

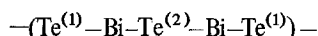
Chemical bonding in bismuth telluride

Bismuth telluride combines an exceptionally high thermoelectric power ($\alpha \approx 150 \mu\text{V K}^{-1}$) with relatively high electrical conductivity ($\sigma \approx 1000 \Omega^{-1} \text{cm}^{-1}$) and low thermal conductivity ($K \approx 0.015 \text{ W cm}^{-1} \text{K}^{-1}$) at room temperature. These properties are highly anisotropic and dependent on impurities [1, 2]. However, the quoted values are easily attainable for polycrystalline material and they result in a large figure of merit (z) for thermoelectric applications [3], which is defined as

$$z = \frac{\alpha^2 \sigma}{K}$$

Furthermore, bismuth telluride possesses a conveniently large energy gap ($E_g \approx 0.15 \text{ eV}$) so that it is considered as *the* thermoelectrically important semiconductor [4].

Early crystal studies and measurements of bond lengths in bismuth telluride have shown the existence of a layer structure [5], with two types of differently bonded tellurium atoms, $\text{Te}^{(1)}$ and $\text{Te}^{(2)}$. $\text{Te}^{(2)}$ atoms have an environment of six Bi atoms and, similarly, Bi atoms have an environment of three $\text{Te}^{(1)}$ and three $\text{Te}^{(2)}$ atoms. Layers of atoms are stacked in the rhombohedral $\langle 111 \rangle$ direction in approximately cubic close packing, giving a repeating five-layer structure in the sequence [6]:



The bond length between Bi and $\text{Te}^{(1)}$ atoms is considerably shorter than the one between Bi and $\text{Te}^{(2)}$ atoms (3.12 Å and 3.22 Å, respectively), which suggests that different types of bonding exist in each case, the Bi- $\text{Te}^{(1)}$ bond being stronger than the Bi- $\text{Te}^{(2)}$. The bond length between $\text{Te}^{(1)}$ atoms in neighbouring layers is much larger: 3.57 Å. It is the large spacing between the $\text{Te}^{(1)}$ atoms that is responsible for the ready cleavage of the Bi_2Te_3 crystal along the basal (0001) planes.

Although the electrical, thermal, and crystal properties of Bi_2Te_3 are fairly well known, the description of the chemical bonding in the compound is still a matter for dispute. In fact, several bonding models were introduced in the late fifties and two of them, proposed by Mooser and Pearson [7] and by Drabble and Goodman [8], have been considered to be particularly interesting. Both models are consistent, in principle, with the

geometry of the crystal Bi_2Te_3 . However, they imply totally different charge distributions among the bonded atoms.

The first model assumes the existence of purely covalent resonating p^3d^3 hybrid bonds in the compound, with the bismuth atoms being single bonded with $\text{Te}^{(2)}$ atoms and partially double bonded with $\text{Te}^{(1)}$ atoms (Figs. 1a and b). If this is the case, the electronegativity difference between Bi and Te (1.9 and 2.1 in the Pauling scale) should render the Te atoms somehow negatively charged with respect to Bi atoms.

The opposite conclusion is derived from the model proposed by Drabble and Goodman. Following the assumption of the transfer of one electron from each $\text{Te}^{(1)}$ atom to a neighbour Bi atom, single covalent bonds are considered between Bi and all Te atoms, with the valence electrons of Bi and $\text{Te}^{(2)}$ atoms occupying sp^3d^2 hybrid orbitals, while the remaining three 5p electrons on $\text{Te}^{(1)}$ atoms retain their original p-character (Fig. 1c). As a result of this electron transfer, a significant ionic character is attributed to the Bi- $\text{Te}^{(1)}$ bonds, with the Bi atoms being now negatively and the $\text{Te}^{(1)}$ atoms being positively charged. $\text{Te}^{(2)}$ atoms will certainly attract some negative charge from their Bi neighbours. However, their electronegativity difference does not seem to be large enough to transform Bi atoms from anions into cations. The same argument is valid for the charge distribution in a slightly modified model, with $\text{Te}^{(1)}$ atoms forming p^3d^3 hybrid orbitals, proposed by Bhide *et al.* [9].

