ON THE ELECTRON DIFFRACTION DIFFUSE STREAK PATTERN OBSERVED IN GeTe

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J. STOEMENOS and N. A. ECONOMOU

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Abstract: GeTe films present diffuse streak patterns when examined with the electron microscope. These streaks are associated with low index reflections and their behaviour as a function of temperature indicates that they are due to interaction of the eleetrons with lattice vibrations. The configuration of the streak pattern can be described as resulting from a network of walls perpendicular to low index planes in reciprocal space, which are the transform of linear scatterers in the real space. Diffused streaks associated with supperlattice reflections are attributed to anomalously soft phonons.

1. Introduction

Germanium Telluride exhibits a faulted structure in the bulk [1,2] and also in epitaxially grown single crystalline layers [3,4]. The main characteristics of these faults arise from the transformation from the cubic phase to a distorted rhombohedral one which leads to a highly twinned structure. In studying single crystal films of GeTe by electron microscopy we have observed, especially on (001) sections, intense diffuse streak patterns interlinking the spots of Laue - Bragg reflections. These streak patterns appeared as tetragonal networks around the central spot. It has been known that two dimensional substructures produce similar patterns [5]. Such substructures are stacking disorder, plate like precipitation or numerous twin interfaces on (110) and (100) planes, which cause linearly extended intensity regions in reciprocal space. Nevertheless, in the above cases the streaks appear only for certain rational electron indices which are grazing the habit planes of these substructures and are transformed to spots at non - rational positions. In our case the streaks remained unaltered in position by changing the angle of observation, with only a change in the shape of the network, while there was not a single case in which these streaks could be changed to irrational spots. There is by no means any relation between these observed streaks and the Kikuchi lines, which are due to secondary Laue - Bragg reflections, since these lines are displaced quite fast along the direction of tilting. In figure 1 we present a diffraction pattern of a specimen in which both Kikuchi lines and diffuse streaks coexist.

