J. Phys. Chem. Solids Pergamon Press 1960. Vol. 15. pp. 13–16. Printed in Great Britain.

LATTICE CONSTANTS OF Bi_2Te_3–Bi_2Se_3 SOLID SOLUTION ALLOYS

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(*Received* 23 *January* 1959; *revised* 12 *November* 1959)

Abstract—The Bi_2Te_3–Bi_2Se_3 quasi-binary system is rhombohedral for all compositions. Lattice constants a_0 and c_0 (based on a hexagonal lattice) for the entire range were determined using powder pattern film techniques. The constant a_0 follows Vegard's Rule over the entire range of compositions, while the constant c_0 exhibits a positive deviation over the range from 40 mol% Bi_2Se_3 to Bi_2Se_3. Bi_2Te_3 has a layered structure with planes of atoms of a single type parallel to the basal plane. The lattice constant data can be explained in terms of Se-atom substitution in preferred planes for the range Bi_2Te_3–Bi_2Te_2Se. Interlayer spacings for Bi_2Te_3 and Bi_2Te_2S are given and discussed.

1. INTRODUCTION

TILLER and MCHUGH[(1)] have shown by thermal analysis that Bi_2Te_3 is soluble in Bi_2Se_3 in all proportions. The structures of Bi_2Te_3 and Bi_2Se_3 have been established as rhombohedral[(2, 3)] which, for convenience of indexing, can be referred to a hexagonal unit cell. It was also shown that planes perpendicular to the c-axis contain atoms of the same type. This structure is shown in Fig. 1, with the rhombohedron outlined.

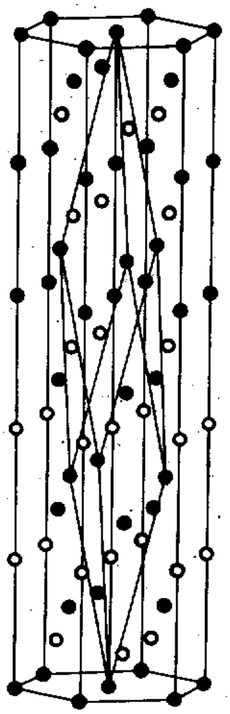

FIG. 1. Crystal Structure of Bi_2Te_3.

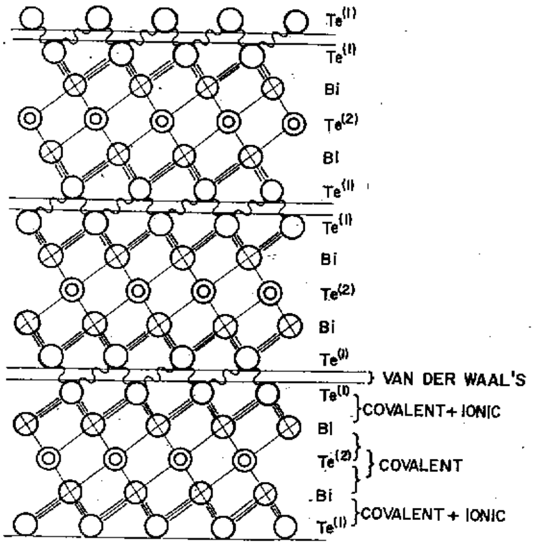

FIG. 2. Bonding Scheme of Bi_2Te_3.

