

The results of the measurement of the specific heat of CrCl_3 between 2 and 4°K are shown in Fig. 1, in coordinates C and T. We see that the temperature dependence of the specific heat is close to linear.

To estimate the contribution of the lattice to the specific heat of CrCl_2 , Fig. 2 shows the measurement results in coordinates C/T and T^2 . It is assumed here that the lattice specific heat is proportional to T^3 , as is the case with other layered halides at helium temperatures [3], and the magnetic specific heat is characterized by a linear temperature dependence.

The specific heat of CrCl_3 is well described by the relation

$$C[\text{cal/mole-deg}] = 0.051T + 7.1 \times 10^{-4}T^3.$$

At 4°K the cubic term amounts to 18% of the total specific heat, and at 2°K it is of the order of 5%, i.e., the magnetic specific heat greatly exceeds the lattice contribution.

Using for the magnetic specific heat the expression obtained for a ferromagnetic model with low anisotropy, $C_M/R = \pi kT/24I_F s$, where s is the spin and I_F the exchange integral characterizing the interaction within the layer, we obtained from our data $I_F s/k = 5.1^\circ\text{K}$.

According to the estimates of Narath and Davis, obtained from magnetization data [9, 10] for different spin-wave theory approximations, $I_F s/k$ amounts to 6 - 7.8°K.

The author is grateful to A. I. Shal'nikov and A. S. Borovik-Romanov for taking part in the discussion, and O. P. Dunaev for help with the experiments.

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UNUSUAL HYDROGEN ISOTOPIC EFFECT IN CRYSTALS OF SODIUM HYDROSELENITE. PHASE DIAGRAM OF THE SYSTEM $\text{Na}(\text{D}_x\text{H}_{1-x})_3(\text{SeO}_3)_2$

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 Submitted 25 June 1968
 ZhETF Pis. Red. 8, No. 5, 235 - 238 (5 September 1968)

We have recently shown [1] that sodium deuteroselenite crystals, $\text{NaD}_3(\text{SeO}_3)_2$, become ferroelectric below the Curie point T_c , in analogy with the sodium hydroselenite crystals, $\text{NaH}_3(\text{SeO}_3)_2$, and not antiferroelectric as claimed in [2 - 4]. However, the effect of deuteration in sodium hydroselenite consists not only of shifting T_c [2, 5], but also, as established by us, in a sharp change of the symmetry (and accordingly of the physical properties) below T_c . Whereas the hydroselenite is triclinic of class I below $T_c = -78.6^\circ\text{K}$,

and goes over into the monoclinic ferroelectric phase m at -173°C [6], the deuterioselenite experiences at T_c a transition $2/m \rightarrow m$, and subsequently has no phase transitions down to -196°C^1 .

A similar isotopic effect, accompanied by a change of symmetry, has never been encountered in any crystal. This made it all the more interesting to determine the phase diagram of the $\text{Na}(\text{D}_x\text{H}_{1-x})_3(\text{SeO}_3)_2$ system and to study the properties of the crystals of this system. We summarize here briefly the results of this study.