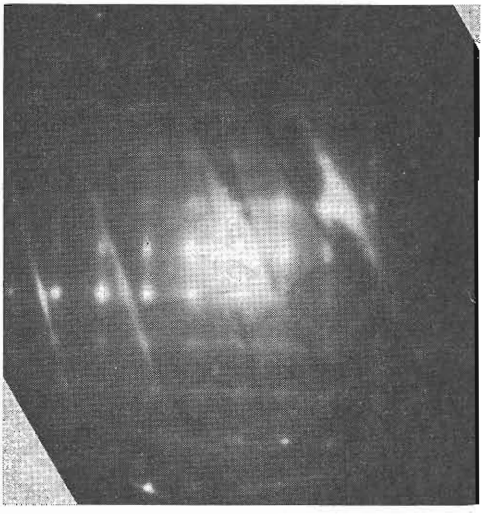
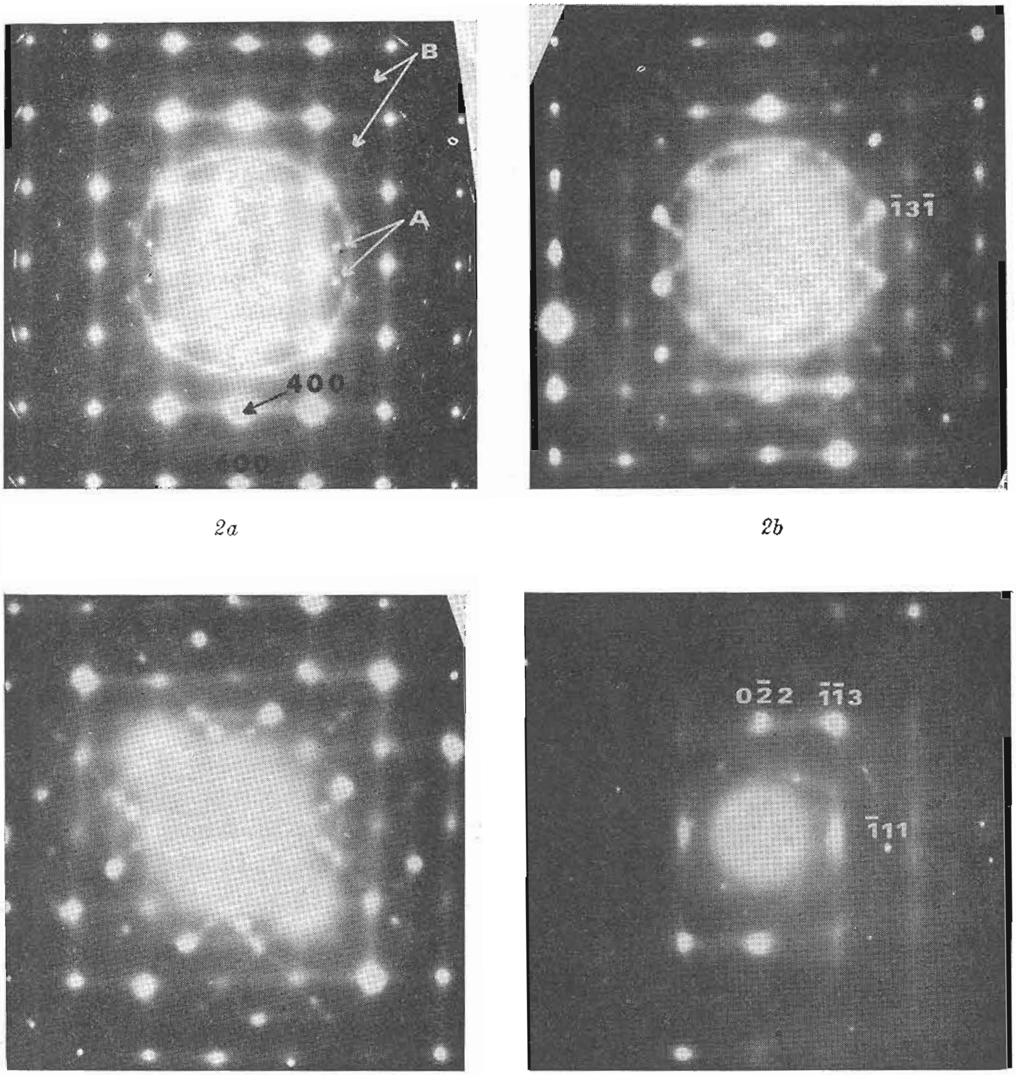


Fig. 1
Diffuse streak pattern and Kikuchi lines coexisting.

The configuration of this streak network varies when the direction of the primary beam is changed in the neighborhood of a certain rational crystallographic axis, but a distinctive change occurs only when the incidence is changed from one such rational incidence to another (fig. 2).

Another feature of these streaks is that they vary in intensity from place to place in the same specimen, and in all cases the intensity is enhanced by increasing the temperature. This latter observation constitutes a rather strong evidence that they have thermal origin, that is, they are due to interactions of the incident electrons with lattice vibrations along prefered crystallographic directions [6]. The vibrations of the lattice in the optical branch are expected to have a frequency of the order 10^{13} s^{-1} which is small compared to the electron frequency of the order 10^{19} s^{-1} (which corresponds to an electron energy of 100 KeV). Thus in a time interval of 10^{-5} s the atom will have described



2a 2b

2c 2d

Fig. 2

Diffuse streak networks as they appear in different crystallographic sections a) (001) section b) (310) scetion c) (311) section d) (211) section.

one thousand of its orbit, while in the same interval a train of about

1000 electrons will be diffracted. As far as the electron beam is concerned, the atoms are regarded stationary and slightly displaced from the positions of exact geometrical regularity, so that instead of a single spot in the diffraction pattern, an elongation of this spot is expected along the direction of the vibration.

2. Experimental procedure and results

Single crystalline GeTe films were grown epitaxially on vacuum cleaved KCl substrates under the conditions reported elsewhere [3]. Tilting experiments were performed in a Jeol 100B electron microscope at room temperature and at the transition temperature around 400°C. The heating was accomplished in situ using a heating tilting stage.

