

Optical absorption of quasi-one-dimensional lattice of selenium filaments in mordenite channels

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(Submitted February 19, 1980)

Pis'ma Zh. Eksp. Teor. Fiz. **31**, No. 11, 617–619 (5 June 1980)

Chains of Se atoms in a system of one-dimensional, parallel channels (6.6 Å diameter with the channels separated by a distance of 13.7 Å) in single crystals of natural mordenite NaM were obtained. The properties of materials, whose optical absorption has severe anisotropy, are compared with a massive Se. The optical conductivity along the filaments is $\sim 0.14 \text{ ohm}^{-1}\text{cm}^{-1}$, which is considerably higher than that of the massive material. The obtained material can be considered a quasi-one-dimensional crystal consisting of inorganic polymer Se_x chains.

PACS numbers: 78.20.Dj, 72.15.Eb

By using a mordenite zeolite matrix as the “solvent,” it is possible to “split” a Se crystal into individual filaments utilizing its polymer properties, and to arrange these filaments into a lattice of parallel dielectric channels. The structure of the channel-dielectric mordenite matrix is shown in the inset of Fig. 1.¹ The diameter of the channels is 6.6 Å; the system of channels forms a regular lattice with a distance of 13.7 Å between the channel centers.

Previously,² Hg and Bi had been introduced into these channels and it was shown that nonwetting materials enter into these channels as monatomic chains under pressure. The conductivity and structure of the optical absorption cannot be detected in this case without pressure—a breakup of the filaments into individual fragments can occur due to the action of surface tension forces. Se, an inorganic polymer, wets the mordenite; this contributes to the stability of the Se filament structure in the channels. It follows from the geometry of the mordenite channels that the Se can exist in NaM either in the form of atoms or molecules, or in the form of polymer chains. We detected only the 233 to 237 cm^{-1} -lines in the Raman scattering spectra (RS) of such systems. These lines coincide with the RS lines for the Se_x polymer chains in a massive (trigonal) selenium.³ We are dealing most likely with a polymer modification of Se— Se_x chains—and the RS frequencies are preserved as one goes from the massive material to these chains. It is clear from the geometrical considerations that the Se_x chains extend along the channels—the crystallographic “c” axis of mordenite. One or two Se_x chains can be placed in a channel.

Se from a melt was introduced into natural mordenite NaM crystals with dimensions of $\sim 2 \times 0.03 \times 0.01$ mm under a pressure of ~ 15 kbar. The optical transmission of the resulting materials was measured in a polarized light using double-beam microspectrophotometers in the $\lambda = 250\text{--}780\text{-nm}$ region. Multiple reflection was taken into account in the calculation of the absorption coefficient α . The thickness of the crystals

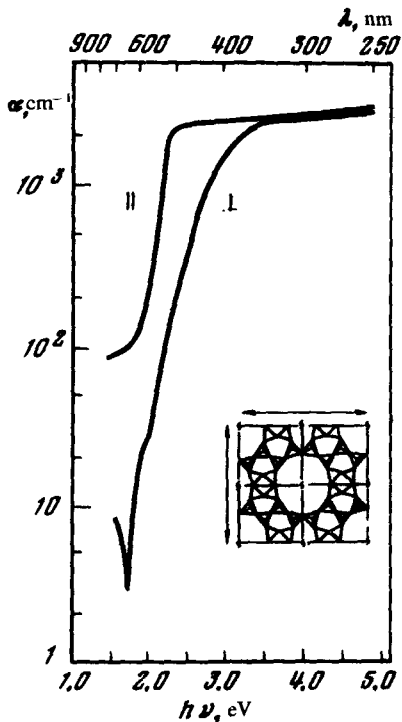


FIG. 1. Absorption spectra of quasi-one-dimensional system of Se filaments in channels of an NaM dielectric matrix; the E vector is oriented parallel (||) to the Se filaments and at right angles (\perp) to them. The structure of the NaM-channel-dielectric matrix is shown in the inset.

was measured from the interference pattern observed in the "transparency" region of the crystals.

Severe optical anisotropy was observed in the tested materials,¹ the absorption is maximum if the E vector is oriented along the Se_x filaments and minimum for perpendicular orientation of E. The absorption spectra for these two polarizations are shown in Fig. 1. The intrinsic absorption edge is observed at $\hbar\omega \sim 2$ eV, i.e., in approximately the same spectral region as for the massive (trigonal) selenium. Beyond the intrinsic absorption edge $\alpha \sim 2 \times 10^3 \text{ cm}^{-1}$ and the crystal is slightly anisotropic. In the vicinity of the edge the anisotropy $\alpha_{\parallel}/\alpha_{\perp}$ is much greater than that in massive Se. The behavior of α_{\parallel} and α_{\perp} must be described here by different spectral dependences.

The crystal retains optical anisotropy in the "transparency" region ($\hbar\omega < 2$ eV), where it can be attributed to the fact that the motion of electrons along the Se_x chains is easier than in the perpendicular direction. An estimate of the value $\sigma_{\text{opt}} = \alpha_{\parallel}/c\epsilon_0 n$ in this region gives $\sigma_{\text{opt}} \sim 0.14 \text{ ohm}^{-1} \text{ cm}^{-1}$, which is two orders of magnitude higher than the corresponding value for the original, massive selenium.

We note that we were able to trace for the first time in these materials a change in the properties as one goes from a massive system to a quasi-one-dimensional and to determine the effects associated with the quasi-one-dimensionality.

¹The initial NaM crystals are transparent ($\alpha < 10 \text{ cm}^{-1}$) and optically isotropic.

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