

Scientific session of the Division of General Physics and Astronomy and the Division of Nuclear Physics, Academy of Sciences of the USSR (24–25 October 1987)

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A joint scientific session of the Division of General Physics and Astronomy and the Division of Nuclear Physics of the USSR Academy of Sciences was held on June 24 and 25, 1987, at the S. I. Vavilov Institute of Physics Problems of the USSR Academy of Sciences. The following reports were presented:

June 24

1. *V. I. Simonov*. Structural studies of crystals with unique physical properties.

V. I. Simonov. Structural studies of crystals with unique physical properties. Consideration of ever more subtle effects in the interaction of crystals with radiation and the development of existing theories to the computational stage make it possible to analyze experimental X-ray diffraction data in the light of these effects and to obtain the parameters of the corresponding crystal structure features. For example, the anharmonicity of thermal atomic oscillations allows us to predict displacement-type phase transitions in crystals; extinction effects characterize the dimensions and misorientation of mosaic blocs in single crystals, and so forth. Multiwave diffraction furnishes experimental methods of determining structure-amplitude phases. The experimental apparatus that will turn this approach into a working research tool is presently under development. The development of computer-controlled automated diffractometers has, for the first time, opened up the possibility of optimizing the measurement of each diffracted reflection with feedback over several parameters.

All the above has led to successful research into the structure and properties of crystalline materials. The range of objects studied by structural crystallography is extremely broad: from metals and alloys to proteins and viruses. In every case diffraction methods have yielded unique information on the structure of studied objects, information that could not be gathered by other means.

Structural studies of solid electrolyte single crystals have yielded rather significant results. These materials have high ionic conductivities—they are superionic conductors: they have attracted scientific interest by their peculiar phase transitions and also by their rather important practical applications (new types of energy sources and accumulators, small capacitors of enormous capacitance, etc.). In Fig. 1 we have reproduced the temperature dependence of conductivity

2. *A. A. Chernov*. Elementary processes of crystal growth from solutions.

3. *S. M. Stishov*. Physics of ultrahigh pressures.

June 25

4. *N. S. Kardashev and V. M. Koutunen*. Land and space based radio-interferometer and the determination of fundamental cosmological constants.

5. *G. B. Khristiansen*. Prospects for studying cosmic rays at ultrahigh energies (10^{15} – 10^{21} eV).

Summaries of three reports are published below.

ity via Li ions in three mutually perpendicular directions of $\text{Li}_3\text{Se}_2(\text{PO}_4)_3$ single crystals. Temperature variation over a 200° range results in conductivity variation over five orders of magnitude. At a given temperature the conduction anisotropy in these single crystals spans two orders of magnitude. X-ray structural studies at different temperatures have determined the atomic mechanism of the phase transition into the superionic state, the easy Li ion transport directions in the single crystals, and the reasons for anisotropic conduction. In the low-temperature phase the sample exhibits crystal microtwinning that depends on the heating and cooling regimes: the ratio of the twin component volumes varies and the crystal macroscopic properties change accordingly. Neutron scattering studies of RbNbWO_6 and TiNbWO_6 single crystals, which exhibit a ferroelectric–superionic con-

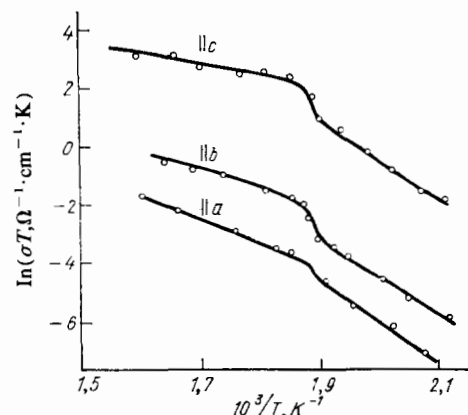


FIG. 1. Temperature dependence of conductivity via Li ions in $\text{Li}_3\text{Se}_2(\text{PO}_4)_3$ single crystals along the crystallographic axes *a*, *b*, and *c*.

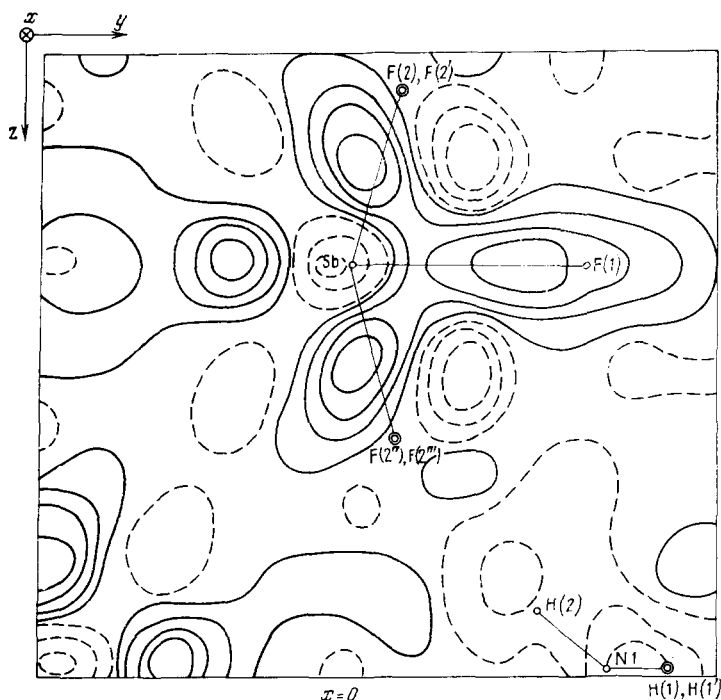


FIG. 2. Cross section of deformation electron density in $(\text{NH}_4)_2\text{SbF}_5$ crystals.

ductor phase transitions, have determined the structural reasons for the higher (by two orders of magnitude) conductivity via Tl ions than via Rb ions in the superionic phases. An analysis of the anharmonicity of thermal atomic fluctuations in the high-temperature phase elucidated the structural transformation mechanism at the phase transition.