In figures 2a, 2b, 2c and 2d the diffraction patterns of GeTe films of orientation (001) are presented at different angles of observation. As it is evident from fig. 2a, which is a diffraction pattern at normal incidence, the streaks lie along the [100] and [010] directions. The spots indicated by arrows A are extra spots which may be attributed to a superstructure [4]. Faint streaks, marked by arrows B, appear also at half distances from regular reciprocal lattice points. The reciprocal lattice vector that describes them has indices {h 0 0}, with h always odd. Fig. 2b is the diffraction pattern of the same specimen, as in 2a, tilted 18° along [010], which corresponds to the (310) lattice section. The splitting of spots that may be noticed is due to the existence of twins of (010) type [2]. Fig. 2c is the diffraction pattern of the same specimen, tilted 25° along $[01\bar{1}]$, which corresponds to the (311) reciprocal lattice section. The network of the diffuse streaks changes progressively in shape from tetragonal to rhombic. Finally in figure 2d, which corresponds to a (211) reciprocal lattice section the shape of the network is orthogonal with the streaks lying along the $<110>$ directions, their intensity considerably reduced as compared with the intensity of the streaks in the (001) section.

In all these observations it is evident that there are no diffuse streaks passing through the origin; in other words the intensity of the zero - order streaks is zero. This means that the streaks are non - radial.

By heating the specimen in situ, the intensity of the streaks increases considerably (fig. 3). At 400° C the extra spots disappear, as due to a superstructure related to the rhombohedral phase, while zero - order streaks appear. These zero - order streaks could be interpreted as resulting from multiple diffractions, with a Bragg - scattered beam acting as a zero order to give its corresponding diffraction pattern [5].

Thus the observed zero order streaks arise from a 200 reflection. Evidence of these multiple diffraction effects is provided by the existence of multiple (220) rings around (200) spots. These (220) rings are due to

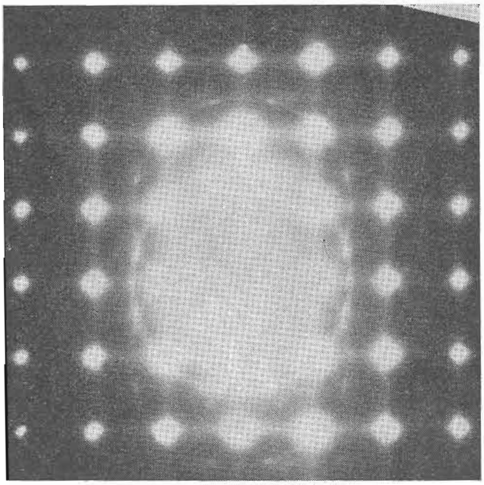


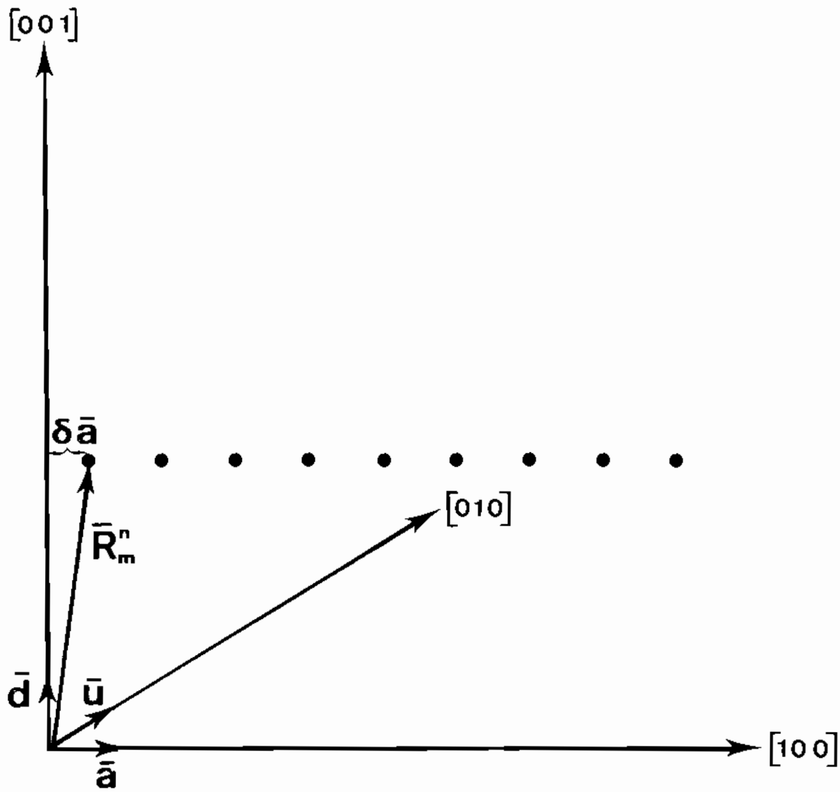
Fig. 3
Diffuse streak pattern at 400° C.

