Mössbauer Effect of Te^{125} in Simple-Cubic and Amorphous Tellurium-Base Alloys*

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Recoilless resonant absorption of the 35.6-KeV γ ray ($\frac{3}{2}^+$ to $\frac{1}{2}^+$ transition) in Te^{125} has been observed in both simple-cubic and amorphous tellurium-base alloys obtained by rapid cooling from the liquid state. As expected from its cubic symmetry, the simple-cubic (one atom/unit cell) metastable AuTe$_2$ gives a single-peak Mössbauer spectrum with a half-width 0.88±0.05 cm/sec and an isomeric shift of 0.03±0.01 cm/sec. The monoclinic AuTe$_2$, which is the equilibrium form of this compound, unexpectedly shows also a single-peak spectrum with an isomeric shift 0.04±0.01 cm/sec. However, the latter is about 23% broader than the former. On the basis of the atomic arrangement of the monoclinic AuTe$_2$, this line broadening is attributed to a weak quadrupole interaction. These findings are consistent with the fact that both polymorphs exhibit metallic conduction of the same order of magnitude. The Mössbauer spectrum of the metastable amorphous alloy Te$_{70}$Cu$_{25}$Au$_5$ exhibits a well-resolved quadrupole splitting of 0.74±0.02 cm/sec, which is about the same as that of crystalline tellurium. The fact that the amorphous alloy has a quadrupole splitting of the same magnitude as that of crystalline tellurium confirms the hypothesis proposed previously that the metastable amorphous tellurium-base alloys consist of randomly oriented spiral chains of tellurium, with the atoms of the minor constituent(s) randomly distributed between the chains. As a consequence of the chain retention in the amorphous alloy, there is predominantly a covalent bonding like that in crystalline tellurium. This conclusion offers a possible explanation of the experimental fact that the amorphous alloy shows a semiconducting behavior similar to that of crystalline tellurium.

I. INTRODUCTION

THE Mössbauer effect of Te^{125}, which was first studied by Phan Zuy Hein et al.,[1] has been observed by several authors[2-6] in tellurium and different Te compounds. All these earlier works are summarized in a recent paper by Violet and Booth.[7] In the same paper, Violet et al. reported the results of their extensive study of the Mössbauer effect in several compounds at both liquid-nitrogen and liquid-helium temperatures. Their observation indicates that quadrupole splitting is present if the host lattice does not have cubic symmetry and is not observed in the case of cubic lattices.

This paper is concerned with the measurements of Mössbauer spectra in two new nonequilibrium tellurium-rich alloys in which the atomic configurations of tellurium are different from those in either the pure element or the equilibrium compounds. The first metastable crystal (AuTe$_2$) is simple cubic with one atom per unit cell (coordination number 6). This crystal structure is unusual and has been found only for polonium[8] and possibly a metastable form of sele-

nium.[9] The second nonequilibrium alloy Te$_{70}$Cu$_{25}$Au$_5$ is amorphous. It was assumed from the analysis of the radial distribution function that the amorphous tellurium-base alloys are composed of short and randomly oriented spiral chains of tellurium atoms with the atoms of the minor constituent(s) randomly distributed between the chains. The previous measurements of electrical properties such as electrical resistance and thermoelectric power[10,11] indicate that (1) the simple-cubic AuTe$_2$ is a metal with a resistivity ($\sim 10^{-3}$ Ω-cm), about the same order of magnitude as that of the monoclinic AuTe$_2$ (the equilibrium form); (2) the amorphous alloy Te$_{70}$Cu$_{25}$Au$_5$ is a semiconductor with semiconducting properties similar to those of crystalline tellurium.

It is the purpose of this investigation to correlate the Mössbauer-effect data and the previous results of electrical measurements. The Mössbauer spectrum of the amorphous alloy is used to provide some experimental evidence to support the hypothesis that the spiral chain structure of crystalline tellurium is retained in the amorphous tellurium-base alloys. This kind of confirmation is significant in the sense that in more general cases of liquid tellurium[12-14] and selenium[15,16] the spiral structure plays an important role in determining the band structure and transport properties.