Bi_2Te_3 is a p-type semiconductor on both sides of stoichiometry. The existence of acceptor states is attributed to the transfer of electrons from $\text{Te}^{(1)}$ to Bi atoms and it is considered an evidence in support of the model proposed by Drabble and Goodman [10]. A test of the correctness of the proposed bonding models can be also attempted in terms of the magnetic effect of substitution of atoms with different numbers of valence electrons from those of the pure compound. It is known that the unit cell of Bi_2Te_3 remains practically unchanged when indium atoms are substituted for Bi atoms in the lattice up to 25% [11]. This fact implies that geometry of the bonds is retained, although each substitution deletes two valence electrons from the crystal.

Actually, such a deletion should not affect the

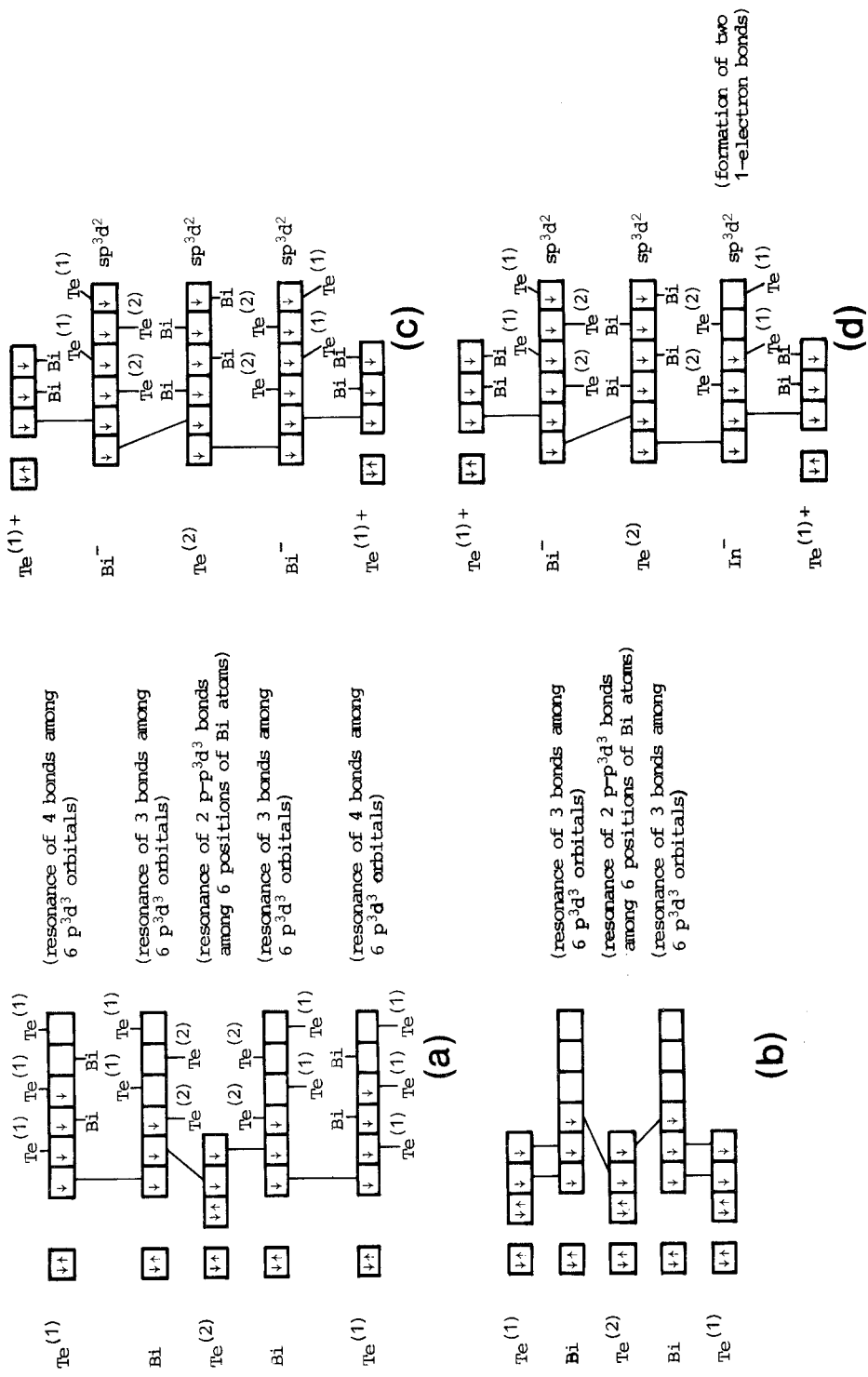


Figure 1 Theoretical models for bismuth telluride: (a) and (b) Electronic configurations of contributing models proposed by Mooser and Pearson, with and without covalent bonding between neighbouring layers, respectively; (c) model proposed by Drabble and Goodman; (d) a paramagnetic model for the partially substituted compound.

population of bonding electrons in the compound if models of Figs. 1a and b were correct, because In atoms entering Bi sites should, under the influence of the lattice, promote their three valence electrons into hybrid p^3d^3 orbitals, to satisfy the trigonal antiprismatic co-ordination. Consequently, In would form the same two-electron resonating covalent bonds with the six nearest neighbours $\text{Te}^{(1)}$ and $\text{Te}^{(2)}$ atoms, just as Bi atoms of the compound do. The model of Fig. 1c, on the other hand, is apparently unable to accommodate two-electron bonds throughout the lattice, when a few In atoms are substituted for Bi atoms. Several one-electron bonds would necessarily form, instead, rendering the compound paramagnetic (Fig. 1d).

