

Absorption spectra of three-dimensionally-ordered system of 12-Å particles

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We investigated the absorption spectra of a regular system of 12-Å particles—clusters of Se in the zeolites NaX and NaA. The obtained spectral curves correspond to the absorption spectra of the crystals in the region of interband transitions. Depending on the type of lattice made up by the clusters, a shift of the absorption edge by approximately 1 eV is observed.

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A number of recent papers deal with the introduction of liquid metals under pressure into channels of different zeolites. It is noted that after the pressure is removed the zeolite channels remain filled with the metal atoms, and the result is either a regular three-dimensional system of "drops"—clusters (10–15 atoms each), or a system of parallel chains of metal atoms inside the dielectric matrix of the zeolite.^[1,2] Depending on the type of zeolites, NaX (Fig. a) or NaA (Fig. b), the system of clusters form a diamond-type lattice, or a primitive cubic lattice, respectively. It was suggested in^[1-3] that an interaction exists between the clusters, i. e., that "secondary crystals" are produced with corresponding collective properties.

In the present study, the regular system of cavities in the zeolites NaX and NaA was filled with selenium. The resultant crystals had two different colors, dark red and yellow. It should be noted that the anhydrous zeolites are transparent in the spectral range of at least from 160 nm (according to our data) to μ .^[4] We measured the absorption spectra of the obtained "secondary crystals" of selenium, SeX (Se introduced into the zeolite NaX) and SeA (Se introduced into NaA). In view of the very small dimensions of the samples, which were single crystals in the form of cubes (SeA) or octahedra (SeX) with dimensions 0–30 μ , the measurements were performed in the spectral region 400–800 nm with a spectrophotometer having an attachment for microscopic samples. The attachment made it possible to investigate a crystal region measuring 5 μ , obtaining at the same time all the advantages of spectrophotometry. We obtained in this manner the optical-density spectra of the investigated single crystals. All the measurements were performed at room temperature. The spectra (Figs. c and d), starting with a definite energy of the incident light quanta, reveal an abrupt increase of the absorption coefficient. To plot the spectra in the short-wave region, where the optical density of the investigated samples is high (larger than 3), it was necessary to shift the null level artificially towards lower density by introducing an attenuator in the comparison channel. According to our estimates, the absorption coefficient in the region of the plateau is of the order of $0.5 \times 10^4 \text{ cm}^{-1}$.

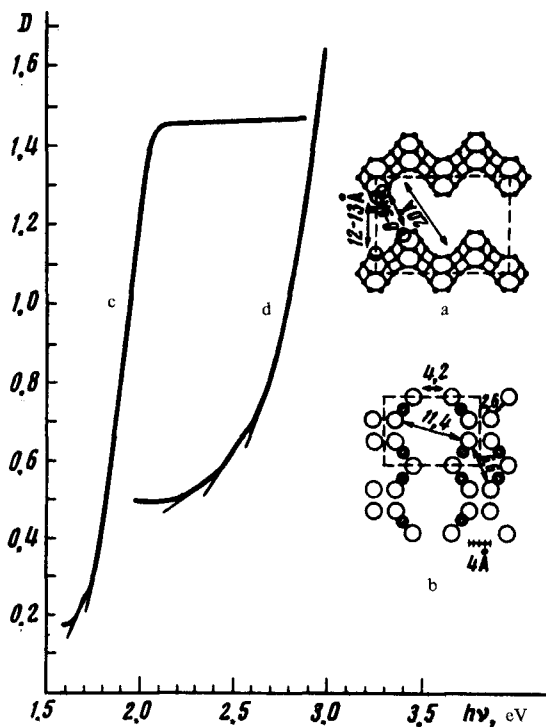


FIG. The structure of zeolite NaX in the (011) plane (a), the structure of zeolite NaA in the (110) plane (b), and optical-density spectra of the crystals SeX (c) and SeA (d).

The form of the spectra obtained by us is typical of absorption spectra of crystals in the region of the optical-absorption edge. The absorption coefficient in the plateau region also favors this comparison. Since the zeolite is transparent in the investigated spectral region, we can apparently conclude that the lattice of the clusters produced in the zeolite cavities is also a crystal, and the obtained spectral curves correspond to the absorption spectra of such "cluster" crystals in the region of the interband transitions.

The position of the absorption edge of the SeX crystal was shifted by an amount 0.8–0.9 eV towards the longer wavelengths relative to the absorption edge of the SeA crystal. In addition, a step (SeX) or two steps (SeA) can be seen on the long-wave sections of the spectra of both crystals. In the interpretation of the obtained spectra it is apparently necessary to call attention to the different relative arrangements of the selenium clusters located in cavities of zeolites of different types.

Although the dimensions of the cavities in the zeolites NaX and NaA are almost the same, 12 and 11.4 Å, respectively, these cavities are interconnected in the zeolites in different manners. In first-order approximation it can be assumed that the cavities are spherical. The nearest cavities in the NaX zeolite noticeably overlap each other (Fig. a), whereas in NaA (Fig. b) a gap of approximately 1 Å separates the edges of the cavities. Therefore, whereas the clusters in NaX can go over continuously into each other, forming a crystal with a modulated density of the introduced substance, in NaA the edges of the neighboring clusters are separated by distances on the order of 1 Å, which

obviously leads to a weakening of the interaction between them. Unfortunately, we still do not know the detailed structure of the clusters. However, if an individual cluster in a zeolite cavity is regarded as a microcrystal, then the latter is probably under the conditions of the quantum size effect. The larger interaction of such microcrystal-clusters, regardless of the details of the structure, will be accompanied by a larger broadening of their electron levels. This effect can apparently lead to a long-wave shift of the absorption edge of the SeX crystal relative to the absorption edge of SeA, in which the interaction between the clusters is weaker.

The presence of steps on the absorption edges of the SeX and SeA crystals can be attributed both to singularities of the electron spectra of the individual clusters and to the "miniband" character of the spectra of the crystals, which have an additional superlattice potential. It appears that SeX and SeA can be regarded as crystals with three-dimensional superlattice, with the periodicity of the superstructure governed by the periodicity of the channels and cavities of the zeolites, while the rigor with which the periodicity holds is determined only by the perfection of the zeolites matrix.

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