the fact that in some areas a mixture of epitaxial (001) and poorly oriented (111) grains occur.

3. Reciprocal lattice patterns of the diffused streaks

Non radial diffuse streaks have been observed previously in monochromatic X - ray diagrams of various substances [7,8,9] and in electron diffraction patterns [10,11]. In the latter case the streaks appear more clearly, due to a superposition of the primary streaks by secondary ones arising from strong Laue - Bragg reflections. A second reason for the more clearly resolved streaks iu electron microscopy is the fact that electron - phonon interaction is expected to be larger than the photon - phonon interaction in X - rays.

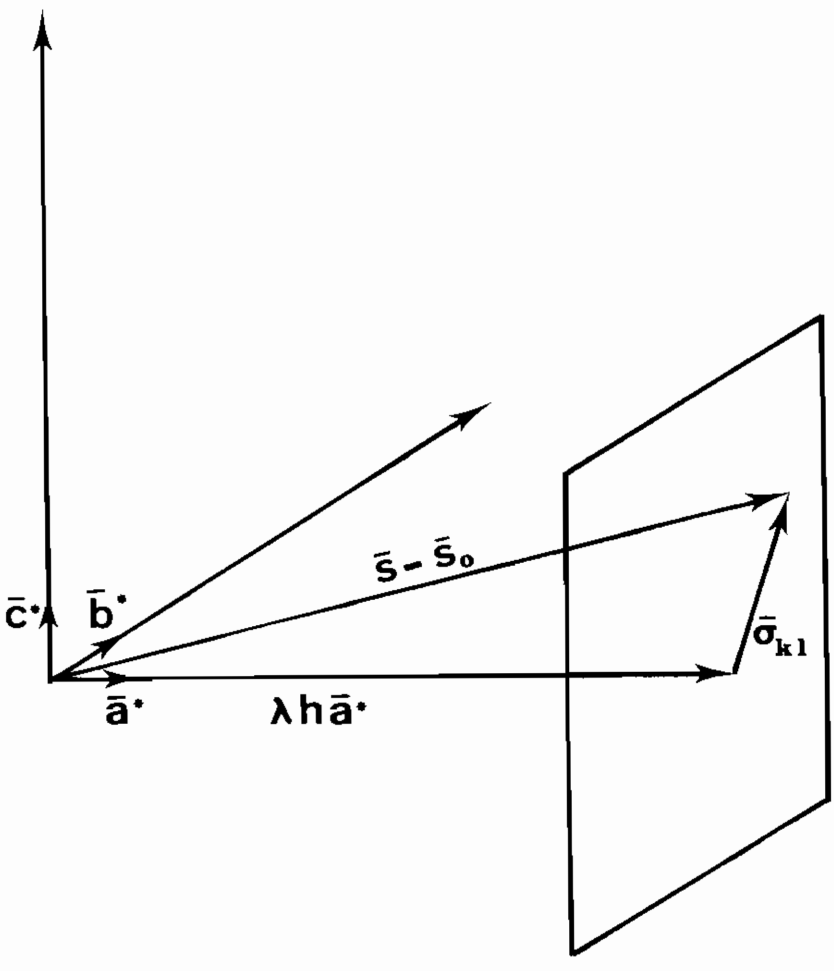
The configuration of the streak patterns can be described as the intersections between the Ewald sphere and networks of walls standing perpendicular to low index net planes in reciprocal space [12]. Since a needle crystal has an intensity distribution in reciprocal space similar to that of a disc perpendicular to the needle, a linear chain, which is the limit of a needle, will be expected to have an analogous intensity distribution. Therefore the observed streak patterns can be attributed to linear scatterers consisting of neighboring atoms slightly shifted from their regular positions (fig. 4a), without disturbing by this shift the relative distances of the atoms in the chain. This latter effect results to a diffuse scattering of the electrons, superimposed on the corresponding sharp scattering due to the crystal as a whole.