DRABBLE and GOODMAN[(4)] have proposed a model for the bonding in Bi_2Te_3, and the bonding model is shown schematically in Fig. 2. In this model the stacking consists of "quintuple layer" leaves where, in each leaf, the layers occur in the order Te$^{(I)}$–Bi–Te$^{(II)}$–Bi–Te$^{(I)}$, with the bond lengths of the Te$^{(I)}$–Bi atoms approximately 0·1 Å shorter than those of the Te$^{(II)}$–Bi bond lengths. The superscripts (I) and (II) are here used to distinguish the Te atoms with different surroundings and with different type bonding with their nearest Bi neighbors. As seen in Fig. 2 the Te$^{(II)}$–Bi bond is covalent, and the Te$^{(I)}$–Bi bond is mixed covalent and ionic; the Te$^{(I)}$–Te$^{(I)}$ (intermolecular bond) is of the van der Waal type. DRABBLE and GOODMAN suggest that when Se atoms are substituted for Te in Bi_2Te_3, they first replace tellurium atoms in the Te$^{(II)}$ layers, after which the Se atoms randomly replace the Te$^{(I)}$ atoms. Optical(5) and electrical(6) measurements indicate that energy gap, thermoelectric power and electrical conductivity values change sharply at a composition near 30 mol% Bi_2Se_3–70 mol% Bi_2Te_3 ($Bi_2Te_{2\cdot1}$ $Se_{0\cdot9}$). This would indicate a change in the nature of the Se substitution. If we assume that the DRABBLE and GOODMAN suggestion(4) is correct, then the new substitution mechanism must be one of replacing tellurium atoms in Te$^{(I)}$ layers.

Evidence for the ordered structure for Bi_2Te_2Se may be found by comparing with the analogous substance Bi_2Te_2S (Tetradymite). HARKER(7) has shown that tetradymite is ordered with layers of atoms in the following order: Te–Bi–S–Bi–Te. Thus, it would seem probable in our alloy that we would obtain a layering of atoms similar in every way except that Se replaces S.

2. EXPERIMENTAL PROCEDURE

All of the alloys in this investigation were prepared in the same way. Stoichiometric amounts of the elements involved were weighed and capsulated in evacuated Vycor tubes. After heating to approximately 50°C above their liquidus temperatures, the alloys were shaken vigorously several times to insure thorough mixing, then quenched into water.

Initially the prepared powders were rolled into "rat-tails", but it was found that the powders cold-worked during this process. The selected technique was to coat very thin (0·3 mm) fibres of glass with diluted Duco cement, then dip the fibres into the annealed powders. This process was repeated until the diameter of the specimen was approximately 0·8 mm. The X-ray diffraction photographs were taken with a 114 mm diameter Debye-Scherrer camera using CoKα radiation.

The reflections for Bi_2Te_3 were indexed on the basis of a hexagonal lattice and this led to values for c and a of 30·45 Å and 4·384 Å, respectively. FRANCOMBE(8) recently obtained values of 30·487Å and 4·3835 Å, in good agreement with our values. Because of the difficulty in indexing some lines, a cleaved single crystal of Bi_2Te_3 was studied with a diffractometer in order to definitely establish the (00l) reflections. The c constant obtained with the diffractometer was 30·51 Å. Since we were interested in an alloy series, we used the X-ray photographs because only Bi_2Te_3 single crystals were available. The film reflections—uniquely (00l)—were (00·6), (00·15) and (00·30). The (00·15) and (00·30) c values were plotted against the extrapolation function $1/2\ (\cos^2\theta/\sin\theta + \cos^2\theta/\theta)$ and an extrapolated value of c was obtained. a was similarly obtained using the (hk0) lines: (110), (300) and (220). c and a constants for the other alloys of the series were obtained by utilizing corresponding X-ray diffraction lines.

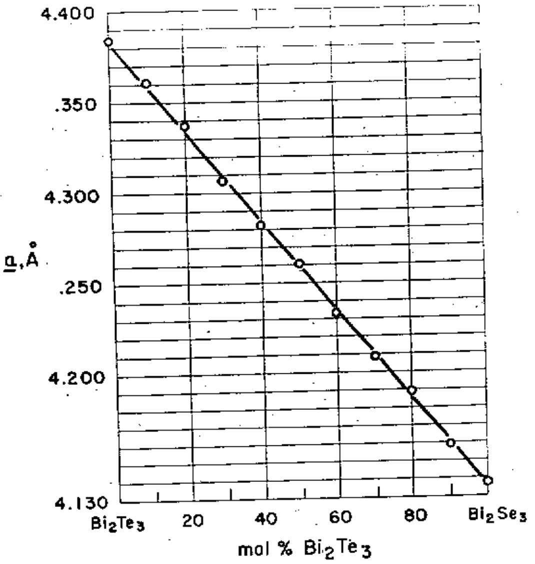

FIG. 3. Constant a as a Function of composition Bi_2Te_3–Bi_2Se_3 system.

