PHILOSOPHICAL MAGAZINE B, 1982, VOL. 45, NO. 1, 137–145

A thermodynamic criterion of the crystalline-to-amorphous transition in silicon

By S. VEPŘEK, Z. IQBAL and F.-A. SAROTT
Institute of Inorganic Chemistry, University of Zürich,
Winterthurerstrasse 190, 8057 Zürich, Switzerland

[Received 18 March 1981 and accepted 1 July 1981]

ABSTRACT

It is shown that the crystal lattice expansion of microcrystalline silicon leads, in the limit of small crystallite size of about 30 Å, to an instability of the diamond structure with respect to the amorphous phase. Simple thermodynamic considerations are presented which support the idea of the crystalline-to-amorphous transformation being a discontinuous order–disorder phase transition.

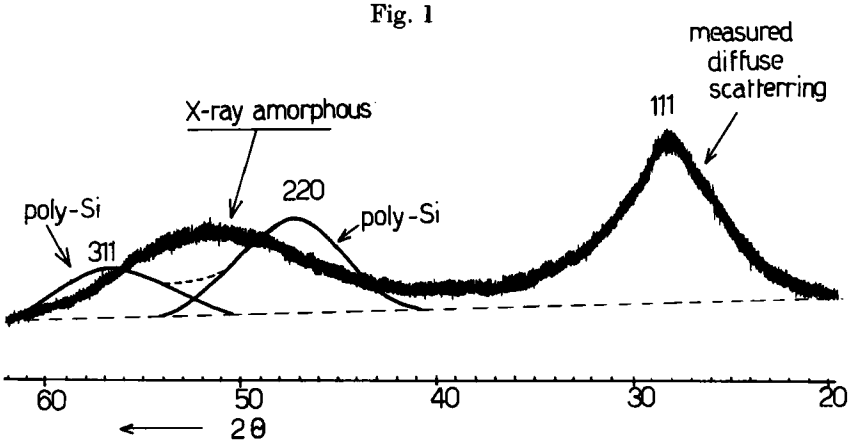
§ 1. INTRODUCTION

It has already been recognized that there exists a discontinuity of the coherence length on going from polycrystalline to amorphous materials (see, for example, Brodsky 1975). In the case of pure, as well as hydrogenated silicon, the lowest limit of the crystallite size for polycrystalline material with the diamond lattice appears to be about 30 Å (Brodsky 1975, Grigorovici and Manaila 1969, Grigorovici 1974, Vepřek, Iqbal, Oswald, Sarott, Wagner and Webb 1981 b). Below this limit, the X-ray diffraction pattern dramatically changes and becomes inconsistent with the diamond structure. Basically it means that instead of the 220 and 311 diffraction peaks of the diamond lattice (i.e. the second and third peaks in the diffraction pattern) a second, broad maximum in the diffuse scattering from the amorphous material appears at a position between the 220 and 311 peaks (fig. 1).

In the case of polycrystalline material, the widths of the different diffraction peaks are interrelated via Scherrer's formula (Guinier 1963) provided the peak broadening is dominated by the limited coherence length and the crystallites have regular shapes. Since the latter conditions are fulfilled in hydrogenated μc-Si prepared by chemical transport (Vepřek *et al.* 1981 b, Vepřek, Iqbal, Oswald and Webb 1981 c, Iqbal and Vepřek 1981), one can calculate from the width (FWHM) of the first maximum (which coincides with the 111 peak of the diamond lattice) the expected widths of the 220 and 311 peaks (fig. 1). It is seen from fig. 1 that the second maximum in the diffuse scattering from ' X-ray amorphous ' material does not correspond to a super-position of the 220 and 311 peaks but is of another origin. In the course of preparation of several hundred samples of μc- and a-Si we have

0141-8637/82/4501 0137 $02·00

Fig. 1



A part of the measured diffuse X-ray scattering from a-Si (recorder trace with noise) and the calculated positions and widths of the 220 and 311 peaks of c-Si when the first peak of the measured curve is interpreted as the 111 Bragg reflection.

observed that there is no continuous transition from the crystalline to the amorphous diffraction pattern but rather an abrupt change†.