4a

We calculated this factor in a manner similar to the one applied in the case of random - layer structures [13]. Let us assume a linear chain of atoms parallel to the [100] direction (fig. 4a), with **a** to be the translational vector along this direction. The chains of atoms are displaced parallel to each other, with the origin of each chain bearing no fixed relation to that of its neighboring chains. This assumption excludes a periodicity along the two other directions, and therefore it is not possible to refer to the **b** and **c** axis. Instead one may assign distances

u and **d** to the neighboring chains lying perpendicular to the one under consideration, along the [010] and [001] directions. The position vector



4b

Fig. 4

a) Chain of nearest neighbours along [100] *direction displaced by a small amount δ.*
b) Representation of the intensity walls in reciprocal space.

of an atom belonging to a chain, with the origin displaced by δ along **a** is

$$\mathbf{R}_m^n = \mathbf{r}_n + m_1\mathbf{a} + m_2\mathbf{u} + m_3\mathbf{d} + \delta\mathbf{a} \quad (1)$$

where $\mathbf{r}_n$ is the position vector of the nth atom of the chain and m_1, m_2, m_3 are integers. If the first Laue condition is satisfied, that is

$$(\mathbf{s}-\mathbf{s}_\circ) \cdot \mathbf{a} = h\lambda$$

the scattered intensity is given by

$$I = FF' \frac{\sin^2 \pi h N_1}{\sin^2 \pi h} \sum_{m_2} \sum_{m_3} \sum_{m_2'} \sum_{m_3'} \exp \frac{2i\pi}{\lambda} [(s-s_\circ)(m_2-m_2')\mathbf{u} + (s-s_\circ)(m_3-m_3')\mathbf{d} + (\delta-\delta')h \cdot \lambda] \quad (2)$$

where the primed indices indicate complex conjugates of the unprimed, λ the wavelength, F the structure factor and $(s - s_\circ)$ the diffraction vector. When $h = 0$ the above equation reduces to

$$I = F^2 \frac{\sin^2\left[\frac{\pi}{\lambda}(s-s_\circ)N_2\mathbf{u}\right]}{\sin^2\left[\frac{\pi}{\lambda}(s-s_\circ)\mathbf{u}\right]} \frac{\sin^2\left[\frac{\pi}{\lambda}(s-s_\circ)N_3\mathbf{d}\right]}{\sin^2\left[\frac{\pi}{\lambda}(s-s_\circ)\mathbf{d}\right]} \quad (3)$$

This indicates that 0kl reflections are normal crystal reflections, since the term which introduces the diffuse part, $(\delta - \delta')h$, vanishes. Therefore these reflections are independent of any parallel displacements of the atomic chains along the [100] direction.

With the above considerations the reciprocal lattice construction for parallel random displaced chains follows easily. The diffraction vector in reciprocal space $(s - s_\circ) = \mathbf{g}$ is

$$\mathbf{g} = p_1\mathbf{a}^* + p_2\mathbf{b}^* + p_3\mathbf{c}^* \quad (4)$$

where $\mathbf{a}^*$, $\mathbf{b}^*$ and $\mathbf{c}^*$ are the reciprocal unit vectors, and p_1, p_2, p_3 numerical coefficients. From the orthogonality relations we have

$$\mathbf{g} = \lambda h\mathbf{a}^* + [\mathbf{g} \cdot \mathbf{u}]\mathbf{b}^* + [\mathbf{g} \cdot \mathbf{d}]\mathbf{c}^* = \lambda h\mathbf{a}^* + \boldsymbol{\sigma}_{kl} \quad (5)$$

The vector $\boldsymbol{\sigma}_{kl}$ lies on a plane perpendicular to $\mathbf{a}^*$, and since in this case $\mathbf{a}^*$ coincides with the vector $\mathbf{a}$ in real space, the chain of atoms is normal to the reciprocal lattice plane (fig. 4b). Also the (0kl) reflections are normal crystal reflections, so that zero order sheets have no intensity weight.

