Absorption edge of a semiconductor NaX-Se superlattice

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Anisotropic NaX-Se crystals were obtained by filling with selenium the channels of the isotropic zeolite matrix NaX. Their Raman, reflection, and transmission spectra were measured. It is concluded from the data for the optical properties and geometry of the matrix that the NaX-Se crystals have a superlattice structure. The characteristic features in the region of the absorption edge are interpreted as a manifestation of a miniband structure of the energy spectrum of NaX-Se.

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By using selenium introduced under pressure from the melt into a regular system of zeolite channels NaX [1)] Bogomolov *et al.*[1] demonstrated for the first time the possibility of obtaining new semiconductor crystals (NaX-Se) that are stabilized in the dielectric matrices of zeolite crystals.

In this work we introduced Se into zeolite channels by absorption. Although a x-ray photograph of the NaX-Se powder showed that the sample is a crystalline substance, we could not analyze in detail the structure of the NaX-Se single crystals because of their small size (30–40 μm). However, we can draw certain conclusions about the structure of NaX-Se by using data for the optical properties of these crystals and for the structure of the matrix.

As shown in Ref. 3, the frequencies of the natural oscillations of Se in NaX-Se coincide with those in a trigonal Se. According to the current ideas about the effect of interchain interaction on the oscillation frequencies of the Se chains,[4] we can conclude from this agreement that Se in the zeolite channels is arranged similarly to the trigonal modification of selenium, i.e., in the form of parallel spiral chains. Such occupation of channels imposes certain constraints on the arrangement of Se in the zeolite matrix, since the channels are arranged along the two-fold axes of a diamond-like zeolite lattice NaX, which cross in the cavities (Fig. 1), and the limiting occupation of a certain channel by infinite Se chains rules out an analogous occupation of all the channels that cross the channel under consideration. There are only two methods of arrangement of Se in NaX that satisfy this condition without leaving empty cavities: 1) the Se chains are arranged only along one of the two-fold axes in the parallel channels; 2) the occupation is accomplished in layers of arbitrary thickness, which are parallel to
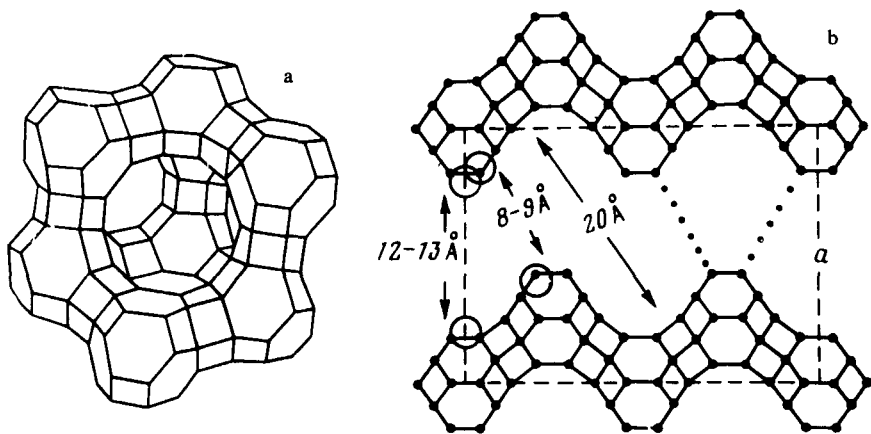
FIG. 1. Zeolite matrix NaX: (a) A fragment of the structure, (b) projection of the unit cell on the (110) plane; the projection of one band is shown schematically by the broken line.

one of the (111) planes of the zeolite; moreover, the Se chains in one layer are parallel to each other in all the channels and are rotated 120° relative to the chains of the neighboring layer. In both cases the NaX-Se crystals must reveal an anisotropy. In fact, an anisotropy was observed in the spectra of reflection (Fig. 2) from the surface of a recently cleaved NaX-Se single crystal for a normal incidence of light on the sample in mutually perpendicular polarizations, whereas the NaX matrix was optically isotropic.