The structural significance of this change in the X-ray scattering is apparent from the radial distribution function (RDF) which, in the case of ' X-ray amorphous ' material cannot be explained by a microcrystalline model with a diamond lattice (Grigorovici 1974, Rudee and Howie 1972, Weinstein and Davis 1973/74, Gaskell 1979). The problem is basically associated with the third peak in the RDF at 4·7 Å which corresponds to the third neighbour distance. Upon the transition from crystalline to amorphous Si the intensity of this peak drops drastically indicating a change in the dihedral angle‡. Only models including some portion of the Si–Si bonds in the eclipsed configuration or a rather broad distribution of the dihedral angle succeeded in reproducing the measured RDF of the X-ray scattering pattern (Rudee and Howie 1972, Grigorovici 1974, Gaskell 1979, Gaskell, Gibson and Howie 1977, Mott and Davis 1979).

Such a network necessarily poses an excess internal energy and configurational entropy (Wong and Angell 1970, Spaepen 1974, Gaskell 1979, Dandoloff, Döhler and Bilz 1980, Döhler, Dandoloff and Bilz 1980). Based on simple thermodynamic arguments it will be shown in the present paper that the contribution of the elastic energy due to the lattice expansion of microcrystalline silicon, reported earlier (Vepřek *et al.* 1981 b), to the free energy of the system, leads to an instability of the diamond structure with respect to the amorphous phase. The theoretically estimated value of the

† A similar observation has also been made in the preparation of amorphous and polycrystalline phosphorus (Wild 1979).

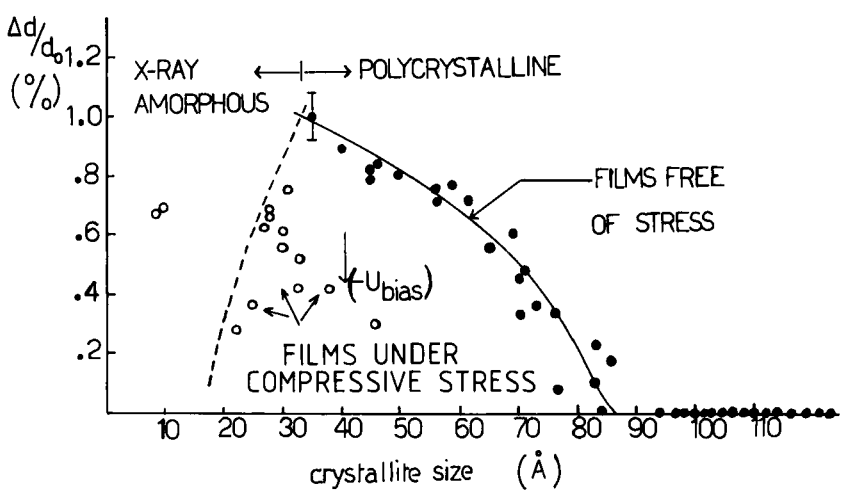
‡ The same change in the intensity of the third peak is seen in the recent RDF study on Ge using EXAFS, although the authors conclude that the transition is ' continuous ' (Evangelisti, Proietti, Balzarotti, Comin, Incoccia and Mobilio 1981).

critical lattice expansion agrees very well with the measured value. Because of an experimentally verified correlation between the crystallite size and the lattice expansion (Vepřek *et al.* 1981 b) such a consideration provides a plausible explanation for the lower limit of the coherence length in polycrystalline material as well as for the abrupt transition from the polycrystalline to the amorphous phase. It also suggests that this transition could be regarded as a discontinuous order–disorder phase transition (i.e. ' first order '), the driving force of which is the increase of the elastic energy due to the lattice expansion, which is in turn related to the increase of the specific surface energy of small crystallites.