4. Discussion

Considering the case of a Born - Von Karman lattice with a basis to represent the atomic arrangement in the case of GeTe, neglecting the actual displacement of the atoms in the rhombohedral phase [14], it is possible to apply an harmonic oscillator approximation to interpret the observed diffuse scattering. W. Cochran has shown [15] that within this approximation the intensity of the diffuse scattering due to thermal motions may be expressed as a series of terms with an order determined from the number of phonons involved in the process. The intensity from the one phonon process, described by the first term, is inversely proportion to the square of the phonon frequency

$$I\,(\mathbf{q}) \propto \frac{1}{\nu^2(\mathbf{q})} \qquad (6)$$

where $\mathbf{q}$ is the position vector of a point in reciprocal space refered to the nearest reciprocal lattice point. Therefore it is expected that waves of low frequency are responsible for the diffuse scattering in directions away from Bragg reflections.

For GeTe in the rhombohedral phase the <100> direction is the one of the closest distance of ueighboring atoms, therefore the chains of atoms to be considered lie along this directions. This is consistent with the observations reported in fig. 1,2,3.

An important observation that should be emphasized are the observed diffuse streaks that belong to reflections with prohibited indices {h00}, where h is odd (fig. 5). In fig. 6 the intensity diffuse distri-

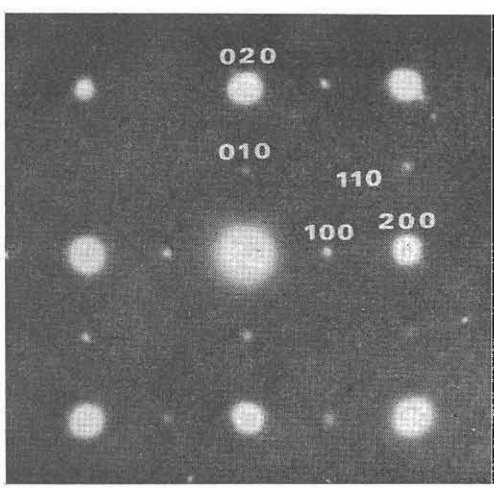


Fig. 5

bution along the 100 direction, taken with a densitometer passing through the [500] spot and also through the middle between the [500] and [600] spots, is presented. From these traces it is obvious that the supperlattice reflections are associated with diffuse scattering. It should be noted that the supperlattice reflections are rather weak, therefore diffuse streaks associated with them to be visible indicate that they

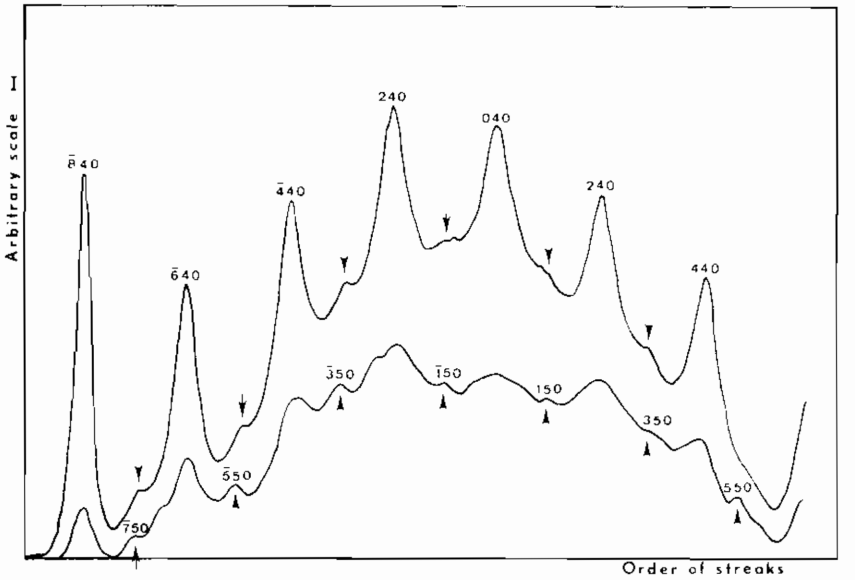


Fig. 6

Densitometer tracings of diffused streaks a) near regular spots b) along supperlattice reflections. Comparison of the two eurves indicotes that the secondary maxima, indicated by arrows, coincide with superlattice reflections.

are due to interaction with phonons of the type $q = \{h, 0, 0\}$, with h odd, anomalously soft, with a frequency approaching zero as the temperature tends to the transition point.

