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Electrical Resistance and Thermoelectric Power of an Amorphous $Te_{70}Cu_{25}Au_5$ Alloy

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The electrical resistance and the thermoelectric power of an amorphous $Te_{70}Cu_{25}Au_5$ alloy obtained by rapid quenching from the liquid state have been measured in the range of 80 to 300°K. The results suggest that the bonding between tellurium atoms is covalent, as in crystalline tellurium. The amorphous alloy is a *p*-type semiconductor with an intrinsic energy gap of 0.21 ± 0.01 eV. The results also establish the existence of extrinsic conduction in an amorphous alloy with a discrete localized energy level of 0.09 ± 0.015 eV above the top of the valence band.

I. INTRODUCTION

THE application of quantum mechanics to solids in the crystalline state results in the band theory of solids which successfully explains many properties of metals, semiconductors, and insulators. According to the band theory of crystals, the electronic band structure is a direct consequence of the quantum-mechanical calculation of the motion of an electron in a periodic potential. The basic feature of the band structure of many metals and semiconductors changes little on the transition from the crystalline state to the liquid state or the amorphous state provided that the short-range order is not altered on transition. This seems to suggest that instead of the long-range crystalline order the short-range order plays a decisive role in determining the nature of band structure. The theoretical and experimental work in this field is reviewed in several articles.[1-3] Most of the theoretical work is limited to one-dimensional liquids and simplified models. Very few experimental investigations of the electrical properties of amorphous semiconductors below room temperature have been reported.

This investigation concerns the temperature dependence of the electrical properties of an amorphous alloy $Te_{70}Cu_{15}Au_5$ obtained by rapid quenching from the liquid state. The results will be discussed in connection with the existing theoretical considerations of the validity of band theory in an amorphous solid. Emphasis will be given to the effect of the disappearance of the long-range crystalline order of the energy gap.

Recently, a simple model for the band structure of an amorphous semiconductor was proposed to interpret the electrical properties of amorphous vacuum-deposited germanium.[4] In that case, the assumption that there were no discrete vacancies in the amorphous germanium was probably appropriate. We will present some evidence of extrinsic conduction suggesting the existence of discrete localized acceptor states in the amorphous alloy $Te_{70}Cu_{25}Au_5$. Possible mechanisms for the extrinsic conduction will be discussed.

II. EXPERIMENTAL METHODS

The alloy was prepared by induction melting of the appropriate quantities of the constituents in a quartz crucible under an argon atmosphere. The purity of the elements was 99.999% for Te and 99.99% for Au and Cu. The amorphous phase was obtained by rapid cooling from the melt following a technique described in Ref. 5. The foils obtained by this technique are irregular in shape (about 25 mm long by 8 mm wide), and their thickness is not uniform but is in general less than 10 μ. Since flat specimens are easier to handle for electrical measurements, the copper strip on which the molten globule is ejected was flat instead of being curved as described in Ref. 5. The specimen was transferred on a nonconductive support by the following technique: The copper strip with the quenched specimen was placed at the bottom of a Teflon mold and a liquid resin of common usuage in preparing metallographic specimen (Quick Mount) was poured into the mold. After a setting time of about 20 min the quenched sample was easily detached from the copper strip and securely attached to the solid resin. The specimen was then shaped into the desired contour (with current and potential leads) by a simple milling operation and electrical contacts were made through copper strips pressed against the specimen with suitable clamping devices.

Since the electrical resistances of the metastable and the equilibrium alloys differed by several orders of magnitude, both the potential-current and the Wheatstone bridge methods were used. In either case, the experimental uncertainty in the reported measurements is estimated at $\pm1\%$ or less. The thermoelectric power was measured against copper, and the conversion to absolute values was based on the results reported in Ref. 6. The thermal emf was measured with a Leeds and Northrup type K-3 potentiometer for specimens of rather low resistance, and an electrometer was used for amorphous specimens for which the resistance was of the order of $10^7\ \Omega$. The temperature was measured by a copper-constantan thermocouple firmly pressed

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[1] A. F. Ioffe and A. R. Regel, Progr. Semicond. 4, 237 (1960).
[2] Kishin Moorjani and Charles Feldman, Rev. Mod. Phys. **36**, 1042 (1964).
[3] N. Cusack, Rept. Progr. Phys. **26**, 361 (1963).
[4] A. H. Clark, Phys. Rev. **154**, 750 (1967).
[5] P. Duwez and R. H. Willens, Trans. AIME **227**, 362 (1962).
[6] N. Cusack and P. Kendall, Proc. Phys. Soc. (London) **72**, 898 (1958).