§ 2. Free energy of microcrystalline and amorphous silicon

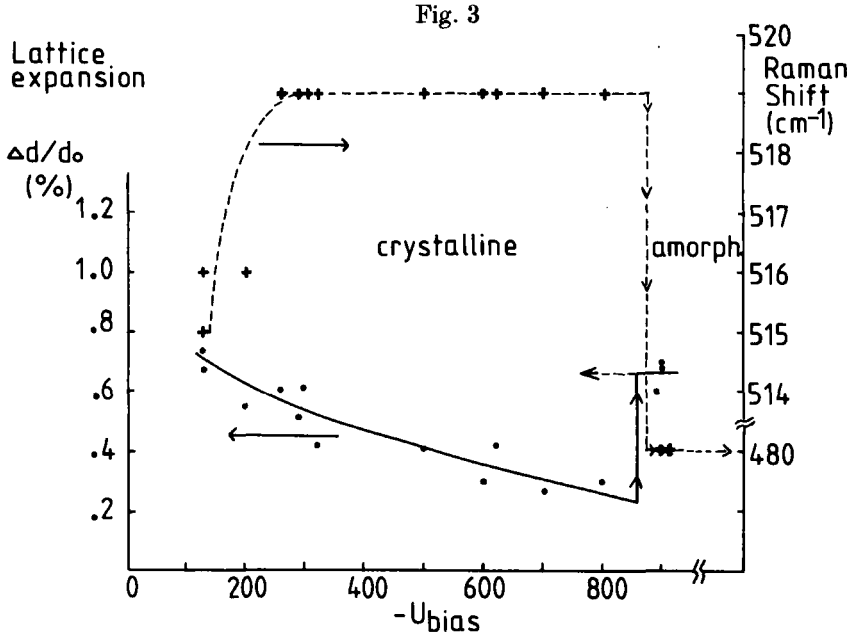
In a previous paper (Vepřek *et al.* 1981 b) it has been shown that the crystalline-to-amorphous transition can be controlled through the control of the deposition parameters, which essentially govern the lattice expansion. At a certain limit of the linear lattice expansion $\Delta d/d_0 \approx 0{\cdot}01$–$0{\cdot}02$, the diamond lattice becomes unstable and the amorphous phase is formed. This is illustrated by fig. 2 which represents an extension of the data given in our previous paper (Vepřek *et al.* 1981 b), showing in particular the effect of the compressive lattice stress on the stabilization of the diamond lattice. In the stress-free films the lower limit of the crystallite size is ~ 30 Å, but it can be decreased to ~ 20 Å for films possessing a large compressive stress (see figs. 2 and 3). With decreasing crystallite size the contribution of the surface energy to the free energy of the system, $F(\mu\text{c-Si})$, increases. The excess energy, $\delta F(\mu\text{c-Si})$,

Fig. 2



Correlation between the measured lattice expansion, $\Delta d/d_0$ and the crystallite size (cube edge—a, see Vepřek *et al.* 1981 b), for nearly stress-free films (full circles and solid line) and for films deposited under negative bias, i.e. films having a compressive lattice stress produced by ion-implantation (open circles).

Fig. 3



Plot of the lattice expansion, $\Delta d/d_0$ (full circles and solid line), and of the peak position of the Raman line (crosses and broken line) versus the negative bias, U_b, of the substrate during deposition. The increasing compressive stress in the films with increasing $-U_b$ leads to a stiffening of the diamond lattice as apparent from the decrease of $\Delta d/d_0$ and increase of the Raman frequency (see also Iqbal and Vepřek 1981 for further details).

can be split into two parts : the first expresses the increase of the energy of the bulk of the crystallites, δF(bulk), and the second represents the contribution to the free energy of the system of the chemically bonded hydrogen, δF(Si–H), i.e.

$$\delta F(\mu\text{c-Si}) = \delta F(\text{bulk}) + \delta F(\text{Si–H}). \tag{1}$$

The first term on the right-hand side of eqn. (1) is approximately equal to the elastic energy due to the lattice expansion since, as long as the diamond lattice is preserved, the entropy term of δF(bulk) can be neglected. Thus, using the usual expression for the elastic energy density, $U(\Delta d/d_0)$ (Kittel 1971), we write

$$\delta F(\text{bulk}) = V_{\text{mole}} U\left(\frac{\Delta d}{d_0}\right) = \frac{V_{\text{mole}} B}{2}\left(\frac{\Delta V}{V_0}\right)^2. \tag{2}$$

