Electronic and vibrational spectra of 10-Å selenium clusters; cluster model of amorphous selenium

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The electronic and vibrational structures of 10-Å cluster of selenium and those of bulk amorphous selenium have been found similar. This similarity is taken as justification for the use of the cluster method to describe the properties of amorphous selenium.

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The cluster method is winning increasing popularity for describing the properties of solids. In this theoretical approach, the properties of bulk objects are modeled by working from the properties of clusters (sets of finite numbers of atoms). This approach has been successful in several cases in analyzing the physical properties and structures of both crystalline and amorphous materials. In particular, some recent papers[1,2] have shown that amorphous selenium (*a*-Se) should be regarded as a quasidisordered structure with a completely definite short-range order within a cluster of radius 11 Å. It is thus clearly of interest to determine the extent to which the various properties of selenium clsuters may determine the properties of *a*-Se.

Using the experimental matrix method of Ref. 3, we can arrange an actual partition of the material into particles a few angstroms in size. In the present experiments we studied 10-Å clusters of selenium stabilized in the cavities of NaA zeolite through adsorption of selenium vapor at $T \sim 500$ °C. The size and concentration of the clusters are determined by the diameter (11.4 Å) and number of large cavities per 1 cm^3 of the NaA (5.36×10^{20}). The average number of Se atoms in a cavity, $n \approx 18$ (the number of atoms in a cluster), is determined from the density of the resulting NaA-Se crystals. Since single crystals of the original NaA zeolite are 20–40 μm in size, the measurements were carried out in powdered samples. Diffraction patterns of powders of the original NaA zeolite and of the NaA-Se showed that the lattice constant of the zeolite is $a \approx 12.31$ Å and that the extent of crystallinity is not altered by the addition of selenium. Zeolite is essentially transparent in the visible, near-UV, and near-IR regions, and it has a very faint Raman-scattering spectrum, so it is a convenient matrix for studying the optical properties of clusters.

We studied the electronic properties (the absorption spectra) and the vibrational properties (the Raman spectra) of 10-Å selenium clusters synthesized by the method described above. The Raman spectra were measured in a 90° arrangement with a DFS-24 double monochromator, with excitation by the 5145-Å line of an Ar^+ laser. The NaA-Se powder was held in a rotating glass cell to avoid overheating. The Raman spectra of these powdered samples were completely depolarized. We obtained information on the absorption spectra by measuring the diffuse-reflection spectra with an SF-16 spectrophotometer with a standard diffuse-reflection attachment.

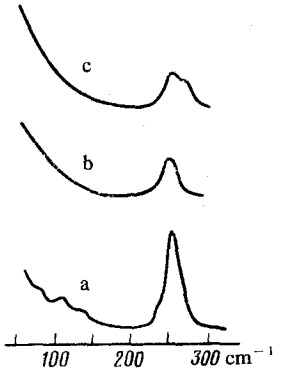

FIG. 1. Raman spectra. a—*a*-Se (Ref. 4); b—selenium clusters stabilized in the cavities of NaA zeolite; c—single bonds of selenium stabilized in the channels of mordenite by the method of Ref. 7.

The Raman spectrum of the 10-Å selenium clusters (Fig. 1b) contains only one band, peaking at 258 cm^{-1}, which is intense enough to be detected. This result agrees well with the Raman spectrum of *a*-Se (Fig. 1a), which also has only a single intense band, peaking at 256 cm^{-1}. This band result from the symmetric extension of the bonds in the case of two-coordination Se atoms. As was shown in Ref. 5, the frequency of this vibration depends strongly on the positions of not only the nearest but also the more remote neighbors of the Se atom. If thus follows from the Raman spectrum of a 10-Å selenium cluster that the relative positions of the atoms in the cluster are the same as the coordination of atoms in *a*-Se. It also follows that the vibrational spectrum of *a*-Se is formed in the 10-Å cluster itself.

It has been assumed in several places[4–6] that the Raman spectrum of *a*-Se may be determined by the vibrations of single selenium bonds. This assumption is refuted, however, by the observation that although single selenium bonds do have an electronic spectrum analogous to that of *a*-Se (Ref. 7), their Raman spectrum (Fig. 1c) differs significantly from that of *a*-Se in having a doublet structure.

Another effect which clearly demonstrates the analogy between the physical properties of *a*-Se and a 10-Å selenium cluster is the photoinduced absorption (photodarkening) which occurs at low temperatures. This effect, which is related not only to the details of the electronic structure but also to the presence of certain defects in semiconductors of the *a*-Se type,[8] was also observed in the case of the 10-Å selenium clusters in the present experiments during illumination with light at $\lambda = 5145$ Å at $T = 77$ K. In contrast with *a*-Se, the effect is not exhibited by the clusters when illuminated at $\lambda = 6328$ Å, because of the high-energy shift of the absorption edge of the 10-Å selenium cluster in comparison with that of *a*-Se (Fig. 2). The magnitude of the observed shift agrees well with an order-of-magnitude estimate of the energy of a particle moving in a bounded region[9] $E \sim \hbar^2/ml^2 \sim 10^{-1}$ eV, where the particle mass m is assumed equal to the mass of the free electron, and the linear dimension of the region of motion is $l = 10$ Å. We believe that these results demonstrate that *a*-Se has electronic states which are unlocalized (at least within 10 Å) and which undergo a size quantization when the bulk material is partitioned into 10-Å clusters. The electronic

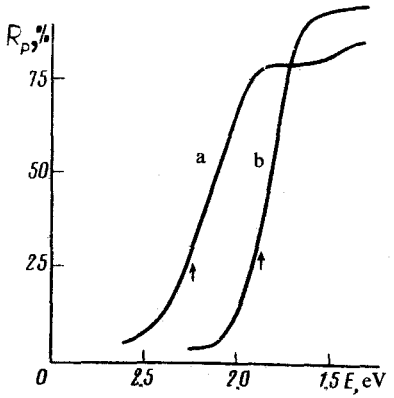

FIG. 2. Diffuse-reflection spectra (the arrows show the positions of the absorption edge E_0, determined in accordance with Ref. 10). a—NaA-Se, $E_0 = 2.24$ eV; b—a-Se, $E_0 = 1.86$ eV (Ref. 10).

properties of the 10-Å selenium cluster may thus be regarded as the electronic properties of a-Se, subjected to some perturbation. There is a qualitative similarity between the electronic structures, including the defect states.

For further proof of this similarity we attempted to observe the photoluminescence spectrum of selenium clusters. Since the luminescence of a-Se results from transitions between localized states according to the generally accepted Street model,[8] no shift of the luminescence band (0.8 eV) of a selenium cluster should be observed. In fact, we found a band in this region in the luminescence spectrum of NaA-Se, but it is difficult to unambiguously identify this band with the emission of clusters because of the possible appearance of defects in zeolite when selenium is added to it. These defects would luminesce in the same spectral range. The question thus requires further investigation.

Summarizing this study, we can assert that the basic features of the electronic and vibrational structures of a-Se are present even in a 10-Å cluster. This result is an experimental justification for the cluster model, in which a-Se is treated as a set of clusters ~ 10 Å in size. For a better quantitative agreement with the electronic properties of a-Se, we should impose certain boundary conditions which rule out the scattering of electrons by artificial boundaries between clusters. It might be possible to generalize these conclusions in the sense that they might be applicable to other amorphous materials.

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