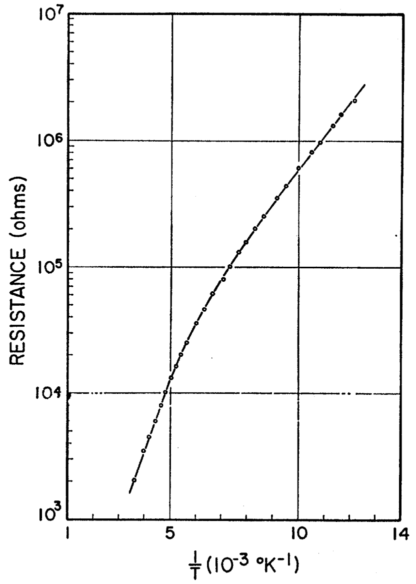

FIG. 1. Resistance versus reciprocal temperature for the amorphous alloy $Te_{70}Cu_{25}Au_5$.

against the specimen. The over-all uncertainty in thermoelectric power measurements is estimated to be about ±2%.

III. RESULTS

The temperature variation of the electrical resistance of the amorphous alloy $Te_{70}Cu_{25}Au_5$ is shown in Fig. 1 in which the logarithmic resistance is plotted versus reciprocal temperature. The graph of Fig. 1 consists of two straight lines joined by a broad transition. In the linear regions, the electrical resistance can be expressed by

$$R=R_0\exp(E_g/2kT), \qquad (1)$$

where k is the Boltzmann constant, E_g the energy gap in electron volts, and R_0 a constant. The values of energy gap derived from Fig. 1 are 0.21 ± 0.01 and 0.09 ± 0.015 eV. The uncertainties in these values include the scattering in the measurements performed on several foils of the same alloy. This scattering is mostly due to variations in the quenching conditions (average foil thickness which in turn affect the quenching rate) which, as explained in Ref. 5, are difficult to control.

The semiconducting properties of the amorphous alloy do not seem to be influenced by impurity atoms. Additions of about 30 to 100 ppm of Cd, In, Bi, Sb, or Mn to the basic $Te_{70}Cu_{25}Au_5$ composition had no noticeable effect on the variation of electrical resistance versus temperature.

The thermoelectric power of the amorphous alloy was measured between 90 and 300°K. As shown in Fig. 2, it increases with temperature up to about 180°K then slowly decreases. The broad maximum is located in a range of temperatures corresponding to the transition region between the two linear portions of the electrical resistivity-temperature curves of the same alloy (Fig. 1). The amorphous $Te_{70}Cu_{25}Au_5$ alloy can be completely transformed into its equilibrium crystalline structure by heating it at 355°K for 24 h. The electrical resistance of this equilibrium alloy is three orders of magnitude smaller than in the amorphous state, and as shown in Fig. 3 its variation with temperature is typical of a metallic conductor. As expected, the transformation of the amorphous alloy into its crystalline equilibrium structure has a drastic effect on the thermoelectric power. As shown in Fig. 2 the thermoelectric power of the crystalline alloy is of the order of 6 μV/°K instead of about 330 μV/°K at 190°K and increases linearly with temperature. Both the order of magnitude and the temperature dependence of the thermoelectric power of the crystalline alloy are compatible with its metallic character.

IV. DISCUSSION

Since the interpretation of the results of this investigation greatly depend on the atomic arrangement in the amorphous alloys, what is known about the structure of this amorphous alloy phase will be briefly reviewed.