Here, $V_{\text{mole}} \doteq 12$ cm^3 is the molar volume of solid silicon, $B = 0{\cdot}99 \times 10^{12}$ dyne cm^{-2} is the bulk modulus and $\Delta V/V_0 \approx 3(\Delta d/d_0)$ is the volume expansion. Writing E_0 and S_0 for the molar internal energy and entropy of the silicon single crystal, respectively, the free energy of μc-Si is given by

$$F(\mu\text{c-Si}) = E_0 - TS_0 + (9/2) V_{\text{mole}} B(\Delta d/d_0)^2 + \delta F(\text{Si–H}). \tag{3}$$

In a similar way, the free energy of amorphous silicon is given by

$$F(\text{a-Si}) = E_0 + \delta E(a) - T(S_0 + \delta S(a)) + \delta' F(\text{Si–H}). \tag{4}$$

Here, $\delta E(a)$ and $\delta S(a)$ stands for the excess configurational internal energy and entropy, respectively, and the term $\delta' F$(Si–H) has a similar meaning as its counterpart in eqn. (3). With decreasing crystallite size the crystalline, diamond lattice becomes unstable with respect to the amorphous phase when

$$F(\text{c}\mu\text{-Si}) = F(\text{a-Si}). \tag{5}$$

Equation (5) represents the thermodynamic criterion for the crystalline-to-amorphous transition and it allows one to estimate the critical value of the elastic energy (i.e. of the lattice expansion) at which the transition occurs. Using the experimentally found correlation between the lattice expansion and the crystallite size (fig. 2) the lower limit of the crystallite size can be obtained for stress-free polycrystalline silicon films.

The exact calculation is impossible to perform at the present time because of the lack of reliable numerical data on the excess terms δF(Si–H), $\delta' F$(Si–H), δE and δS in eqns. (3) and (4), and of the bulk modulus for small crystallites. Nevertheless, the following estimate, which is based on some (we believe) plausible assumptions, gives an encouraging agreement with the experimental observations.

The value of the bulk modulus depends on the interaction potential and the Si–Si distances. For crystallites containing more than 1000 atoms and a lattice expansion of 1–2%, the bulk modulus of single crystal seems to be an acceptable approximation.

Next we assume that

$$\delta F(\text{Si–H}) \approx \delta' F(\text{Si–H}). \tag{6}$$

This is justified by the experimental findings that both the a-Si and μc-Si have a comparable hydrogen content; the hydrogen is bounded on the surfaces of the crystallites and the spectral bands in the infrared corresponding to the SiH_x groups appear approximately at the same frequencies (Vepřek *et al.* 1981 c, Iqbal and Vepřek 1981).

Thus, the condition for the crystalline-to-amorphous transition, eqn. (5), can be approximated by :

$$(9/2)\, V_{\text{mole}} B(\Delta d/d_0)^2 \approx \delta E(a) - T\delta S(a). \tag{7}$$

Depending on the structural model the excess internal energy of an amorphous network consisting in part (or completely) of Si–Si pairs in the eclipsed configuration amounts to $\delta E(a) \approx 0{\cdot}1$–$0{\cdot}6$ kcal mol^{-1} (see, for example, Rudee and Howie 1972, Dandoloff *et al.* 1980, Döhler *et al.* 1980), the lower limit being probably a rather unrealistic underestimate. Stable and well relaxed amorphous networks have a rather low excess entropy (Bagley 1974, Wong and Angell 1976). For a-Si Spaepen (1974) calculated as an upper limit of the configurational entropy $\sim 0{\cdot}2 k_B$ atom^{-1}, i.e. $\delta S(a) \lesssim 0{\cdot}4$ cal K^{-1} mol^{-1}. Thus, the excess entropy term in eqn. (7) is rather at the lower limit of the (positive) δE contribution for the temperature range of 300–500 K (see also Döhler *et al.* 1980). Using these values, the critical lattice expansion at which the

diamond lattice becomes unstable with respect to the amorphous phase can be estimated from eqn. (7) to be :

$$\left(\frac{\Delta d}{d_0}\right)_{\text{critical}} \approx 0{\cdot}01\text{–}0{\cdot}02. \tag{8}$$

This is in very good agreement with the experimentally measured value of the lattice expansion for poly-Si with crystallite sizes close to the critical, lower limit (see fig. 2). The above mentioned simplifications probably modify the value in eqn. (8) only slightly.