On the basis of the fact that the zeolite channels are occupied by parallel Se chains, we can calculate the maximum permissible occupation of the matrix by selenium. It follows from the geometry of the NaX channels and Se chains that one channel can accommodate not more than four Se chains, and 5.3 spirally packed Se atoms can be fitted along the "effective length" of the channel of one cavity; hence, the limiting
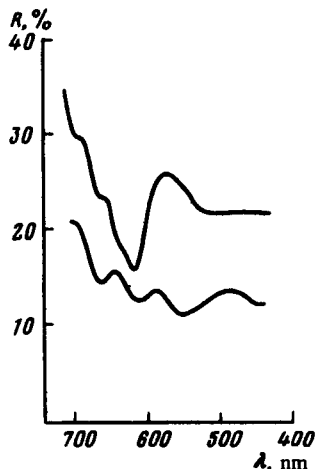

FIG. 2. Reflection spectra of a NaX-Se single crystal for mutually perpendicular polarizations of the incident light, obtained by "Blesk" microspectroreflectometer[9]; the photometric scanning range is $\sim 2 \ \mu$m.
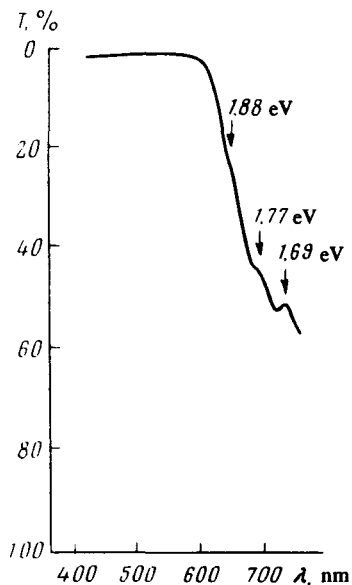
FIG. 3. Transmission spectrum of the NaX-Se single crystal ($d \sim 10$ μm) obtained by "Marsh" microspectrophotometer[9]; the photometric scanning range is ~ 2 μm.

occupation is $n = 21.2$ atoms/cavity, in good agreement with the experimental value $n = 20$–21 atoms/cavity. This also confirms the expressed assumption about the NaX-Se structure. It should be noted that the electron interaction of four selenium spirals from different channels can be disregarded, since they are separated ~ 10 Å from each other by zeolite walls.

An interesting feature of the Se chains in the NaX zeolite channel is that they are located in periodic potential field due to the zeolite matrix. The spacing of the NaX lattice along the two-fold axis is 17.5 Å, which noticeably exceeds the spacing of the Se spiral 4.95 Å. It is evident that NaX-Se is a structural superlattice (SL). A question arises as to whether electronic properties of a SL can occur in such a system.

Trigonal selenium is a p-type semiconductor in which the hole mobility along the the chain at room temperature is $\mu_\| = 30$ cm^2/V sec,[6] and the effective mass of the hole, calculated for one chain, is $m_\| = 2m_0$.[5] Using these values to estimate the uncertainty of the hole energy ΔE in NaX-Se, we obtain: $\Delta E \sim (\hbar/\tau) = (\hbar e/m_\| \mu_\|) \sim 10^{-2}$ eV. The main contribution to the periodic potential produced by the zeolite matrix apparently is attributable to the electrostatic field of the structural Na$^+$ cations which are regularly arranged in the zeolite channels. As follows from the data of Ref. 7 for the electrostatic potential produced by ions in the NaX zeolite channels, the amplitude of the proposed potential of the SL is $A \gg \Delta E$, which indicates that the miniband structure of at least the valence band can be resolved. An analogous estimate for an electron does not seem possible because of the absence of reliable data for the μ electron in the trigonal Se.

We can see 1.69, 1.77, and 1.88-eV increments in the region of the absorption edge in the transmission spectrum of a ~ 10-μm-thick NaX-Se single crystal (Fig. 3). The onset of intensive increase of the absorption corresponds to the energy $E_{g0} = 1.9$

eV,[2] which almost coincides with the width of the forbidden band of the trigonal Se.[6] Thus, the absorption increments are located on the long-wave side of E_{g0}, and the absorption spectrum of NaX-Se has a similar shape to that of the SL with a covariant band modulation,[10] i.e., the absorption increments may be interpreted as a manifestation of the miniband structure of the superlattice with a SL potential of an electrostatic nature.

It should be noted that the electrons and holes in the zeolite channel exist under size-quantization conditions when they move at right angles to the chain. This effect may also involve the appearance of a structure in the absorption spectrum, but the structure attributable to size quantization cannot have a long-wave shift relative to the absorption edge of a massive semiconductor.

Thus, the obtained results justify considering NaX-Se a semiconductor that has a structure and electronic properties of a superlattice.

[1] The zeolite structure is analyzed in detail in Ref. 2.
[2] E_{g0} was determined according to Fochs method[8] from the spectra of diffusive reflection of NaX-Se powder.

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