Amorphous phases in tellurium base alloys were first reported in binary alloys containing Ge, In, or Ga.[7] An x-ray diffraction study of the structure of these alloys leads to the conclusion that it consists of randomly oriented spiral chains of atoms with two nearest neighbors, which is typical of solid as well as liquid tellurium.[8] Amorphous tellurium base alloys were later reported in Te-Cu and in Te-Cu-Au systems.[9] The x-ray diffraction patterns of these alloys were found to be

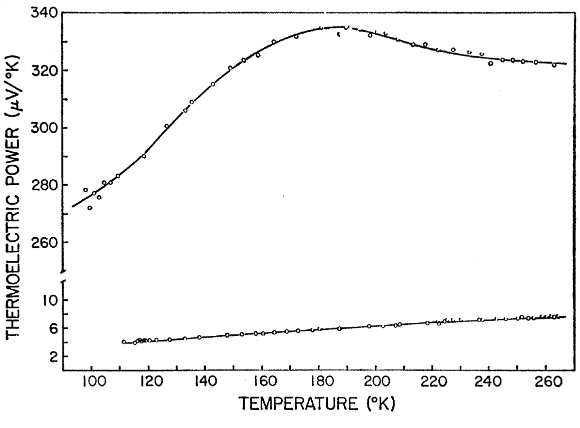

FIG. 2. The thermoelectric power of the amorphous alloy $Te_{70}Cu_{25}Au_5$ (upper curve) and of the same alloy annealed at 355°K for 24 h.

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[7] H. L. Luo and Pol Duwez, Appl. Phys. Letters 2, 21 (1963).

[8] R. Buschert, I. G. Geib, and K. Lark-Horovitz, Phys. Rev. 98, 1157 (1955).

[9] C. C. Tsuei, Ph.D. Thesis, California Institute of Technology, 1966 (unpublished).

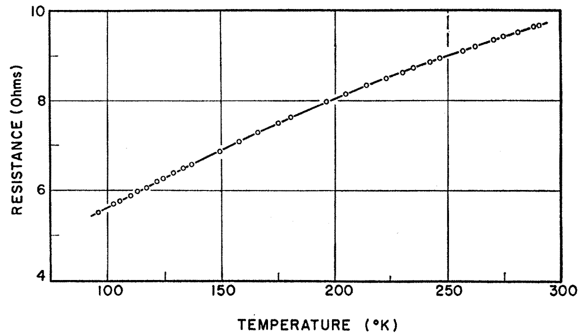

FIG. 3. Resistance versus temperature of the amorphous alloy $Te_{70}Cu_{25}Au_5$ annealed at 355°K for 24 h.

almost identical with those of the binary alloys previously studied. Hence, the structure of the particular amorphous $Te_{70}Cu_{25}Au_5$ alloy studied in this investigation can also be described as consisting of randomly oriented spiral chains of atoms with only two nearest neighbors. The exact location of the metallic atoms (Cu and Au in this case) is not known, and it might be assumed that they are substituted at random for Te atoms in the chain structure. However, the results of a Mössbauer-effect study[10] have shown that the quadrupole splitting of Te^{125} in the amorphous $Te_{70}Cu_{25}Au_5$ alloy is the same as in crystalline Te, and this would indicate that most of the metallic atoms are located between the tellurium chains.

The fact that the amorphous alloys exhibit semiconducting properties is consistent with the atomic bonding in these alloys. Since the chain structure typical of crystalline tellurium is preserved, each tellurium atom forms covalent bonding with its two nearest neighbors in the chain and the chains are weakly held by van der Waals forces.

Explanations for the existence of a band structure in amorphous semiconductors have been advanced by several authors. Gubanov first proposed a band theory for a one-dimensional liquid.[11] By solving the Schrödinger equation in a deformed coordinate system, he predicted the following qualitative effects on the electron energy spectrum: (1) As a result of the disappearance of the long-range crystalline order, the energy spectrum of electrons is altered in such a way that allowed bands expand and forbidden bands contract; there is a general upward displacement of both allowed and forbidden bands. (2) Band edges are diffuse, as would be expected from random disturbances in the short-range order. (3) As the degree of disorder increases, the forbidden band becomes narrower and eventually disappears. The above results remain true when this theory is extended to the three-dimensional case.