If a compressive stress is induced in the growing film by ion implantation (fig. 2, open circles, also see fig. 3), the crystalline diamond phase is stabilized at an even smaller crystallite size (e.g. 20 Å, fig. 2). At the present time we hesitate to give some interpretation of this effect in terms of the interaction at the grain boundary, but rather we just refer to eqn. (7). Indeed, the diamond phase is stabilized because of the relative decrease of the elastic energy due to the compressive stress, i.e. a decrease of $\Delta d/d_0$ upon ion implantation.

§ 3. Discussion and conclusions

The thermodynamic considerations presented in § 2 are rather approximate and hence they call for more quantitative calculations. Nevertheless, they seem to provide a basically correct phenomenological picture of the crystalline-to-amorphous transition. The thermodynamic model presented here is consistent and complementary with the dynamical–topological model of amorphicity presented by Döhler *et al.* (1980) and Dandoloff *et al.* (1980) and it has some relevance to the recent ideas of Phillips (1979, 1981).

Döhler *et al.* (1980) point to the inherent weakness of the c-Si diamond lattice to deformations of the space angle because of a low-frequency transverse acoustic (TA) phonon branch with anomalous anharmonic properties. The ' soft ' zone-boundary acoustic phonon corresponds to an eigenvector which can lead *locally* to a transformation of the Si rings in the ' chair ' configuration in the diamond lattice to the ' boat ' configuration expected in a disordered network or Si-clusters. In terms of our picture, it can be suggested that the lattice expansion with decreasing crystallite size is related to the anomalous anharmonicity of the acoustic branch. The resulting increase in elastic energy with decreasing crystallite size is then the driving force which triggers the crystalline to amorphous transition. The transition can be considered to be an order–disorder transition analogous to that observed for example in the melting of solids, which is first order and hence discontinuous.

The discontinuous nature of the crystalline-to-amorphous transition is evident from the following experimental facts :

(*a*) The change in the X-ray pattern (fig. 1) is discontinuous regardless of whether the crystalline-to-amorphous transition occurs because of a low deposition temperature (see fig. 2, ' stress-free films ') or to ion implantation (fig. 3) (see also Müller and Kalbitzer 1977).

(*b*) The Raman spectrum shows an abrupt disappearance of the crystalline TO $\mu_{25'}$ mode below the lower crystallite size limit. Only the Raman

peak attributed to a surface-like phonon mode persists and it displays a continuous shift towards 480 cm^{-1}. Such a mode, which essentially corresponds to a bond-stretching of a $Si–Si_4$ unit will of course persist in any network conserving the fourfold coordination of Si (Iqbal and Vepřek 1981).

(*c*) The electrical conductivity of Si and Ge decreases sharply upon the transition to the amorphous phase (Johannessen 1974, Kamiya, Kishi, Ushirokawa and Katoda 1981).

(*d*) The sign of the Hall mobility changes from the normal to the anomalous one upon the transition (Spear, Willeke, Le Comber and Fitzgerald 1981).

Further arguments in support of the discontinuous nature of the transition come from Landau's theory of phase transitions (Landau 1937) which states that, if there is no common sub-group of the symmetry groups of both phases, the transition between them has to be discontinuous. Only if there were large clusters ($\geqslant 1000$ atoms) in a-Si having symmetry elements (other than identity) which belong to a sub-group of the symmetry group of the diamond lattice, such a transition could be continuous. This seems to be unlikely in the case of a-Si and a-Ge which are topologically over-constrained. However, if, as in the case of good glass-formers, the formation of clusters with certain symmetry elements of the crystalline phase (e.g. chains, or two- and three-dimensional clusters) occurs, the crystalline-to-amorphous transition should be second order (i.e. continuous). We do not want to draw final conclusions regarding the application of Landau's theory to the crystalline-to-amorphous transition, but we believe that it may bring some new insights into this problem and is hence worth consideration in some detail.