ΔΙΑΧΥΤΟΙ ΓΡΑΜΜΑΙ ΣΚΕΔΑΣΕΩΣ ΗΛΕΚΤΡΟΝΙΩΝ ΠΑΡΑΤΗΡΗΘΕΙΣΑΙ ΕΙΣ ΤΟ GeTe

Ὑπὸ

Ι. ΣΤΟΪΜΕΝΟΥ καὶ Ν. Α. ΟΙΚΟΝΟΜΟΥ

ΠΕΡΙΛΗΨΙΣ

Παρατηρήσεις λεπτῶν ὑμενίων GeTe δι' ἠλεκτρονικοῦ μικροσκοπίου ἀποδεικνύουν τὴν ὕπαρξιν διαχύτων γραμμῶν σκεδάσεως. Αἱ γραμμαὶ αὗται ἀποδεικνύεται ὅτι συσχετίζονται μὲ ἀνακλάσεις, μὲ δείκτας ἁπλοῦς, ἡ δὲ συμπεριφορά των συναρτήσει τῆς θερμοκρασίας ἀποδεικνύει ὅτι ὀφείλονται εἰς ἀλληλεπίδρασιν τῶν ἠλεκτρονίων μὲ τὰς δονήσεις τοῦ πλέγματος. Ἡ διάταξις τῶν γραμμικῶν τούτων σχημάτων δύναται νὰ περιγραφῇ ἐὰν θεωρηθῇ ὅτι προέρχεται ἀπὸ δίκτυον καθέτων ἐπιφανειῶν ἐντάσεως εἰς τὸν χῶρον τοῦ ἀντιστρόφου πλέγματος. Τὰ ἐπίπεδα ταῦτα εἶναι τὰ σχήματα μετασχηματισμοῦ γραμμικῶν σκεδαστῶν εἰς τὸν πραγματικὸν χῶρον. Διάχυτοι γραμμαὶ συσχετιζόμεναι μὲ ἀνακλάσεις ἐξ ὑπερδομῆς ἀποδίδονται εἰς ἀνωμάλως μαλακὰ φωνόνια.

REFERENCES

1. J. STOEMENOS and N. ECONOMOU: Chimika Chronika, **1**, 168 (1972).
2. M. SNYKERS, P. DELAVIGNETTE and S. AMELINCKX: Mat. Res. Bull. (1972) to be published.
3. J. STOEMENOS and R. VINCENT: Phys. Stat. Sol. (a), June (1972).
4. J. STOEMENOS, S. KOKKOU and N. ECONOMOU: Phys. Stat. Sol. to be published.
5. HIRSH et al: Electron Microscopy of Thin Crystals, Butterworths, London (1965).
6. R. W. VOOK and A. BALTZ: J. Appl. Phys. **35**, 1952 (1964).
7. K. LONSDALE and H. SMITH: Proc. Roy. Soc. A **8**, 179, (1941 - 2).
8. P. G. OWSTON: Acta Cryst. **2**, 222, (1949).
9. M. S. AHMED: Acta Cryst. **5**, 587, (1952).
10. G. HONJO: J. Phys. Soc. Japan, 17, Suppl. B - **11**, 277 (1961).
11. G. HONJO, S. KODERA and N. KITAMURA: J. Phys. Soc. Japan, 19, 351 (1964).
12. K. KOMATSU: J. Phys. Soc. Japan **19**, 1243 (1964).
13. L. V. AZAROFF: Elements of X - Ray Crystallography, Mc Graw - Hill, (1968).
14. T. B. ZHUCOVA and A. I. ZASLAVSKII: Soviet Physics - Crystallography **12**, 28 (1967).
15. W. COCHRAN: Phonons and Phonon Interactions, T. A. Bak Editor, W. A Benjamin, pp 102 (1964).