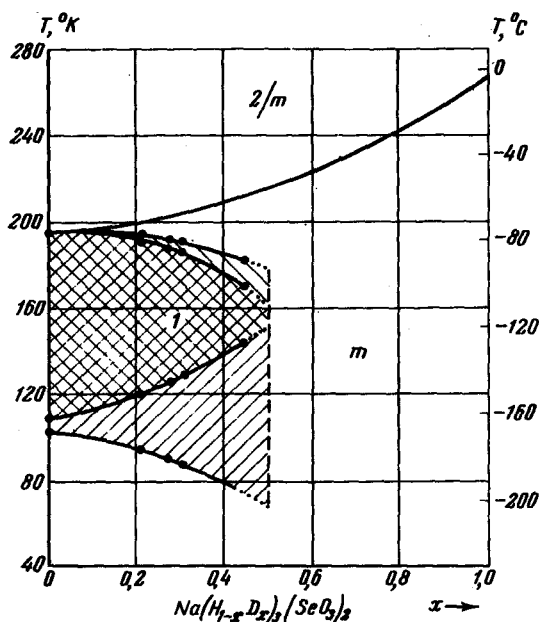


Fig. 1

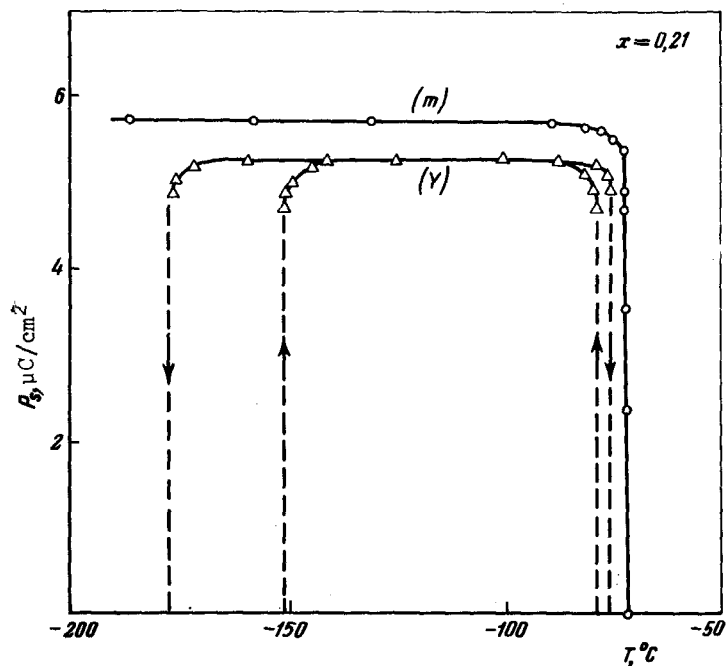


Fig. 2

1. Measurements of the dielectric constant and of the rotary thermo-optical effect, and a study of the hysteresis loops for differently oriented cuts of crystals with different compositions, have made it possible to construct the phase diagram of the system and to determine the point symmetry of all the phases.

It is seen from Fig. 1 that the peculiarity of the isotopic effect in the system $\text{Na}(\text{D}_x\text{H}_{1-x})_3(\text{SeO}_3)_2$ lies in the splitting of the curve of the upper phase transition and the appearance of a new transition at $x < 0.5$, and a gradual narrowing of the temperature region of stable existence of the triclinic phase with increasing x and a complete vanishing of this region at $x > 0.5$.

Also unusual is the broadening, with increasing D content, of the regions of temperature hysteresis, of both lower transitions existing when $x < 0.5$, a broadening particularly pronounced at the lower transition.

All three phase transitions are accompanied by anomalies of the dielectric, thermo-optical, and other properties.

¹⁾The same conclusion was reached later by Blinc and co-workers [7].

The lower two transitions are of first order, while the upper has features of both first- and second-order transitions; however, judging from thermo-optical measurements, it is apparently also of first order, but close to second order.

Crystals with $x < 0.5$ reveal in the upper ferroelectric phase, in a field E_y , double electric-hysteresis loops of a peculiar nature, corresponding to the induction of a ferroelectric phase I in the ferroelectric phase m (i.e., to the appearance of a Y component of the spontaneous polarization P_s).

3. The character of the phase diagram and the independent behavior of the components of P_s (Fig. 2) allow us to draw a conclusion, compatible with the symmetry, that the Y component of P_s and the m component of P_s perpendicular to it (lying in the m-plane of the para-phase) not only have different microscopic mechanisms, but are also independent of each other. It is probable that the m component of P_s and accordingly the upper phase transition are due to ordering of hydrogen bonds, while the Y component of P_s and the two lower phase transition are due to a shift of the Na^+ ions and a distortion of the SeO_3^{2-} groups. This hypothesis, which was advanced by us earlier [6], agrees well with the thermo-optical measurement data. (In crystals with $x < 0.5$, obviously, this hypothesis can also be verified directly, say by the NMR spectroscopy method.)

Thus, crystals of the system $Na(D_xH_{1-x})_3(SeO_3)_2$ have an unusual isotopic effect, and apparently constitute the first example of ferroelectrics having spontaneous-polarization components that are independent and differ in their nature.

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FREE RADICALS AS CHAINS OF SPINS WITH ANTIFERROMAGNETIC INTERACTION

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Submitted 26 June 1968

ZhETF Pis. Red. 8, No. 5, 239 - 241 (5 September 1968)

There are few experimental studies of linear chains of spins. This is due primarily to the lack of suitable objects. There is only one known compound, $Cu(NH_3)_4SO_4$, for which a linear structure has been proposed [1]. From the theoretical point of view, the one-dimensional model is of considerable interest. This is connected with the fact that such a model admits of an exact solution under certain simplifications [2,3], and can also be calculated