A thermodynamic model of course cannot yield any microscopic understanding of the origin of the lattice expansion. This, is however, likely to be related to bond weakening and bond-length expansion, in small, covalently bonded clusters (Allpress and Sanders 1970). It is known that the structure of small clusters containing 10–30 atoms is generally different from that of a macroscopic bulk crystal, the reason being a minimization of the surface energy. This leads to structures that are incompatible with a macroscopic lattice having translational symmetry. Typical examples of such structures are the icosahedron and the pentagonal dodecahedron (amorphon) (Allpress and Sanders 1970, Horae and Pal 1975, Frank 1952, Grigorovici 1974, Horae and Barker 1976). In the case of silicon the dodecahedron corresponds to a cluster of 20 atoms all being in the eclipsed configuration with only one dangling bond per atom. In contrast, clusters of comparable sizes with the ' diamond lattice ' have more than 1·2 dangling bonds per atom. This comparison illustrates why the diamond lattice becomes unfavourable in the limit of small cluster size.

The structure of the silicon films is determined by the conditions of the nucleation and nuclei coalescence. Unless activation energy is provided to the growing film to allow the formation of stable nuclei with the diamond lattice, the structure of the film will be determined by the structure of the most stable clusters which are, in general, incompatible with a three-dimensional crystal lattice having translational symmetry. The coherence length in such

an amorphous material will be limited. This is the case during deposition of silicon films by evaporation or by decomposition of silane in a weak discharge, far away from thermodynamic equilibrium. By chemical transport, on the other hand (see, for example, Vepřek *et al.* 1981 b, Vepřek 1980, Vepřek, Iqbal, Oswald, Sarott and Wagner 1981 a), the deposition takes place close to chemical equilibrium, in which case sufficient energy *can be* provided to the growing surface to catalyse the formation of stable, large nuclei of the diamond lattice. The thermodynamic estimate presented in this paper suggests that the minimum size of such a nuclei amounts to ≈ 30 Å (i.e. more than 1000 atoms!) in agreement with the experimental data. A large activation energy is necessary to transform an amorphous cluster into a crystalline one of such a size, which explains the high stability of the amorphous silicon showing a recrystallization temperature of $T_c \gtrsim \frac{1}{2} T_m$.

The activation energy necessary to transform the amorphonic nuclei into the crystalline ones at their stability limit of ~ 30 Å is likely to be provided by the intense recombination processes taking place on the silicon surface during growth under plasma conditions with a typical discharge power density of $\gtrsim 0{\cdot}1$ W cm^{-3}. We have shown elsewhere (Vepřek *et al.* 1981 a) that recombination of H-atoms is the dominant process. Typically, at a growth rate of ~ 1 Å s^{-1} several thousand H–H recombination events take place on the surface per deposited Si atom. A part of the recombination energy of $\sim 0{\cdot}5$–$0{\cdot}9$ eV per H_2 formed is dissipated into the silicon surface. It is much larger than the thermal energy of phonons, kT, and also larger than $k\theta$, θ being the Debye temperature. This fact together with the localized nature of the H_2-recombination lead us to the conclusion that the (energetic) phonons close to the boundary of the Brillouin zone are excited and strongly overpopulated during deposition, since they can be thermalized only via relatively slow anharmonic phonon–phonon interaction. In the light of the ideas of Dandoloff *et al.* (1980) as discussed above, such an excitation can easily lead to an amorphous-to-crystalline transition of the small nuclei.

Acknowledgments

This work has been supported in part by the Nationaler Energie-Forschungs-Fonds and by the Schweizerischer Nationalfonds zur Förderung Wissenschaftlicher Forschung.

