

Size effects in the vibrational spectrum of 10-Å selenium particles

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Raman spectra of ensembles of isolated and bound 10-Å clusters of Se (a three-dimensional network) have been measured over the range 10–300 cm^{-1} . Size effects have been discovered: discrete structure in the vibrational spectrum of an isolated cluster and an increase in the matrix element for Raman scattering by low-frequency modes. These size effects are seen for clusters of both types.

A limitation on the size of a solid in one dimension (a filament), in two dimensions (a film), or in three dimensions (a cluster) leads to changes in the structure and electronic and vibrational spectra because of size effects. Experiments on size effects in clusters are usually carried out with ensembles of clusters stabilized in solid-state matrices. In Ref. 1, size effects were studied in the electronic optical spectra of 10-Å clusters of Se stabilized in matrices of zeolite crystals. In the present letter we report the observation of size effects in the vibrational spectra of these systems: the Raman scattering spectra measured in the frequency regions of both optical and acoustic

modes of bulk selenium. The size effects of the type seen in these experiments have been the subject of extensive theoretical study, but, to the best of our knowledge, there has been no previous direct experimental observation of these effects.

As in Ref. 1, the experimental samples are two types of ensembles of $\sim 10\text{-\AA}$ clusters of Se stabilized in matrices of zeolite crystals of types *A* and *X*. The structure of these porous aluminosilicate matrices is such² that neighboring clusters are isolated from each other in the zeolite matrix of type *A*, while in the matrix of type *X* they have common covalent bonds and form a three-dimensional network of bound clusters.¹ The concentration of the selenium, which is supplied to the zeolite cavities by adsorption, is determined from measurements of the densities of the *A*-Se and *X*-Se crystals (zeolites of types *A* and *X* with Se); the results are ~ 18 and ~ 21 atoms per cavity (cluster), respectively. Clusters of chalcogenides in zeolite cavities are under conditions of physical adsorption, so that the matrix has little effect on their properties.³ Furthermore, the matrices of these zeolites are similar in both chemical composition and physical and chemical properties,² so that, on the basis of the discussion above, we can directly distinguish the size effects in their properties by comparing the properties of ensembles of "isolated" clusters and clusters that are "sewn together."

The Raman spectra measured at room temperature in a 180° geometry with the help of a DILOR RTI-30 triple monochromator (manufactured in France) with excitation by the 5145-\AA line of an Ar^+ laser. The powdered samples of *A*-Se and *X*-Se are held in a rotating glass cell to avoid overheating.

Studies of the Raman spectra of *A*-Se in the region of valence and deformation vibrations have shown^{4,5} that the structure of the clusters in *A*-Se is similar to the microstructure of amorphous selenium (*a*-Se). In the present study we measured the low-frequency part of the vibrational spectrum ($10\text{--}100\text{ cm}^{-1}$), in addition to carrying out a more detailed study of the spectrum of valence and deformation vibrations of clusters in zeolite *A*. A similar study was carried out for a network of Se clusters in zeolite *X*.

Figure 1 shows relative Raman spectra of (b) *A*-Se and (c) *X*-Se. In the low-frequency part of the spectrum of the isolated clusters, we clearly see a size effect, consisting of a discrete spectral structure. In contrast with the continuous background

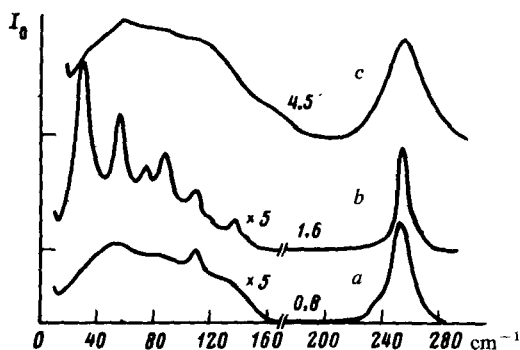


FIG. 1. Relative Raman scattering spectra $I_0(\nu)$ of (a) amorphous selenium⁶ and (b) isolated and (c) bound 10-\AA Se clusters. The numbers are the ratios of the total intensities of the low-frequency and high-frequency parts in each spectrum. $I_0(\nu) = I_{\text{expt}}(\nu)(1 - e^{-h\nu/kT})$

spectrum of bulk α -Se, with a minimum frequency $\nu_{\min} = 0$, in the discrete spectrum of the clusters we have $\nu_{\min} \neq 0$, and this minimum frequency depends on the size of the cluster. If we assume that the dispersal of the α -Se has no effect of any sort on its structure, the value of ν_{\min} of an α -Se particle with a linear dimension α will be determined by the frequency of the first resonance of the transverse acoustic mode: $\nu_{\min} \sim v_t/2cd$, where $v_t = 0.98 \times 10^5$ cm/s is the velocity of a transverse acoustic wave in α -Se (Ref. 7), and c is the velocity of light. For a 10-\AA α -Se particle we have $\nu_{\min} \sim 16$ cm^{-1} . This value agrees fairly well with the observed spectrum (Fig. 1b) of a 10-\AA Se cluster.