Makinson and Roberts[12] carried out numerical calculation on a one-dimensional model of liquid similar to the well-known Kronig-Penney model, with equal δ-type potential wells but distributed according to a cutoff parabolic distribution about the mean value. The length of the chain was assumed to be 2000 atoms. By counting the number of nodes of the solutions to the Schrödinger equation, it was found that there is a definite energy gap in which no states appear. This energy gap decreases as the degree of disorder increases. Other qualitative results are also in good agreement with Gubanov's conclusions.[13] Borland[14] extended Makinson and Roberts's approach to a one-dimensional liquid in which atoms are represented by a general atomic potential instead of δ potential and showed that a definite energy gap exists provided that the maximum deviation of the distance between atoms is less than a critical value. Recently, Hiroike[15] applied the nonperturbational method of Faulkner and Korringa to a one-dimensional liquid in which the atomic potentials are δ functions and the interatomic distances are governed by a Gaussian distribution. It was shown that the existence of an energy gap is not restricted by the condition assumed by Borland and Roberts and Makinson. The behavior of the energy gap is found in good agreement with the numerical results of Roberts and Makinson. Therefore, it is clear that the applicability of the band theory goes far beyond the limits imposed by the periodicity of atomic arrangement from which it was deduced and the three different approaches to the band theory of liquid lead to the same qualitative conclusions.

Since the spiral chain structure of tellurium atoms exists in amorphous alloy $Te_{70}Cu_{25}Au_5$, it is interesting to compare the width of the intrinsic energy gap of this alloy with that of pure crystalline tellurium, at least in a qualitative manner. When a transformation from the amorphous to the crystalline state takes place in a semiconductor and assuming that the short-range atomic distribution remains approximately the same, the energy gap can be affected by two factors. The first factor is the disappearance of long-range order. According to the theories mentioned before, this effect always narrows the intrinsic energy gap. The second factor having an effect on the intrinsic energy gap is the change in average interatomic distances associated with the amorphous to crystalline transition. The sign of this energy-gap change can be positive or negative and depends on the details of the band structure. The effect

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[10] C. C. Tsuei and E. Kankeleit, Phys. Rev. **162**, 312 (1967).

[11] A. I. Gubanov, *Quantum Electron Theory of Amorphous Conductors* (Counsultants Bureau Enterprises, Inc., New York, 1965). This book contains Gubanov's complete work on band theory of amorphous conductors as well as a general review of experimental and theoretical works on noncrystalline materials.

[12] R. E. B. Makinson and A. P. Roberts, Australian J. Phys. **13**, 437 (1960).

[13] An erroneous assumption in Gubanov's original paper {A. I. Gubanov, Fiz. Tverd. Tela **2**, 651 (1960) [English transl.: Soviet Phys.—Solid State **2**, 605 (1960)]} which led to a discrepency between the conclusions of Gubanov and that of Makinson and Roberts has been corrected in Gubanov's book (see Ref. 11, p. 101).

[14] R. E. Borland, Proc. Phys. Soc. (London) **78**, 926 (1961).

[15] Kazno Hiroike, Phys. Rev. **138**, A422 (1965).

of interatomic distances has been discussed by Callen[16] and Gaspar[17] in their study of the electronic band structure of crystalline tellurium as a function of lattice spacings. Callen's simplified tetragonal model is disputed.[18,19] According to Gaspar's result the width of the forbidden band of tellurium decreases with decreasing lattice spacing. Since in the amorphous tellurium-base alloy, the interatomic distance of first-nearest neighbors (~2.7 Å) is slightly less than that of crystalline tellurium (2.86 Å), the energy gap of the amorphous alloy should be smaller than that of tellurium as a result of smaller interatomic distance. The intrinsic energy gap of the amorphous alloy $Te_{70}Cu_{25}Au_5$ is found to be 0.21 eV as compared with that of crystalline tellurium, 0.34 eV.[20] This reduction in energy gap can be qualitatively attributed to the two above-mentioned effects. It should be clear that the alloying effect of Cu and Au on the energy gap can not be inferred from the available experimental information.

