

## LETTER TO THE EDITOR

# Two-level systems: a possible structure and its role in amorphisation

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**Abstract.** We show that a particular interstitial structure in c-Si has both ring structures characteristic of a-Si and low-energy excitations of a tunnelling type and a bond-switch (soliton) type. These excitations exist for reasons of symmetry, not because of anomalous bond angles or lengths. We suggest these defects may act as nuclei for amorphisation under irradiation and offer a possible explanation of the observed relation between tunnelling level systems and the extent of amorphisation in quartz.

It is well known that the thermal properties of amorphous solids deviate from the predictions of the Debye model at very low temperatures (for a survey, see Elliott 1984). The specific heat and thermal conductivity are affected, and the changes are customarily described in terms of tunnelling systems or two-level systems. Phenomenologically, this is successful. However, when one seeks atomic models, there are surprisingly few on offer: site switching involving bridging atoms such as oxygen, rotations of tetrahedra, or possibly impurities such as hydrogen. There are, of course, extensive discussions of continuous random networks (see especially Rivier 1987) and of possible ways that these might be constructed systematically from corresponding crystalline networks (e.g. Weaire and Wooten 1985, Wooten and Weaire 1985). In most discussions the tunnelling systems are unplanned side effects of the randomisation, identified only by deforming the final amorphous structure. Moreover, such tunnelling systems are normally taken to be one-atom tunnelling states (e.g. Smith 1979). In our present paper we draw attention to a distinct and general class of possible tunnelling centres, and one which has particular promise for such systems produced during radiation amorphisation. Since we are concerned primarily with the initiation of the amorphous structure, it is possible to illustrate this class of two-atom tunnelling states by a specific crystal defect.

The particular example we discuss is the so-called Jackson interstitial (Kimerling 1979) in silicon, though other examples will certainly be possible. The Jackson interstitial has a very complicated structure of low symmetry, though it can be understood quite simply by imagining its creation in a (fictitious) two-step process. First, remove four adjacent Si atoms, namely an equilateral triangle of three atoms, A, B and C, and their common neighbour, D. The result at this intermediate stage has two key features. The system

still has threefold symmetry about the axis through D and the mid-point of ABC, and there are ten dangling bonds (three each previously joined to A, B, C, and one previously joined to D). The second step inserts a five-membered ring, its ten dangling bonds saturating those left at the first step. The whole system then relaxes to equilibrium. The net effect of both steps is to insert a single extra Si atom. The final structure contains both a five-membered ring and several other odd-membered rings which we need not discuss.

The secondary consequences concern structure: the symmetry is lowered (the five-membered ring does not share the trigonal symmetry in any reasonable circumstances) and the topology is changed. Five-membered rings are indeed a common feature of models of amorphous solids, and are not found in the crystal.

In the present Letter we are not concerned with the formation energy of this complex interstitial, nor with its mode of diffusion or its numbers in thermal equilibrium. These will be the subject of a separate paper (for a preliminary note, see Torres *et al* 1986). For the present purposes we observe simply that this interstitial does not appear to have the lowest free energy of the many possible interstitials, nor is it high enough in energy to be ignored. Further, the relaxed geometry has low symmetry, but all reasonable interatomic potentials give rather similar geometries, even though the energies they indicate vary greatly. We shall need to suppose only that a certain number of Jackson interstitials are formed under irradiation, and that these are at least metastable.