3. RESULTS AND DISCUSSIONS

Figure 3 shows the variation of the a constant with composition, and Fig. 4 the variation of *c*. We see from the figures that both constants decrease as the composition goes from Bi_2Te_3 to Bi_2Se_3 and that the *a* value follows Vegard's Law. The deviation from Vegard's Law values for the lattice constant *c* is shown in Fig. 5. It is recalled that *a* is the interatomic distance of atoms in the basal plane of our structure. It seems clear that the main cause of the decrease in *a* is that Te atoms are replaced by the smaller Se atoms. The ionic radius for Te is 2·21 Å and for Se is 1·98 Å.(9) As has been indicated previously, these Se atoms at first go into $\mathrm{Te}^{(II)}$ layers.

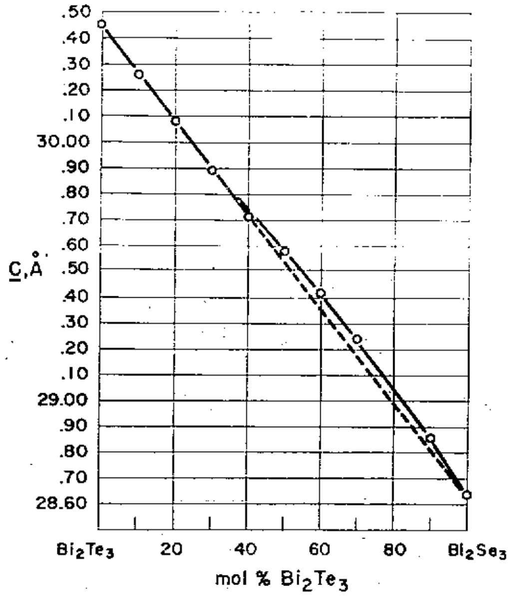

FIG. 4. Constant *c* as a Function of composition Bi_2Te_3–Bi_2Se_3 system.

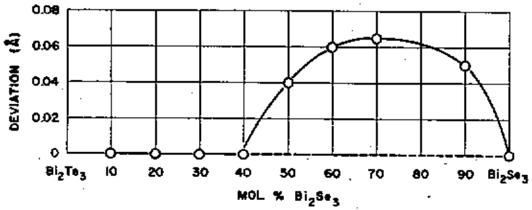

FIG. 5. Constant *c* deviation from Vegard's Law, Å.

A somewhat different effect on the *c* constant due to Se substitution is shown in Figs. 4 and 5. The decrease is linear to approximately 40% Bi_2Se_3, beyond which there is a positive deviation from Vegard's Law. This deviation implies that effects other than size are acting within the lattice. In general, it is expected that substitution of Se for Te would lead to smaller *c* values for the reason that the Se atom is smaller than Te.

There is a kind of van der Waal's interaction which is stronger between identical systems than between non-identical systems.(10) These are specific charge fluctuation forces which have been utilized to explain phenomena such as polymerization and biological replication. So long as the $\mathrm{Te}^{(I)}$ sites are all occupied by one atomic species—either all Te or all Se—one of the five-layer molecules is bounded on each side by its identical twin and the specific forces increase the van der Waal's attraction. When the $\mathrm{Te}^{(I)}$ sites are partially replaced by Se, the adjacent five-layer molecules are no longer identical and the van der Waal's interaction is weakened. Thus we believe that up to about 33 per cent Se, the Se atoms would all go into the $\mathrm{Te}^{(II)}$ layers in order to have maximum binding. The specificity effect then could explain the positive deviation of the *c* constant from Vegard's Law beyond 33 per cent Se. The adjoining five-layer molecules will be most unlike at $67\frac{2}{3}\%$ Bi_2Se_3 and we see from Fig. 5 that, near this composition, the greatest deviation from Vegard's Law occurs. We do not understand why there is no positive deviation from Vegard's Law at 40% Bi_2Se_3 for *c*.