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II. EXPERIMENTAL

The alloys prepared for this study corresponded to the compositions $AuTe_2$ and $Te_{70}Cu_{25}Au_5$. The alloys were prepared by induction melting of the constituents in a quartz crucible under an argon atmosphere. The weight losses after melting were less than 0.2%, and it was assumed that the actual composition of the alloys was the nominal one. The purity of tellurium was 99.999%, and gold and copper were 99.99% pure. Small amounts of the alloys (about 10 mg) were rapidly cooled from the melt at a rate of approximately 10^6 °C/sec by the technique described by Duwez and Willens.[17] In this technique, the rapidly solidified alloy is spread into a thin foil on a copper substrate. Because the tellurium-base alloys are very brittle after quenching, the rapidly quenched material was recovered in the form of a fine powder. The powders were analyzed by x-ray diffraction (Debye-Scherrer method). The structure of $AuTe_2$ was simple cubic[10] with one atom
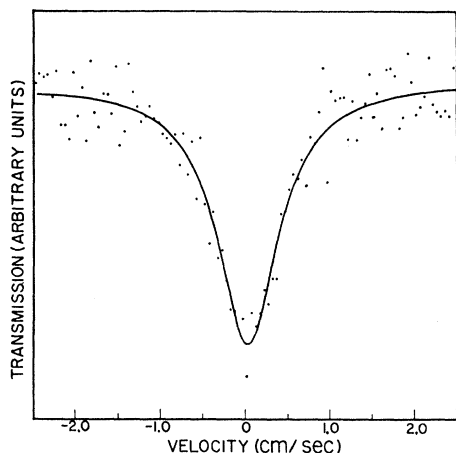

Fig. 1. Mössbauer spectrum of simple-cubic $AuTe_2$.

per unit cell and that of $Te_{70}Cu_{25}Au_5$ was amorphous,[11] as previously reported. For the Mössbauer experiments, the finely powdered alloys were dispersed in wax, and the thickness of the absorber was between 10 and 20 mg/cm². The source was made of 10 mCi of I^{125} diffused into copper to give a single resonance line.[18] Throughout this work, the source and the absorber were cooled to liquid-nitrogen temperature by means of a flow-through type cryostat. The drive and the electronic instrumentation of the spectrometer have been described elsewhere.[19]

III. RESULTS

The Mössbauer spectrum of the simple-cubic $AuTe_2$ is shown in Fig. 1. This spectrum shows a sharp, unsplit

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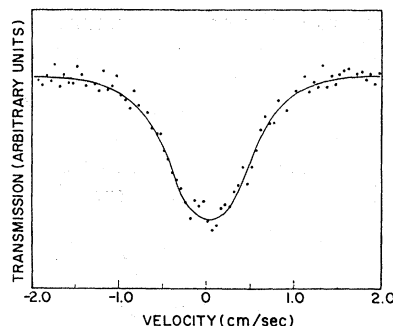[19] E. Kankeleit, Mössbauer Effect Methodology (Plenum Press, Inc., New York, 1965), Vol. I.

Fig. 2. Mössbauer spectrum of monoclinic $AuTe_2$.

line with a width at half-maximum equal to 0.88±0.05 cm/sec. The isomer shift of this simple-cubic alloy is 0.03±0.01 cm/sec relative to the source. For comparison, the Mössbauer spectrum of the monoclinic $AuTe_2$ is shown in Fig. 2. This spectrum gives a broad unsplit line with a half-width of 1.08±0.03 cm/sec. The isomer shift is 0.04±0.01 cm/sec. The resonance absorption spectrum of the amorphous alloy $Te_{70}Cu_{25}Au_5$, shown in Fig. 3, exhibits a well-resolved quadrupole splitting. The spectrum was fitted to a sum of Lorentzians by least-squares computer analysis. The magnitude of the quadrupole splitting as measured from Fig. 3 is 0.74± 0.02 cm/sec. To facilitate the interpretation of the results, the spectrum of pure tellurium was also measured but is not shown here, since it is almost identical to the one shown in Fig. 3. The quadrupole splitting of pure tellurium according to this measurement is 0.73± 0.02 cm/sec which is in good agreement with the experimental finding of Violet et al.[7]

IV. DISCUSSION

The fact that the Mössbauer spectrum of the simple-cubic $AuTe_2$ shows no quadrupole splitting is consistent with the cubic symmetry of the atomic arrangement. Contrary to expectation, a single-peak absorption spectrum is observed for monoclinic $AuTe_2$. However, a
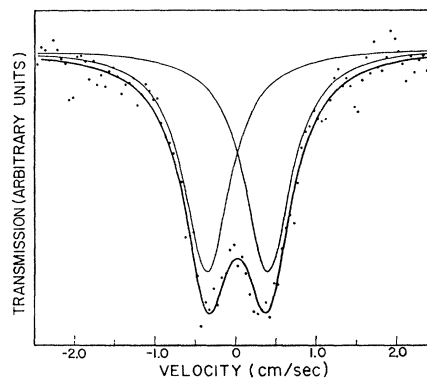

