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BOND ORDERING IN NONCRYSTALLINE SOLIDS

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Résumé - A partir de l'analyse des propriétés optiques des solides non cristallins (nc) et des solides cristallins correspondant avec des liaisons à caractère covalentiel prédominant, on obtient un paramètre d'ordre F . Ce paramètre détecte les différences entre les solides nc caractérisés par un ordre à courte distance semblable p. ex. Si amorphe ($F < 0,8$) et silice vitreuse, SiO_2 ($F \approx 1$). Les propriétés optiques et électroniques indiquent que, contrairement aux solides amorphes, dans les solides vitreux, les états électroniques peuvent demeurer délocalisés même s'il n'y a pas d'ordre à longue distance.

Abstract--From the analysis of optical properties of noncrystalline (nc) and the corresponding crystalline solids with predominantly covalent bonds a bonding order parameter, F , is derived. This parameter reveals differences between nc solids which are characterized by similar degree of short-range-order as, e.g., amorphous Si ($F < 0.8$) and vitreous SiO_2 ($F \approx 1$). Both the optical and electrical properties indicate that, in contrast to amorphous solids, the electronic states in vitreous solids may remain delocalized even though there is no long-range-order.

1. Introduction--The structure of noncrystalline (nc) solids, as derived from diffraction experiments is usually described in terms of a radial distribution function (RDF).¹ The RDF's are often characterized by a few (up to about four) peaks corresponding to the first, second, etc. neighbor interatomic distances whose mean values generally correspond to those in the crystalline (c) solid, indicating that short-range-order (SRO) is largely preserved in nc solids even though long-range-order (LRO) is absent. Because the nc structure is not uniquely defined, it is necessary to use a model which approximates both the experimental RDF and the experimental density;¹ these models are usually based on a continuous random network (CRN) of the constituent atoms.

These CRN models do not consider local disruptions of the structure (i.e., bond breaking). Broken bonds in a nc solid do not necessarily affect the average interatomic distances and, hence, the RDF, but they can have a very significant effect on some other (e.g., optical, electrical) properties. Thus, the SRO, as derived from the RDF of a CRN model is inadequate to describe all short range features of nc solids. This shortcoming of CRN models is especially manifested in predominantly covalent nc solids in which the local atomic configurations are closely tied to local bonding. When the parameters characterizing a local configuration exceed some limiting values, the bond is broken or a new bonding associated with a new configuration arises.

2. Optical Properties as Indicators of Bond Ordering--The above mentioned inadequacy of CRN models is illustrated by the example of vitreous (v) SiO_2 and vacuum deposited (or sputtered) amorphous (a) Si. In both cases interatomic distances determined by the RDFs closely resemble those of the corresponding crystals^{2,3} so that one would expect the relationship between various properties of these nc solids to those of the corresponding crystals to be rather similar. This would be particularly true for properties which are determined by the valence band (e.g., optical properties) since the density of valence states is supposed to be primarily determined by SRO.⁴

Contrary to this expectation, the optical properties of a-Si are rather different from those of fcc c-Si but the difference between v-SiO₂ and quartz crystal is simply due to the difference in their density.⁵ This is the reason that, in contrast to a-Si, v-SiO₂ has been labelled as an optically ordered solid.⁹ The degree of order as related to optical properties can be quantitatively expressed by the normalized oscillator strength, f , derived from the frequency dependence of the optical dielectric constant, $\epsilon = \epsilon_1 - i\epsilon_2$; f is proportional to the macroscopic oscillator strength, E_d , and the normalized dimensionless coordinate matrix element, x , used in the analysis of the optical properties of solids:⁶

$$f \equiv \frac{E_d}{N d^3 Z} = \frac{30.16 \hat{x}^2}{dZ} \text{ eV} \quad (1)$$

where d is the nearest neighbor distance in Angstroms, N is the density of valence electrons per Å³, and Z is the formal chemical valency. On the basis of the behavior of f , nc solids have been classified as (1) vitreous and (2) amorphous. The f values in group (1) are almost the same as in the corresponding crystal while in group (2) they are less. This behavior has been attributed to a decrease in delocalization (increased localization) of the bonding electrons in amorphous solids which apparently does not occur in vitreous solids.⁶