The plot of logarithmic resistance of the amorphous alloy $Te_{70}Cu_{25}Au_5$ versus reciprocal temperature in Fig. 1 shows a slope change which usually characterizes the onset of extrinsic conduction in semiconductor. From the slope of linear segment at lower-temperature region, it is found that the extrinsic conduction corresponds to a discrete localized level ~0.09 eV above the top edge of the valence band.

The temperature dependence of thermoelectric power of this amorphous alloy is consistent with the resistance results. As shown in Fig. 2, the thermoelectric power of the amorphous alloy $Te_{70}Cu_{25}Au_5$ increases with increasing temperature in the extrinsic range and decreases slowly with increasing temperature in the intrinsic range. This experimental fact can be qualitatively explained as follows:

A theoretical expression for the thermoelectric power S can be derived by the use of the Boltzmann transport equation which gives the electrical and thermal current densities. The thermoelectric power of a semiconductor is found by evaluating the Thomson coefficient σ_T from electrical and thermal current densities and then integrating the Kelvin relation $\sigma_T = T(ds/dT)$.

In the extrinsic range, only holes (in the case of p-type semiconductors) are predominant. Without considering the specific scattering mechanism of holes, we assume that relaxation time τ is proportional to energy E^b. Then, the thermoelectric power of holes can be expressed[21] as

$$S_h = (k/e)\left[\tfrac{5}{2} + b - (E_F/kT)\right], \tag{2}$$

where k is the Boltzmann constant, e is the magnitude of electron charge, and E_F is the Fermi energy. Equation (2) shows that in the extrinsic range of temperatures the thermoelectric power should decrease with decreasing temperature. This conclusion seems to be in qualitative agreement with the experimental result.

In the intrinsic range, the temperature is high enough to justify the neglecting of extrinsic conduction effect. The number of electrons in the conduction band is equal to the number of holes in the valence band. Both electrons and holes contribute to thermoelectric power in the intrinsic range of temperature. Assume that in this temperature range the phonon scattering is the most important scattering mechanism. The thermoelectric power of p-type semiconductor is found[21] as follows:

$$S = \frac{k}{e}\,\frac{[(\mu_e/\mu_h)-1]}{[(\mu_e/\mu_h)+1]}\left(\frac{E_g}{2kT}+2\right), \tag{3}$$

where μ_e/μ_h is the ratio of mobility of electrons to that of holes, and E_g the intrinsic energy gap. Equation (3) shows that the thermoelectric power should in general decrease with increasing temperature. This equation yields a qualitative explanation of the experimental result in the intrinsic range. The ratio μ_e/μ_h of the amorphous alloy remains to be determined experimentally. As a first approximation, let us assume it is equal to that of crystalline tellurium,[22] then $\mu_e/\mu_h \sim 2.1$. The intrinsic energy gap for the amorphous alloy is approximately 0.21 eV. When these quantities are substituted into Eq. (3), it is found that the thermoelectric power of the amorphous alloy is about 200 μV/°K at room temperature which is the right order of magnitude. Therefore, the thermoelectric power of the amorphous alloy confirms the existence of the localized states shown by the resistance measurement. Since this amorphous alloy has positive thermoelectric power in the temperature range from liquid-nitrogen temperature to room temperature, it should be considered as a p-type conductor, and the deep-lying localized energy level acts as an acceptor state. The experimental information available now, however, does not give a clue as to the mechanism which is responsible for this extrinsic conduction. As the doping of several impurities did not alter the conduction of the amorphous alloy significantly, the nature of the extrinsic conduction in the amorphous alloy probably is not of impurity. The proposed structure of the amorphous alloy permits some speculation on this problem. The copper or gold atoms which occupy a regular site in the tellurium chain, or the end atoms of the chain, may represent a big local potential and can give rise to localized states which are responsible for this extrinsic conduction. The absence of impurity effect on the extrinsic conduction of the amorphous alloy is tentatively explained as follows:

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[16] H. B. Callen, J. Chem. Phys. **22**, 518 (1954).

[17] R. Gaspar, Acta Phys. Acad. Sci. Hung. **7**, 289 (1956).

[18] J. R. Reitz, Phys. Rev. **105**, 1233 (1957).

[19] G. Dresselhaus, Phys. Rev. **105**, 135 (1957).