In his publication, HARKER gives the lattice constants and parameters for rhombohedral tetradymite.(7) From these values interplanar spacings can be calculated; these are given in Table 1. Also in Table 1 are values obtained from interatomic distances in Bi_2Te_3 as given by AIRAPETIANTS and EFIMOVA(11).

Table 1

	Bi_2Te_3 (this work)	Bi_2Te_3 (from Russian data)	Bi_2Te_2S (after HARKER)
$\mathrm{Te}^{(I)}$–$\mathrm{Te}^{(I)}$	$2{\cdot}60_4$	2·73	2·73
Bi–$\mathrm{Te}^{(I)}$	$1{\cdot}73_9$	1·69	1·86
Bi–$\mathrm{Te}^{(II)}$ or Bi–S	$2{\cdot}03_8$	2·02	1·77

Our values of the Bi_2Te_3 lattice parameters were obtained utilizing a single crystal. Intensity data from $(00l)$ reflections, up to $(00{\cdot}10)$, were obtained on a diffractometer using $CuK\alpha$ radiation. A one dimensional Fourier synthesis of electron density was carried out for a reduced hexagonal unit cell (1/3 of the true cell in c), using signs which were the same as those of the corresponding tetradymite terms. The space group for Bi_2Te_3 is the same as that of tetradymite, $R\bar{3}m$.⁽¹²⁾ The electron density was projected onto the c axis and initially trial parameters of $\mu = 0{\cdot}401$ and $\nu = 0{\cdot}208$ were obtained. The refinement was carried out utilizing the fact that the third and fourth order reflections were experimentally zero. Since single crystals and a sensitive counter were used, we feel that these zero values are highly significant. The limiting factor is the atomic structure factor. The standard Thomas–Fermi values corrected for dispersion⁽¹³⁾ were used. Parameters $\mu = 0{\cdot}400_1$ and $\nu = 0{\cdot}209_5$ were obtained. An R factor of 0·46 was obtained for the limited set of reflections. The values computed from the Russian data are $\mu = 0{\cdot}399$ and $\nu = 0{\cdot}211$. These parameters are close to the values we obtained by refinement using atomic scattering factors without the dispersion correction; $\mu = 0{\cdot}399_5$ and $\nu = 0{\cdot}212_4$. AIRAPETIANTS and EFIMOVA do not state how or from what source their data are obtained. We feel that our data are probably the better.

The difference between the $Te^{(I)}$–$Te^{(I)}$ spacings for the two alloys is expected to be small; an idea of the magnitude of the error ($\cong 0{\cdot}1$ Å) may be obtained from the difference. Again, the Bi–$Te^{(I)}$ distances are expected to be similar in magnitude and, within experimental error, they are. The smaller size of the sulphur ion (1·74 Å) leads to the 1·77 Å spacing for Bi–S versus 2·07 Å for Bi–$Te^{(II)}$ The important numbers to be observed are these: (i) the large spacings for $Te^{(I)}$–$Te^{(I)}$ in both cases; (ii) the smaller value for Bi–$Te^{(I)}$ when compared with Bi–$Te^{(II)}$. Both of these features are in keeping with the bonding scheme of DRABBLE and GOODMAN, namely, that the "quintuple layer" leaves are bonded by weak $Te^{(I)}$–$Te^{(I)}$ homopolar forces and that the mixed covalent and ionic Bi–$Te^{(I)}$ bond length is shorter than the purely covalent Bi–$Te^{(II)}$ bond length.

Acknowledgements—This work was done under the sponsorship of The Thermoelectric Effects Cooperative Program. The authors wish to thank DR. F. DONAHOE for his stimulating discussions and valuable suggestions and R. PYLE for his valuable help in experimental procedures.

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