It is suggested here that bond ordering (BO) in a nc solid can be derived from optical properties by using the parameter F defined as

$$F \equiv f(\text{nc})/f(\text{c}) \quad (2)$$

The f values for SiO₂ are 5.1 and 5.0 eV for quartz crystal and vitreous silica, respectively,⁶ so that $F = 0.98 (\approx 1)$. In contrast, the f values of sputtered a-Si (2.3 eV) and vacuum deposited a-Si (3.6 eV) are less than those of fcc c-Si (4.4 eV) or covalent crystals in general ($4.4 < f < 5.1$ eV),⁶ resulting in $F = 0.52$ and $F = 0.82$, respectively. Accordingly, $\sim 0.5 < [F(\text{a-Si})/F(\text{v-SiO}_2)] < \sim 0.8$, indicating that the BO in a-Si is significantly reduced relative to v-Si, even though the SRO is about the same. Another example of vitreous nc solid is As₂S₃, whereas Ge and Te are examples of amorphous solids.⁶

The discrepancy regarding BO and SRO in a-Si and v-SiO₂ is related to the fact that the wide range of Si-O-Si bond angles ($\sim 120^\circ - \sim 180^\circ$) in v-SiO₂ is not associated with broken or strained Si-O bonds but arises from the flexibility of the Si-O bond as its energy varies only by ~ 2 kcal mole⁻¹ within this range of bond angles.⁷ The range of Si-Si-Si bond angles in a-Si ($\sim 88^\circ - \sim 130^\circ$), as obtained from the standard deviation of the bond angle distribution (7°) in the CRN model with minimum distortions,⁸ is comparable to the range of Si-O-Si angle in v-SiO₂. However, as has been pointed out earlier, this wide range of Si-Si-Si bond angles (that is even wider in some other CRN models of a-Si) is incompatible with the relatively rigid sp³ hybrid bonds.⁹ It is thus very likely that the wide range of bond angles in the CRN models of a-Si is associated with broken and/or severely strained bonds or that some of the bonds are not sp³ hybrid bonds as in the fcc crystal.

According to these considerations, the local bonding environment is significantly different in a-Si from that in v-SiO₂ even though, as discussed above, the SRO in both nc solid is about the same. This important difference between a-Si and v-SiO₂ is not revealed by the current CRN models.

The relationship between BO and structure is again illustrated by the examples of a-Si and v-SiO₂. The density of EPR-active defects, i.e., broken ("dangling") bonds is of the order of $\sim 10^{20}$ cm⁻³ in sputtered or vacuum deposited a-Si and decreases during annealing to $\sim 10^{18}$ cm⁻³ as a-Si crystallizes and the optical properties approach those of fcc-Si.¹⁰ From the density of EPR-active defects their average separation in a-Si is estimated as being of the order 10^{-7} cm. Assuming that a 3-coordinated Si atom, i.e. with a broken bond, represents the end of bonding electron delocalization along all three chains of Si atoms ending at such an atom, the extent of BO is of the order of 10^{-7} cm in a-Si. In contrast to a-Si, the density of EPR-active defects in v-SiO₂ is estimated as less than $\sim 10^{13}$ cm⁻³,¹¹ so that the extent of BO is about 5×10^{-5} cm.

3. Comparison Between Bonding Orders Derived From Optical and Other Properties--In addition to the optical properties and density of EPR-active defects, a-Si and v-SiO₂ exhibit some other differences. For instance, the density of localized states responsible for hopping conduction is $\sim 10^{19} \text{ cm}^{-3} (\text{eV})^{-1}$ in a-Si.¹² In contrast, the mobility of photo-injected electrons in v-SiO₂ is $\sim 20 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,¹³ indicating that the range of localized states at the conduction band edge is negligibly small, being less than $\sim 0.025 \text{ eV}$.¹⁴ These observations indicate that, v-SiO₂ is more perfect than a-Si which is in accordance with a conclusion reached above from optical properties.

