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Abstract

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ON THE NATURE OF THE MOLECULAR MECHANISM OF THE PHASE TRANSITION IN FERROELECTRICS ISOMORPHOUS WITH TRIGLYCINE SULFATE CRYSTALS

(Presented by Academician A. V. Shubnikov on 30 XII 1965)

The known results obtained by the method of combination scattering of light, in agreement with X-ray structural data, show that in triglycine sulfate crystals in the ferroelectric state the group SO_4^{2-} does not possess tetrahedral symmetry ([1]). This is also to be expected, since a tetrahedral group must inevitably be distorted when placed in the field of a monoclinic-system crystal ([2]) and, consequently, must have lower symmetry both below and above the Curie point. Thus, the very distortion of the tetrahedral group observed at room temperature (below the Curie point) still says nothing about changes in it at the phase transition.

Our investigation in polarized light of the infrared reflection spectra of oriented sections of single crystals of triglycine sulfate ([3,4]), triglycine selenate, and deuterated triglycine sulfate allowed us to reconsider the traditional assignment of individual bands, adopted by us earlier, and showed that the shift of the 1150 cm^{-1} band observed at the phase transition belongs not to the wagging deformation vibration of the NH_3^+ group (I), but to vibrations associated with the SO_4^{2-} group. In the spectrum of triglycine selenate, at the phase transition, changes were likewise observed in the band associated with vibrations of the corresponding SeO_4^{2-} ion. Thus, at the phase transition a shift is observed in some vibrational frequencies of the SO_4^{2-} (or SeO_4^{2-}) ion, indicating deformation of this rigid ion.

Although, as has been rather convincingly proved, the changes in the position and structure of the glycine and glycinium ions during the phase transition I are undoubtedly responsible for the ferroelectric properties in ferroelectrics isomorphous with triglycine sulfate crystals, the distortion of the rigid SO_4^{2-} ion is no less responsible for the occurrence of the phase transition itself. Therefore, it is of interest to try to relate the Curie temperatures observed in the isomorphous series to quantities characterizing the rigidity of the SO_4^{2-} (or SeO_4^{2-})

ions. The distortion of the structure of these ions is apparently a consequence of a change in the electronic configuration due to the transition of the valence electrons binding the central sulfur (selenium) atom with the oxygens into a state of another symmetry close in energy. The energy difference between these two states, all other conditions being equal, should in the first approximation be proportional to the rigidities of the electron shells of the central atoms S (or Se). The foregoing permits one to suppose that, when sulfur is replaced by selenium in this isomorphous series, the Curie temperature will change, to a first approximation, in the same way as the rigidity of the electron shell changes in going from sulfur to selenium. The rigidity of the electron shells may be roughly characterized by ionization energies (it must be proportional to the ionization energy). Thus, there is reason

assume that

$$T_1/T_2 = I_1/I_2.$$

If for I_1 and I_2 one takes the tabulated values of the ionization energies of the free sulfur and selenium ions (^{5}), $I^{+1\to+2} = 23.4$ eV, $I_2^{+1\to+1} = 21.5$ eV, and uses the known values of the Curie temperatures of triglycine sulfate and triglycine selenate (^{1}), $T_1 = 322$°K, $T_2 = 295$°K, then $I_1/I_2 = T_1/T_2 = 0.92$. Although the agreement is not very good, it nevertheless may serve as some confirmation of the hypothesis expressed above.

The third isomorphous crystal in this group is triglycine fluoroberyllate; its Curie temperature is $T_3 = 343$°K. Instead of SO_4^{2-} we now have BeF_4^{2-}; therefore, in estimating the rigidity of the central ion, it is also necessary to take into account that the oxygens have been replaced by fluorines. The electron affinity E of the fluorine ion is 3.62 eV, and that of the oxygen ion is 2.33 eV. Assuming that the greater electron affinity of the fluorine ions makes the system more rigid, we obtain

$$I_3E_3/I_1E_1 = T_3/T_1,$$

or, substituting the numbers ($I_3^{+1\to+2} = 18.21$ eV), we obtain

$$I_3E_3/I_1E_1 = 18.21 \cdot 3.62/23.4 \cdot 2.33 = 1.22, \quad T_3/T_1 = 1.17,$$

i.e., the agreement is again quite satisfactory, if one takes into account the roughness of the estimates.

The suggestion made above apparently also makes it possible to explain the effect of deuteration on the shift of the Curie point of triglycine sulfate (^{6}). Our studies of infrared reflection spectra of oriented sections have shown that, upon deuteration of triglycine sulfate, a shift to the short-wavelength side occurs for bands belonging to vibrations of the SO_4^{2-} ion (1140; 1134; 1164 cm^{-1}), which indicates an increase in the rigidity of the SO_4^{2-} group; and an increase in the rigidity of the SO_4^{2-} ion should naturally raise the Curie temperature, as is observed experimentally. The increase in the rigidity of the SO_4^{2-} ion upon deuteration of triglycine sulfate is connected with the fact that in most crystals the D bond has a somewhat greater length than the H bond ([7]), and thus exerts a smaller perturbing effect on the SO_4^{2-} ion. It may be pointed out that, when comparing the Curie temperatures of triglycine fluoroberyllate and triglycine sulfate, one should also take into account the fact that the hydrogen bond to fluorine is somewhat stronger than to oxygen ([8]), and therefore the Curie temperature calculated without allowing for this factor should be somewhat overestimated.

There is reason to believe that taking into account the possibility of transitions of electronic configurations to a nearby energy state of different symmetry in the isolated quasisymmetric ions so characteristic of ferroelectrics will make it possible to provide a new fruitful approach to the solution of the question of the mechanism of the phase transition in other ferroelectrics as well.

In conclusion, I take this opportunity to express my gratitude to L. A. Shuvalov for his constant interest and friendly support.

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Note: Figure translations are in progress. See original paper for figures.