Adequate materials were prepared and measurements of magnetic susceptibilities were carried out using the Faraday method. Pure Bi_2Te_3 was found to be diamagnetic ($\chi = -0.5 \times 10^{-6}$ c.g.s. units per gram at room temperature), which is consistent with both proposed models, having all their electrons paired. This value is in very good agreement with previously reported measurements [1, 2, 4]. Partially substituted samples, however, corresponding to the compositions $\text{Bi}_{1.8}\text{In}_{0.2}\text{Te}_3$ and $\text{Bi}_{1.6}\text{In}_{0.4}\text{Te}_3$ were found to be less diamagnetic or markedly paramagnetic ($\chi = -0.2 \times 10^{-6}$ and $+5.2 \times 10^{-6}$ c.g.s. units per gram at room temperature, respectively). The observed gradual increase of paramagnetism with the substitution of In for Bi atoms, produces evidence that model of Fig. 1c provides a better description of the bonding in Bi_2Te_3 , than the combination of models of Figs. 1a and b.

The above analysis is based on the assumption that the magnetic effects of the deletion of paired electrons, caused by the above-mentioned substitution, are negligible. It is also assumed that the contribution of free carriers to magnetic susceptibility is practically the same in all cases. In fact, electric

resistivity and Hall coefficient measurements have shown that at temperatures between 77 and 300 K the material is in the exhaustion region with similar carrier concentrations, of the order of $2 \times 10^{25} \text{ m}^{-3}$, in all samples [12].

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The prediction of creep at long times in polymeric solids

This note describes the principles and experimental test of a method for predicting long time creep in the linear viscoelastic region of polypropylene. It is based upon the recent precision determination

of the activation energy for creep (ΔH) of the α -relaxation process using the temperature pulse technique [1, 2]. The shift factor a_T

$$\ln a_T = \frac{\Delta H}{R} \left[\frac{1}{T} - \frac{1}{T_0} \right] \quad (1)$$