The extent of band tailing, ΔE , is also considered as a measure of disorder: $\Delta E \propto \epsilon^2$ where ϵ is a measure of deviation from SRO in the sense that the interatomic distance, a , in the one dimensional lattice becomes $a(1 + \epsilon)$ in the nc solid.¹⁵ From the ranges of localized states mentioned above, the relative BO can be derived as follows:

$$\frac{\Delta E(\text{a-Si})}{\Delta E(\text{v-SiO}_2)} = \frac{\epsilon^2(\text{a-Si})}{\epsilon^2(\text{v-SiO}_2)} = \frac{> \sim 0.2}{< \sim 0.025} > \sim 10,$$

resulting in $\epsilon(\text{a-Si})/\epsilon(\text{v-SiO}_2) > \sim 3$. In other words, v-SiO₂ appears to be at least 3 times more ordered than a-Si. As a comparison, the F values indicate a factor in the range of 1.2 - 2.0. Note that ϵ does not reflect the effects of broken or severely strained bonds and the band tailing is thought to arise from positional disorder alone.¹⁵ Because, as mentioned above, the positional disorder derived from RDF in a-Si is comparable to that in v-SiO₂, ΔE should be roughly the same. The fact, that it is not, indicates that positional disorder is an insufficient criterion.

Along similar lines to the above considerations, the calculated bandgap was suggested as a measure of disorder in CRN models of a-Si; for a series of four models characterized by 3.8%, 2.5%, 1.2%, and 1.1% relative standard deviations in the bond length distributions as well as by 12.3°, 13°, 11.5°, and 7.1° standard deviations in the bond angle distributions, the bandgap values were found to be 0, 0.67, 1.26, and 2.19 eV in the above order.¹⁶ Note that, despite the significant variation in the spread of the parameters, all these models reproduce reasonably well the experimental RDF. Also note that the large variation in the calculated bandgap does not result from the effects of broken bonds since continuity is assumed in the models.

5. Concluding Remarks--From a comparison of the optical properties of covalently bonded noncrystalline (nc) and crystalline (c) solids a bond ordering parameter has been defined; its value is about one for vitreous nc solid and less than one for amorphous solids. Bond ordering refers to structure associated with the covalent bonds, whereas the disorder parameter, ϵ , used above refers to lattice (for the crystal) or network (for the nc solid). The absence of long-range-order (LRO) in the nc solid is thought to arise from the cumulative effects of deviations in short-range-order (SRO): The deviation from the correct position increases with n as the distance between the n th and $(n + 1)$ th network point, given as $na(1 + \epsilon)$, increases with n .¹⁶ This is obviously not the case with v-SiO₂ where the SiO_{4/2} tetrahedra associated with the network points are invariant. Anderson localization in nc solids is thought to be affected by variation in bond angles or fluctuations in density which would lead to a random potential.¹⁷ Obviously, this is again not the case with v-SiO₂.

The failure of various disorder parameters to describe the properties of vitreous solids results from two factors. One is that the frequently implied one-to-one correspondence between network and structure is not valid when the network points are associated with a structural unit comprising more than one atom. The second factor is that the nature of localized bonds is not considered as the disorder parameters refer to positional disorder alone.

The key feature of bond ordering is bond flexibility resulting in structural flexibility. If there is only one kind of predominantly covalent bond which is inher-

ently flexible (i.e., the bond energy changes very little with the bond angle by which the quasi-invariant structural units are linked as e.g., in $v\text{-SiO}_2$), then the nc solid is vitreous. In quasi-vitreous solids the flexibility can arise from mixing two or more kinds of bonds. These bonds may be between identical atoms but are characterized by more than one kind of hybridization state and, hence, by different local configurations as, for instance, in nc-Se.¹⁸ It is also possible that two or more different kinds of atoms are involved as in nc-Si_{1-x}H_x and nc-Si_xN_yH_z films.

In vitreous and quasi-vitreous solids a relatively high degree of BO can be maintained even though there is no LRO. In contrast, those solids, in which the bond flexibility is reduced (e.g. Si where the sp^3 hybrid bonds are rather rigid), are usually amorphous when they are in the nc state. Here, the lack of LRO is associated with reduced BO as many bonds are broken or severely strained.

Bond ordering plays a key role in the correlation between bond parameters, such as, bond lengths and angles as, for instance, in $v\text{-SiO}_2$. The correlation is, in turn, responsible for localized ordering in vitreous solids as manifested by structurally ordered tridymite-like regions¹⁹ and "pre-ordered" domains²⁰ in $v\text{-SiO}_2$ as well as by "structural channels"²¹, particularly, in SiO_2 films obtained by thermal oxidation of silicon.

In conclusion, these arguments demonstrate that bond ordering associated with bond and structural flexibility plays a more fundamental role in determining the properties of nc solids with predominantly covalent bonds than short-range-order derived from continuous random network models.

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