[20] A. S. Epstein, H. Fritzsche, and K. Lark-Horovitz, Phys. Rev. **107**, 412 (1957).

[21] V. A. Johnson and K. Lark-Horovitz, Phys. Rev. **92**, 226 (1953).

[22] S. Tanama, Sci. Rept. Res. Inst., Tohoku Univ., Ser. **A6**, 160 (1954).

Since the structure of the amorphous alloy is quite loose, the space between the randomly oriented chains can easily accommodate the impurity atoms without producing significant variation in the local potential larger than that caused by the fluctuation of the atomic distribution. Another possibility is that the local states created by large fluctuations of atomic arrangement in the amorphous alloy capture electrons or holes and "neutralize" the donors or acceptors, causing the absence of impurity conduction.

V. CONCLUSIONS

(1) From the results of electrical-resistance and thermoelectric-power measurements, it is concluded that the amorphous alloy $Te_{70}Cu_{25}Au_5$ is a semiconductor. The semiconducting properties of the amorphous alloy $Te_{70}Cu_{25}Au_5$ are consistent with the hypothesis proposed previously that the tellurium atoms in this amorphous alloy form randomly oriented spiral chains like those in crystalline tellurium. This experimental observation clearly demonstrates that short-range order of atomic arrangement plays an essential role in determining the transport properties and band structure of a substance no matter whether it is in the crystalline or amorphous state.

(2) The intrinsic energy gap of the amorphous alloy $Te_{70}Cu_{25}Au_5$ (0.21 ± 0.01 eV) is smaller than that of crystalline tellurium (0.34 eV). This reduction in energy gap is partially attributed to the effect of the disappearance of long-range order as predicted by the current band theory of liquid.

(3) Results of the electrical resistance as well as the thermoelectric power of the amorphous alloy suggested the existence of discrete localized acceptor states 0.09 ± 0.015 eV above the top edge of the valence band. As impurity does not alter the conduction significantly, the extrinsic conduction probably is not of impurity in nature.

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Infrared Absorption Induced by a Charge Defect in an Ionic Crystal*

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An expression is derived for the impurity-induced infrared absorption in an ionic crystal, using a slightly more general model for the defect than considered previously. This model includes not only changes in mass and force constant but also changes in the effective charge tensors of the impurity and its neighbors. A T-matrix formulation is used, assuming a low concentration of defects. Calculations are made to explicitly demonstrate the effects of a charge-mass-force-constant defect in NaCl. In some cases the absorption is seen to increase with decreasing effective charge. For a charge-mass defect, there exists a frequency at which the dipole moment of the crystal changes sign and at which the absorption is exactly zero.

I. INTRODUCTION

ONE-PHONON absorption occurs in alkali-halide crystals at only one frequency, the long-wavelength, transverse optical eigenfrequency. However, the inclusion of defects in the crystal so alters the modes of vibration that absorption occurs at most eigenfrequencies. This absorption has been observed in alkali halides containing substitutional impurities. Corresponding calculations have been made, using Green's-function techniques and a mass-force-constant defect model.[1-3] Consideration of a change in the effective charge of the impurity and its neighbors has been included only in an approximate calculation for an NaCl chain.[4] It is the purpose of this paper to include a change in effective charge in a T-matrix formulation of the impurity induced absorption of an ionic crystal. Calculations are made to demonstrate explicitly the effects of a charge defect in an alkali-halide host. We will be particularly interested in two systems for which a change in effective charge may be important. A defect with a valence different from that of the atom it replaces will certainly require a change of charge in the defect model. This system would be particularly interesting if oppositely charged compensating defects were sufficiently removed from one another so as to allow them to be considered isolated defects. A defect with a polarizability different from that of the atom it replaces requires a change in the effective charge of at least the defect and its nearest neighbors. There are several other

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[1] M. V. Klein, in Physics of Color Centers, edited by W. B. Fowler (to be published).

[2] G. Benedek and G. F. Nardelli, Phys. Rev. **155**, 1004 (1967).

[3] A. A. Maradudin, Solid State Phys. **19**, 1 (1966).

[4] L. Genzel, K. F. Renk, and R. Weber, Phys. Status Solidi **12**, 639 (1965).