Fig. 3. Mössbauer spectrum of amorphous $Te_{70}Cu_{25}Au_5$.

detailed analysis of the crystal structure of monoclinic $AuTe_2$ provides a possible explanation for this experimental finding. This compound crystallizes in the monoclinic system with $a=7.18$ Å, $b=4.40$ Å, $c=5.07$ Å (all ±0.03 Å), $\beta=90°\pm30'$ and each unit cell contains six atoms.[20] The gold atoms occupy the 0, 0, 0 and $\frac{1}{2}$, $\frac{1}{2}$, 0 positions. The positions of the tellurium atoms are (m, o, p), $(\bar{m}, o, \bar{p})$, $(m+\frac{1}{2}, \frac{1}{2}, p)$, $(\frac{1}{2}-m, \frac{1}{2}, p)$, where $m=0.69$ and $p=0.29$ (all ±0.05). Thus, for a given Te atom, the three Te neighbors (two at 2.98 Å, one at 2.68 Å) lie in three almost-orthogonal planes $(87°10', 86°50', 86°50')$ which intersect at a distance of 0.42 Å from the given Te atom. Thus, the crystal structure of the monoclinic $AuTe_2$ is considered as a distorted simple-cubic lattice. Therefore, the line broadening can be attributed to a weak quadrupole interaction due to this near-cubic symmetry. The isomer shifts of the simple-cubic and monoclinic $AuTe_2$ are about the same within the experimental accuracy. All these Mössbauer data seem to support the previous conclusion[10] that only a slight distortion is necessary to transform the monoclinic $AuTe_2$ to its simple-cubic form. Consequently, the electronic structures of the two forms of $AuTe_2$ are probably very similar. This statement is consistent with the fact that both polymorphs exhibit similar metallic conduction.

In crystalline hexagonal tellurium, the tellurium atoms form spiral chains parallel to the c axis with three atoms per turn, and the axes of these chains are located at the corners and at the center of a hexagon. It is believed that a given tellurium atom shares covalent bonds with its two neighbors, and the chains are weakly held together by van der Waals bonding. Hence, the bonding between the next-nearest neighbors of adjacent chains is considered to be much weaker than that between the nearest neighbors within a single spiral chain. Based on this knowledge of the chemical bond in tellurium, the dominant part of the quadrupole interaction at a given tellurium nucleus is assumed to be from its nearest neighbors in the same chain.[21]

The structure of the amorphous alloy $Te_{70}Cu_{25}Au_5$ has been discussed elsewhere.[11] From the analysis of the radial distribution function of amorphous tellurium-base alloys, it has been concluded that the atomic arrangement consists of short and randomly oriented spiral chains of tellurium atoms and most of the copper and gold atoms are distributed randomly between the chains. As far as the quadrupole interaction of a given tellurium atom is concerned, the major contribution is from the nearest neighbors in the spiral and the effect of the second-nearest neighbors such as gold and copper atoms is insignificant. Therefore, the quadrupole splitting of the amorphous alloy $Te_{70}Cu_{25}Au_5$ should be the same as that of pure crystalline tellurium, if the spiral structure is indeed retained. This is exactly what has been observed in this investigation. As a consequence of the chain retention in the amorphous alloy, there is predominantly a covalent bonding like that in crystalline tellurium. Hence, it is reasonable to expect that the amorphous alloy shows a semiconducting behavior similar to that of crystalline tellurium.

In summary, the following points can be stated:

(1) The two polymorphs of $AuTe_2$ show almost identical isomer shift. The line broadening exhibited by the single-peak Mössbauer spectrum of the monoclinic $AuTe_2$ is attributed to a weak quadrupole interaction due to its near-cubic symmetry. These findings are consistent with the fact that both exhibit metallic conduction of the same order of magnitude.

(2) The Mössbauer-effect data obtained in this investigation confirm the notion that the tellurium chain structure of covalent bonding is retained in the amorphous alloy $Te_{70}Cu_{25}Au_5$.

ACKNOWLEDGMENT

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