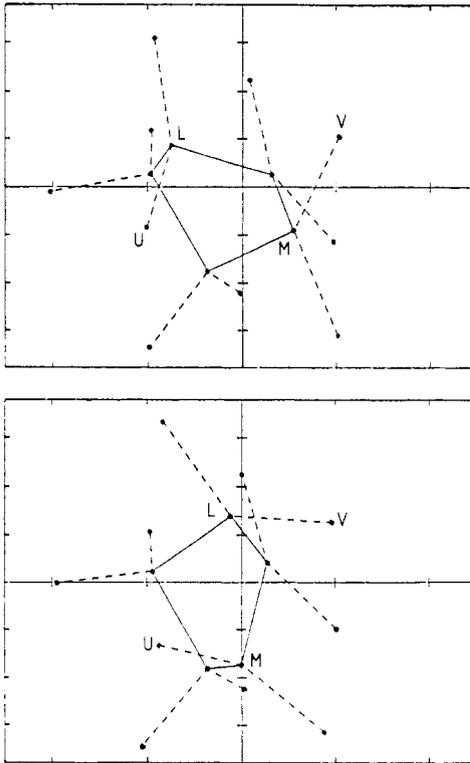
The lack of symmetry is the origin of the most interesting feature. For each choice of atoms removed (step one above) there are six equivalent ways in which it is possible to orient the five-membered ring. This is quite general: these orientations are related to one another by the rotations about the threefold axis through D and the midpoint of ABC and by reflections in the planes defined by AD, and the threefold axis (or the corresponding planes involving BD and CD). Even at this stage, one can argue that there is the possibility of tunnelling motion. How important it is clearly depends on the nature of the atomic motions needed to make a transition from one to another of these equivalent sites.

Closer inspection shows another type of motion, shown in figure 1. The sole effect here is to switch two bonds. If we label the two relevant atoms of the five-membered ring L and M, and if U and V are the two key atoms that are not part of the ring, the sole effect is that bonds LU and MV switch to become LV and MU. Since the other atoms do not change sites, but we have a change in the bonding pattern, we have an analogue of the so-called solitons in some conducting polymers.

We may now look at the physical consequences. First, we note that five-membered rings are a characteristic feature of models of amorphous solids like a-Si. Secondly, we note that the insertion of a five-membered ring into c-Si in the manner of a Jackson interstitial automatically (i.e. as a result of symmetry, rather than special values of bond lengths or angles) leads to low-energy excitations, either of the tunnelling type or of the soliton type. Thirdly, such low-energy excitations have the general character of the tunnelling systems or two-level systems or two-level systems that affect the specific heat and thermal conductivity.

A natural conclusion would be that, at least in radiation-induced amorphisation, a modest population of Jackson interstitials would provide at the same time both structural (ring-type) and thermal effects, these being regarded usually as separate phenomena. This conclusion would not necessarily apply to silicon alone, for it is possible to envisage similar defect structures in many crystals of high symmetry.

The picture may be too simple in one important respect. When there is a significant



**Figure 1.** The bond-switch motion of the Jackson interstitial in silicon. Here the atomic positions are projected onto a (111) plane, the origin corresponding to the (111) axis through original atom D and the mid-point of the original atoms A, B, C (atoms A, B, C, D being those removed prior to inserting the five-membered ring). The ring is shown by full lines. The bond lengths are, in fact, all close to their perfect-crystal values, the apparent differences resulting from the projection), and the broken lines show bonds to other atoms. The switch is (LU, MV)  $\rightarrow$  (LV, MU).

number of these defects, they may interact so as to lose the low-energy excitations, i.e. so that one defect interferes with another. We expect only the interstitials which remain isolated to be important thermally, whereas the structural features will remain. This is consistent with recent experiments on neutron-irradiated quartz (Van Reyten and Michiels 1987) where the observed dependence of the velocity change with temperature on the dose is different from that of the amorphous cluster density. The results were consistent with the view that the two-level systems acted as nuclei from which the amorphous regions developed rather than merely correlating with amorphous zones. Whilst the case for quartz is more complex than that of silicon discussed above, the similarities (e.g. four-coordinated  $\text{SiO}_4$  tetrahedra instead of four-coordinated Si) are such that we again expect behaviour of this type. In quartz, the analogue of the Jackson interstitial tunnelling would presumably appear as coupled rotations of  $\text{SiO}_4$  tetrahedra, as observed by Buchenau *et al* (1984, 1986).

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