N- and S-shaped I-V characteristics of the cluster superlattice of tellurium in type X zeolite

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Into the cubic lattice of the cavities of type X zeolite used as the matrix, Te is introduced in the amounts of 16 and 23 atoms in each cavity. In the first case the crystal conductivity is $\sigma \sim 10^{-5}$ ohm^{-1} cm^{-1}, and the I-V characteristic has the form of a series of successive current surges as the field is increased. With 23 atoms per cavity, the contact between clusters is better, which gives $\sigma \sim 10^{-1}$ ohm^{-1} cm^{-1}, and the I-V characteristic looks like a series of S-shaped regions. It is assumed that in the first case a resonance tunneling occurs in the field between the levels of the clusters in neighboring cavities, and in the second case there is a breakdown between the minizones of tellurium, which are produced as a result of modulation by the zeolite matrix.

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Superlattices with nonlinear I-V characteristics[1] occupy an important place in the program to develop new materials for electronics. The use of zeolites as matrices with regular lattices of atomic-size cavities or channels, in which one can obtain three-dimensional systems of clusters or filaments, makes it possible to construct new types of solids—filamentary and cluster crystals (superlattices) that are more sensitive to external stimuli than the conventional lattices.[2] Figure 1 shows one large type X zeolite (faujasite) cavity. The cavity diameter is ~ 13 Å and the window diameter is 8-9 Å. A diamond-type lattice with a constant of 24.6 Å is formed from these cavities. Up to 23 tellurium atoms can be tightly packed into each large cavity. By coming in contact with each other through the windows, these Te_{23} clusters form a three-dimensional tellurium body that is spatially modulated by the zeolite dielectric matrix. If the

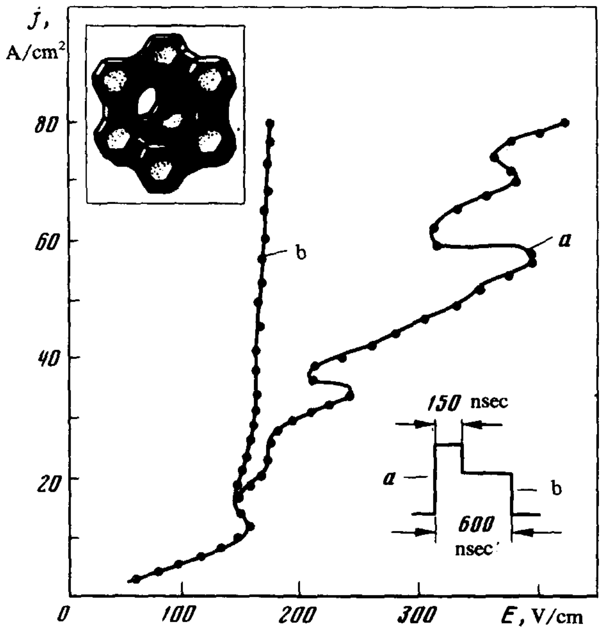

FIG. 1. *I-V* characteristic of $NaXTe_{23}$ cluster crystal, obtained by using 600-nsec square pulses in the current source mode of operation at $T = 293$ K. Branches "*a*" and "*b*" correspond to the leading and trailing edgies of the pulse. The structure of the large cavity in type X zeolite is shown in the upper left-hand corner.

zeolite NiNaX is used as the matrix, where some of the Na^+ in the cavity walls is replaced by Ni^{++}, and tellurium is introduced into it from a melt at a pressure of 5–6 kbars, then the number of atoms in the clusters, which is determined from the density of the single crystals, is actually close to the limit and amounts to 22–23. Such a single crystal has a conductivity of $\sigma \sim 10^{-1}$ ohm^{-1} cm^{-1} at $T = 300$ K, which is close to the conductivity of the original massive tellurium. The *I-V* characteristics of such crystals have the form of a series of *S*-shaped regions (Fig. 1). The characteristic curve in Fig. 1 was obtained in 0.2-mm single crystals by using the contact method and a current source of square pulses with a duration of 600 nsec. The branch "*a*", a series of *S*-shaped regions measured form the leading edge of the pulse, represents the *I-V* characteristic for 150-nsec pulses.

