectric measurements. Nevertheless, such separation may still be possible by careful experimental techniques since interstitials should be considerably more effective than vacancies in reducing the thermoelectric power of the specimen. The largest change in thermoelectricity should occur in the vicinity of liquid nitrogen temperature, although even at higher temperatures one should be able to detect small changes in S with sensitive equipment. Of course, the major limitation on experimental observation at high temperatures is the small number of defects which are likely to be encountered. Annealing studies on irradiated copper have shown that most of the damage has already annealed out before room temperature is reached.[14]

Figures 3 and 4, which show the concentration dependence of ΔS, clearly exhibit, at the lower tempera-

[10] J. Nyström, Arkiv Mat. Astron. Fysik **A34**, No. 27 (1948).
[11] W. Meissner, *Handbuch der Experimentalphysik* (Akademische Verlagsgesellschaft, Leipzig, 1935), Vol. 11, Part 2, p. 51.
[12] Borelius, Keesom, Johansson, and Linde, Leiden Comm. **206b** (1930).
[13] F. Abelès, Compt. rend. **237**, 796 (1953).
[14] Cooper, Koehler, and Marx, Phys. Rev. **97**, 599 (1955).

ture, the saturation effect which sets in when $\Delta\rho \gtrsim \rho$. Although the largest possible concentrations of defects are, of course, desirable for experimental investigation of the effect, the effort required to attain concentrations in excess of 0.1 atomic percent is probably not justified.

As regards the use of the thermoelectric effect described here in studying the annealing spectrum of irradiated copper, the procedure and interpretation of the results would be somewhat more difficult than in similar studies of resistivity. In order to observe the effect, it is necessary to maintain a temperature gradient in the sample of a few degrees; this temperature difference between the two ends of the sample forming the thermocouple would have to be known quite accurately. As the specimen is warmed up the temperature gradient must be maintained; and thus, in the temperature range where annealing of one or more defects takes place, the concentration of these defects in the sample will not be uniform, annealing occurring more rapidly at the higher temperature end. Furthermore, even if no annealing were to take place over a certain temperature range, ΔS will nevertheless exhibit more or less drastic variations, as predicted by the curves of Figs. 1 and 2. Thus, deducing the annealing spectrum from an anlysis of ΔS *versus* T for an irradiated sample would be considerably more involved than interpreting the changes in resistivity over the annealing range.

We have so far refrained from speculating about the accuracy of the results. A certain skepticism is justified by the fact that the free electron model predicts the wrong sign for the absolute thermoelectric power of pure copper. Apart from this, the nonlinear temperature dependence of S in the range below about 150° K throws further doubt on deductions which are based on the use of Eq. (1). Nevertheless, the agreement found for the calculated and observed effect of arsenic on the thermoelectric power of copper would indicate that our results are probably of correct magnitude.

Finally, we have not considered an effect which has recently been brought to focus, namely the "phonon contribution" to the thermoelectric power. This has been investigated by Herring for semiconductors[15] and by Ter Haar and Neaves for metals.[16] The conclusion, in the case of metals, is that in the temperature region around $\theta/2$ the drag on the charge carriers due to the phonon current may be substantial and could, perhaps, account for the increase of the thermoelectric power of copper with decreasing temperature which is observed between 150 and 80° K. It is reasonable that the presence of imperfections in the lattice would reduce the phonon contribution to S because the scattering of conduction electrons associated with these imperfections reduces the importance of the electron-lattice interaction in determining the relaxation time, and also because the imperfections will scatter phonons and thus tend to restore an equilibrium phonon distribution. It is, therefore, quite possible that the actual decrease of the thermoelectric power due to Frenkel defects is enhanced by the phonon contribution in that temperature range where this effect is important.

To date there is no experimental evidence which either confirms or disproves the conclusions reached here. The only investigations on the effects of Frenkel defects on the thermoelectric properties of metals known to the writer are those of Andrew, Jeppson, and Yockey[17] and of Jamison and Blewitt.[18] Both groups of workers reported no observable changes. However, Andrew *et al.* performed their experiment at high temperatures. It is, therefore, not surprising that the density of defects was inadequate to give rise to measurable changes. Jamison and Blewitt subjected their samples, which were cooled to liquid nitrogen temperature, to a total neutron flux of 5×10^{16}. Neutrons are, regrettably, much less effective than charged massive particles in producing lattice defects; the concentration of defects achieved by Jamison and Blewitt was probably about 2×10^{-4} atomic percent, and again the negative result which they reported might have been anticipated. Evidently, further experimental investigations are needed in order to compare the present results with observation.

IV. CONCLUSIONS

The change in the thermoelectric power of copper due to Frenkel defects and due to small concentrations of arsenic have been calculated in the free electron approximation. In the case of arsenic agreement of calculated and experimental results is satisfactory. The predicted change in thermoelectricity caused by Frenkel defects is sufficiently large, especially at low temperatures, that it should be readily observable for defect concentrations attainable with cyclotron irradiation. It is suggested that annealing studies may throw further light on the processes which occur during warm-up of an irradiated specimen.

The effect of Frenkel defects on the thermoelectric power of copper also makes adequate precautionary measures imperative whenever thermocouples are used to determine the temperature of the specimen in a radiation damage experiment. It is probable that unless the thermocouple is properly shielded from the beam, unreliable temperature readings will result. The error will depend on the type of couple employed and on the fraction of it exposed to the radiation. Because of their intrinsic high residual resistance, a couple formed of suitable alloys is less likely to cause trouble than one in which one or both arms consist of pure metals.

[15] C. Herring, Phys. Rev. **96**, 1163 (1954).
[16] D. Ter Haar and A. Neaves, Proc. Roy. Soc. (London) **A228**, 568 (1955).
[17] Andrew, Jeppson, and Yockey, Phys. Rev. **86**, 643 (1952).
[18] R. E. Jamison and T. H. Blewitt, Rev. Sci. Instr. **24**, 474 (1953).