References

Allpress, J. G., and Sanders, J. V., 1970, *Aust. J. Phys.*, **23**, 23.
Bagley, B. G., 1974, *Amorphous and Liquid Semiconductors*, edited by J. Tauc (New York : Plenum Press).
Brodsky, M. H., 1975, *Light Scattering in Solids*, edited by M. Cardona (Berlin : Springer-Verlag).
Dandoloff, R., Döhler, G., and Bilz, H., 1980, *J. non-crystalline Solids*, **35–36**, 537.
Döhler, G. H., Dandoloff, R., and Bilz, H., 1980, *J. non-crystalline Solids*, **42**, 87.
Evangelisti, F., Proietti, M. G., Balzarotti, A., Comin, F., Incoccia, L., and Mobilio, S., 1981, *Solid St. Commun.*, **37**, 413.
Frank, F. C., 1952, *Proc. R. Soc.* A, **215**, 43.
Gaskell, P. H., 1979, *J. Phys.* C, **12**, 4337.

GASKELL, P. H., GIBSON, J. M., and HOWIE, A., 1977, *The Structure of Non-crystalline Materials*, edited by P. H. Gaskell (London : Taylor & Francis Ltd), p. 181.
GRIGOROVICI, R., 1974, *Amorphous and Liquid Semiconductors*, edited by J. Tauc (New York : Plenum Press).
GRIGOROVICI, R., and MANAILA, R., 1969, *J. non-crystalline Solids*, **1**, 371.
GUINIER, A., 1963, *X-Ray Diffraction* (San Francisco : Freeman).
HORAE, M. R., and BARKER, J. A., 1976, *The Structure of Non-crystalline Materials*, edited by P. H. Gaskell (London : Taylor & Francis Ltd), p. 175.
HORAE, M. R., and PAL, P., 1975, *Adv. Phys.*, **24**, 645.
IQBAL, Z., and VEPŘEK, S., 1981, *J. Phys.* C (in the press).
JOHANNESSEN, J. S., 1974, *Phys. Stat. Sol.* (a), **26**, 571.
KAMIYA, T., KISHI, M., USHIROKAWA, A., and KATODA, T., 1981, *Appl. Phys. Lett.*, **38**, 377.
KITTEL, C., 1971, *Introduction to Solid State Physics*, fourth edition (New York : Wiley).
LANDAU, L. D., 1937, *Phys. Z. SowjUn.*, **11**, 26.
MÜLLER, G., and KALBITZER, S., 1977, *Proceedings of the Fourth International Conference on Non-crystalline Solids*, edited by G. E. Frischat (Trans. Tech.), p. 278.
MOTT, N. F., and DAVIS, E. A., 1979, *Electronic Processes in Non-crystalline Materials* (Oxford : Clarendon Press).
PHILLIPS, J. C., 1979, *J. non-crystalline Solids*, **34**, 153 ; 1981, *Ibid.* (to be published).
RUDEE, M. L., and HOWIE, A., 1972, *Phil. Mag.*, **25**, 1001.
SPAEPEN, F., 1974, *Phil. Mag.*, **30**, 417.
SPEAR, W. E., WILLEKE, G., LE COMBER, P. G., and FITZGERALD, A. G., 1981, *J. Phys., Paris* (in the press).
VEPŘEK, S., 1980, *Chimia*, **34**, 489.
VEPŘEK, S. IQBAL, Z., OSWALD, H. R., SAROTT, F. A., and WAGNER, J. J., 1981 *a*, *J. Phys., Paris* (in the press).
VEPŘEK, S., IQBAL, Z., OSWALD, H. R., SAROTT, F.-A., WAGNER, J. J., and WEBB. A. P., 1981 b, *Solid St. Commun.* **39**, 509.
VEPŘEK, S., IQBAL, Z., OSWALD, H. R., and WEBB, A. P., 1981 c, *J. Phys.* C, **14**, 295.
WEINSTEIN, F. C., and DAVIS, E. A., 1973/74, *J. non-crystalline Solids*, **13**, 153.
WILD, R., 1979, Ph.D. Thesis, University of Zürich.
WONG, J., and ANGELL, C. A., 1976, *Glass Structure by Spectroscopy* (New York, Basel : Marcel Dekker).