In contrast to massive Te, the *S*-shaped *I-V* characteristics are observed in a wide temperature interval from 77 to 373 K, the critical current and field are an order of magnitude lower, and there are several *S*-shaped regions. In terms of the mechanism for *S*-shaped *I-V* characteristics for massive tellurium,[3] we can assume that in the case of the $NiNaXTe_{23}$ cluster crystal the *I-V* characteristic is attributable to splitting of the energy spectrum of the massive tellurium due to the influence of volume modulation of the zeolite matrix on the series of minizones, between which a breakdown occurs in the electric field.[4]

A completely different picture is obtained if the zeolite NaX is used as the matrix. Under the same processing conditions only 16 Te atoms enter into each cavity in the

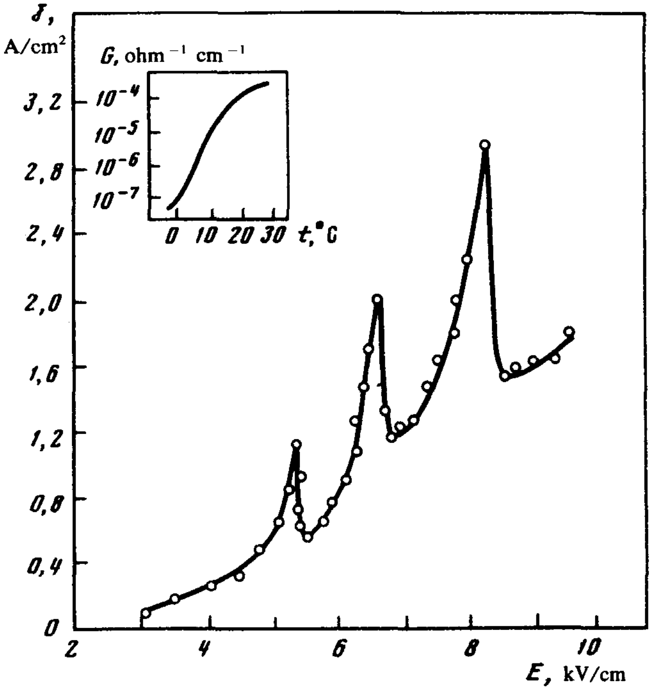

FIG. 2. I-V characteristic of $NaXTe_{16}$ cluster crystal, obtained by using individual square pulses with a duration of $\sim 10\,\mu$sec in the voltage source mode of operation at $T = 280$ K. The temperature dependence of the conductivity of the $NaXTe_{16}$ crystal in a field of $E = 10^3$ V/cm is shown in the upper left-hand corner.

purely sodium zeolite. The 16-atom clusters form the $NaXTe_{16}$ cluster crystal with a weak interaction between clusters and a conductivity $\sigma \sim 10^{-5}$ ohm^{-1} cm^{-1} at $T = 280$ K. The I-V characteristic of such a crystal is shown in Fig. 2. The characteristic curve was obtained by using invidivdual square pulses with a duration of $\sim 10\,\mu$sec in the voltage source mode of operation at $T = 280$ K using two gallium contacts.

Assuming that in this case the Te_{16} clusters can be considered as well-localized microparticles, the current surges in Fig. 2 can be attributed to the resonance tunnel transitions in which the levels of neighboring clusters coincide due to the action of the field. Assuming that the average distance between the cluster centers is ~ 12 Å and $E = 10^3$ V/cm, we obtain $\Delta \sim 10^{-4}$ eV as the separation of the levels in the clusters, if that field distribution in the crystal is uniform. However, since inhomogeneities can form in a medium that has internal instabilities, the value of Δ will be larger.

Such I-V characteristics with current surges are observed only below room temperature. The temperature dependence of the conductivity is shown in the upper left-hand corner of Fig. 2. As the temperature in the region 273 K$<T<$293 K increases, an abrupt increase in the conductivity is observed in the $NaXTe_{16}$ crystals. In the low-resistance state, i.e., $T \geqslant 293$ K, the I-V characteristic is predominantly S-shaped.

The structure of the Te_{23} and Te_{16} microclusters, the mechanism of their contact with each another, as well as the structure of the entire crystal, are still unknown, but considering the behavior of $NaXTe_{16}$, we must take into account two facts. Te, like the other chalcogens, can form both chain as well as ring structures, and these tendencies compete with the need for localization in the cavities of specified geometry. A 16-atom cluster in the cavity still has sufficient room, so that either configuration can be realized, depending on the temperature. Thus, tellurium in the NaA zeolite, cavities, which are well isolated from each another, exists in the form of the unusual Te_8 ring modification[5] and behaves like an insulator.

Thus, the *I-V* characteristics of tellurium cluster crystals in a type X zeolite matrix (three-dimensional superlattices) depend on localization of the clusters and on the conduction mechanism of the system.

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