The Raman spectra of X -Se and α -Se agree in terms of the positions of the structural features, but they disagree noticeably in terms of the intensity ratio of the high-frequency valence-vibration band and the low-frequency band peaking at $50\text{--}60$ cm^{-1} . In the X -Se spectrum, this low-frequency band is nearly an order of magnitude more intense than the corresponding band in the α -Se spectrum. This intensification can be linked with a change in the matrix element for the inelastic scattering of light by low-frequency vibrations during the dispersal of the Se, under the assumption that the spectra of the density of vibrational states of α -Se and Se in zeolite X are essentially the same. The manifestation of a low-frequency band in the Raman spectrum of α -Se is due to a violation of the selection rule in terms of quasimomentum in the disordered system (this band is dominated by acoustic vibrations⁶). During the dispersal of Se, there can be another effect, which also stimulates a manifestation of low-frequency vibrations in the Raman spectrum. This effect, discussed in Ref. 8, consists of a controlling contribution of surface atoms to the effectiveness of the Raman scattering by vibrations of the microcrystal, which are inactive in the case of the bulk material. Application of the theoretical conclusions of Ref. 8 to the case of X -Se leads to a substantial increase in the 60-cm^{-1} band in the Raman spectrum, since in this case more of the Se atoms are at the surface of the profiled bulk material, which is a three-dimensional network of clusters in X -Se. It should be noted that the total intensity of low-frequency modes in the Raman spectrum of isolated 10-\AA clusters in α -Se is lower than that in the spectrum of X -Se. The reason is a natural decrease in the number of low-frequency vibrational states of such small particles. The half-width of the valence-vibration band (35 cm^{-1}) in the Raman spectrum of the network of clusters is significantly greater than that in the Raman spectrum of α -Se (18 cm^{-1}), but it agrees with the half-width of the corresponding band in the spectrum of the vibrational-state density of α -Se (35 cm^{-1} ; Ref. 9). We attribute this effect to a violation of the selection rules in X -Se caused by the surface atoms, which leads to the appearance of all the valence modes in the Raman scattering. In the case of the isolated clusters, which may be thought of as a quasimolecule, the selection rules are of course more stringent. For this reason, the Raman spectrum is dominated by a single band of a symmetric valence vibration, which is responsible for the small half-width of the valence-vibration band of α -Se (10 cm^{-1}). In particular, the narrowness of this band emphasizes the identity of the Se clusters which make up this macroscopic ensemble.

The structure and properties of these α -Se and X -Se samples make these samples model entities for illustrating the shaping of the structure and of the phonon spectrum of α -Se. The Se clusters in α -Se, which are elementary formations of ~ 18 atoms, have many features in their vibrational spectrum which are characteristic of the amorphous

bulk material. This circumstance is a consequence of the similarity of the structure of a cluster to the microstructure of *a*-Se. In the vibrational spectrum of the clusters, however, a size effect is seen as the appearance of a discrete structure in the low-frequency part of the spectrum. This circumstance causes their spectrum to differ substantially from the continuous spectrum of *a*-Se. This difference disappears in the three-dimensional network of bound clusters (*X*-Se crystals) because of the removal of the size-effect boundaries.

The operations realized experimentally—the breakup of the bulk material and of clusters and the “sewing together” of these clusters—are essentially similar to the method that is used in calculating the spectra of solids and that is known in theoretical physics as the Bethe lattice method.¹⁰ This analogy suggests one practical application of the results found here: The phonon spectrum of *a*-Se can be calculated by the Bethe lattice method with clusters of ~ 20 Se atoms.

The possibility of clearly observing size effects in the vibrational spectra of macroscopic ensembles of clusters in zeolites creates an opportunity for studying structural features, the nature of bonds, and phase transitions in low-dimensionality systems. The primary advantage of ultradisperse zeolite systems in their uniqueness in terms of both the smallness and the identical dimensions of the clusters.

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