

Identification of a new tellurium modification—a Te_8 ring in small-diameter clusters

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In the course of dispersion of S, Se and Te known stable and unstable phases of these elements were stabilized by way of production of clusters in $\sim 10\text{-\AA}$ cavities of zeolites in NaA and NaX; in addition to this, a heretofore unknown tellurium modification, a Te_8 ring, was identified. Identification was carried out from the spectra of Raman scattering of light.

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Zeolite crystals are shell-structured aluminosilicates with a regular system of channels and cavities of molecular dimensions.¹ Stabilization of macroscopic ensembles of monodispersed $\sim 10\text{-\AA}$ clusters of different monoatomic substances which consist of 10–30 atoms² with concentrations $\sim 0.5 \times 10^{21} \text{ cm}^{-3}$ is possible in these crystals.

Small-size particles are characterized by the existence (under normal conditions,) of phases which in heavy specimen correspond to different nonequilibrium states (high-temperature phases, high-pressure phases, etc). Moreover, phase formation and stabilization may occur under conditions which are not generally observed in heavy specimen.³

The basic structural feature of both amorphous and crystalline modifications of heavy specimen of chalcogens are eight-term corrugated rings (eight-atom molecules of "corona" type) or infinite spiral chains; moreover, under normal conditions the following picture of stability of these structures is observed:⁴

	S	Se	Te
Ring	Stable	Metastable	Not observed
Spiral	Unstable	Stable	Stable

Dispersion of S, Se and Te by means of cluster production in the cavities of NaX- and NaA-type zeolites has identified the possibility of both stabilizing known stable and unstable phases of the given substances, and deriving a heretofore unknown Te modification. Moreover, the structure of S, Se and Te clusters indicates a dependence on both the dispersion method and the structure of the parent zeolite matrix. For example, x-ray diffraction studies showed⁵ that at $t \leq 270^\circ\text{C}$ sulfur is absorbed into NaA zeolite at the rate of 16 atoms per large cavity which then form two parallel annular S_8 molecules. Liquifaction under several kilobar pressure indicates the maximum possible packing of a large-cavity volume limited by zeolite structure (755 \AA^3) is: ~ 28 atoms per cavity (the number of atoms in a cluster was calculated from the

TABLE I. Frequency (cm^{-1}) and type of oscillation symmetry (shown in parentheses).

$\text{Se}_{\alpha\text{-mon}}$	NaA-Te	Se_{trig}	NaX-Se	Te_{trig}	NaX-Te	NaA-Te	S
Ring							
251(A_1)* [7]		—	—	—	—	~168	473(A_1) [7]
254(E_2) [7]	254						475(E_2) [7]
Spiral							
—	—	233(E) [7]	233	139.5(E) [8]	~140	—	—
		237(A_1) [7]	237	120.4(A_1) [8]	~120	—	—

density of resultant crystals). Moreover, absorption spectra were used to identify in the S_{28} cluster ensemble a significant concentration of structural fragments S_3 and S_4 ,⁶ which are unstable under normal conditions. Long-term (> 1 year) stability of unstable structural states of sulfur is explained in this case by the fact that the S_{28} clusters reside in zeolite cavities of the order of atomic dimensions and, thus a possible restructuring of these is made more difficult.

In this work under conditions of room temperature and laser excitation ($\lambda_B = 5145 \text{ \AA}$; $\lambda_B = 6328 \text{ \AA}$) triple RSL spectrophotometers "Cazy-82," "Spex-Ramallog" and "Jobin Yvon" Raman laser microspectrophotometers were used to record the RSL spectra of the NaA-Se, NaX-Se, NaA-Te and NaX-Te specimen (NaA and NaX zeolites with Se and Te clusters in cavities). Table I below shows results of measurements and data from the literature on the frequencies and symmetry of natural oscillations of annular Se_8 and spiral Se_n and Te_n molecules which are known as a result of investigation of the RSL spectra of α -monoclinic Se and trigonal Se and Te crystals, respectively.

In the case of Se the identified frequencies of oscillations attest to the fact that the fundamental structural feature of clusters in the NaA zeolite cavities is an annular Se_8 molecule, and in the NaX zeolite cavities, spirals. This may be associated only with a different geometry of the X- and A-type zeolite cavities. Actually, in X-type zeolites 12–13- \AA diameter cavities are joined by 8–9- \AA apertures,¹ thus forming a weakly diameter-intensive continuous channel without upsetting the spatial continuity of Se (introduced by either adsorption or under pressure from the melt), and contributing to a thermodynamically most stable spiral modification of Se. In type-A zeolite 11.4- \AA diameter cavities are separated by apertures of smaller diameters (4.2 \AA), spatial continuity is disturbed which enhances the formation of annular Se_8 molecules with ~7.5- \AA diameters in the cavities, since short spiral Se chains constitute unstable biradicals.

Thus, the structural rule for packing Se into the cavities of different zeolites differs sharply regardless of the similar conditions for obtaining the specimen. In

addition to this, our data may also be used to conclude that significant differences in the optical properties of superlattice Na4-Se and NaX-Se crystals in the natural absorption region—observed earlier⁹—are, first of all, clearly constrained by the different molecular structure of Se clusters that are stabilized in zeolite cavities of different geometry. All the aforementioned reasoning for Se may also apply to the case of Te in zeolite cavities. However, in contrast to Se, the only Te crystals known today consist of “infinite” spiral chains.⁴ The resultant oscillation frequencies (see Table I) lead to the conclusion that the fundamental structural features of Te clusters in the NaX zeolite cavities are also spirals—Te_n. Oscillations with a frequency 168 cm⁻¹ were identified in Na4-Te crystals which substantially differ from the known frequencies of “spiral” Te.

In considering the known natural oscillation frequencies of annular and spiral structures in a homologous series S, Se and Te (see Table I), we discovered that the coefficient of quasi-elastic force k for the oscillations of one symmetry is well described by a ratio $k \approx a/r^2$, where r is the covalent atomic radius and a is a constant for similar oscillations of chalcogens with an accuracy of $\sim 5\%$. This permits us to use known frequencies for one chalcogen to find frequencies of monotypic oscillations for another. Evaluation of the natural oscillation frequency for symmetry A_1, E_2 , and Te_8 rings yields values of 165–180 cm⁻¹; this permits us to consider the 168-cm⁻¹ oscillations observed in Na4-Te as a manifestation of the natural oscillation of the Te_8 ring, a new Te modification. In principle, having opened a zeolite matrix one may expect to find monoclinic Te crystal—similar to monoclinic Se crystals—consisting of rings. We should note that only trigonal Te crystals are known at present, which consist of “infinite” spiral chains.⁴ In a number of S, Se and Te crystals conductivity changes from dielectric to semimetallic in Te. Conductivity of monoclinic Te should be, clearly, lower than that of trigonal Te. Taking into account the special properties of Te phase diagram⁴ and results of this work, it becomes interesting to find the Te_8 phase in, for example, Te thin films.

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