Neutron structure studies of nonstoichiometric fluoride crystals carried out by our research group have contributed significant corrections to the structural models of these practically important solid solutions that exist in the literature. Nonstoichiometric fluorides can be used as laser materials, superionic (anionic) conductors, environmental gas contamination sensors, and optical system materials. Neutron diffraction data have established two distinct structural types in fluorite-based nonstoichiometric fluoride crystals. The growth mechanisms and clustering nature of these structures have been determined. The existence regions and cluster formation in each of these types depends on the size ratio of the divalent cations of the host material to the trivalent impurity cations. Controlled changes in the chemical composition and structure of fluoride-based nonstoichiometric fluorides permit continuous regulation of the physical properties of these compounds. For example, the (111) edge hardness in BaF_2 and $\text{Ba}_{0.69}\text{La}_{0.31}\text{F}_{2.31}$ crystals is 80 and 250 kg/mm^2 respectively, whereas the ionic conductivity via F anions increases by six orders of magnitude when lanthanum is added. Thus, within the above limits, we can select the composition and grow a crystal with the required hardness and conductivity. Such compounds differ in their melting temperature, index of refraction, infrared absorption, and so forth—consequently these properties can be selected as required.

Diffraction-based structural crystallography can establish the structure and properties of a material with respect to any number of different characteristics. It has been shown that the unique acoustooptical properties of paratellurite $\alpha\text{-TeO}_2$ single crystals are due to the anharmonicity and strong

anisotropy of the thermal oscillations of Te atoms. The most important feature of many currently important materials is their resistance to radiation damage. Thus CsNO_3 single crystals grown by spontaneous crystallization can withstand a γ -radiation dose two orders of magnitude higher than their counterparts grown from seed. Diffraction studies have revealed marked differences in the extinction parameters of the two types of samples. These parameters, in turn, are determined by the sizes and misorientations of mosaic blocs in the single crystal. The samples that better resist radiation breakdown have mosaic bloc dimensions smaller by a factor of five.

Precision structure measurements using X-ray diffraction have determined the spatial distribution in the crystal of outer atomic electrons that form chemical bonds. Figure 2 reproduces a cross-section of the deformation electron density in the $(\text{NH}_4)_2\text{SbF}_5$ compound. Deformation density is defined as the difference between electron distribution in a given crystal and the electron densities of the noninteracting atoms that make up the crystal. The chemical bonds Sb–F(1) and Sb–F(2) are clearly depicted in Fig. 2. When the Sb atom is configured in the trans-position with respect to the F(1) atom we observe a clear density maximum that corresponds to the unshared electron pair of the Sb atom.

Methods of structural crystallography have been successfully applied to semiconductors, ferroelectrics, nonlinear optical materials, laser materials, and other crystals with unique physical properties. The next step in the development of diffraction methods involves the use of synchrotron radiation and of coordinate detectors. Together these advances will shed light on the transformation dynamics in crystalline structures. Synchrotron radiation is not only more intense but possesses a continuous spectrum, which promises qualitatively new applications of anomalous scattering effects.

¹Crystallography and Crystal Chemistry (in Russian), Nauka, M., 1972, pp. 104, 215.

²É. K. Kov'ev and V. I. Simonov, *Pis'ma Zh. Eksp. Teor. Fiz.* **43**, 244 (1986) [*JETP Lett.* **43**, 312 (1986)].

³A. V. Zvarykina, P. A. Kononovich, V. N. Laukhin, V. N. Molchanov, S. I. Pesotskiĭ, V. I. Simonov, and R. P. Shibaeva, *Pis'ma Zh. Eksp. Teor. Fiz.* **43**, 257 (1986) [*JETP Lett.* **43**, 329 (1986)].

⁴V. N. Molchanov, R. P. Shibaeva, V. N. Kachinskiĭ, É. B. Yagubskiĭ, V. I. Simonov, and B. K. Vaĭnshteĭn, *Dokl. Akad. Nauk SSSR* **286**, 637 (1986) [*Sov. Phys. Dokl.* **31**, 6 (1986)].

⁵I. P. Makarova, L. A. Muradyan, V. E. Zavodnik, and V. I. Simonov, *Dokl. Akad. Nauk SSSR* **283**, 126 (1985) [*Sov. Phys. Dokl.* **30**, 545 (1985)].

⁶L. A. Muradyan, M. I. Sirota, I. P. Makarova, and V. I. Simonov, *Kristallografiya* **30**, 258 (1985) [*Sov. Phys. Crystallogr.* **30**, 545 (1985)].

⁷I. P. Makarova, S. V. Misyul, L. A. Muradyan, A. F. Bovina, V. I. Simonov, and K. S. Aleksandrov, *Phys. Stat. Sol. (b)* **121**, 481 (1984).

⁸E. A. Genkina, L. N. Dem'yanets, A. K. Ivanov-Shits, B. A. Maksimov, O. K. Mel'nikov, and V. I. Simonov, *Pis'ma Zh. Eksp. Teor. Fiz.* **38**, 257 (1983) [*JETP Lett.* **38**, 305 (1983)].

⁹M. E. Andrianova, D. M. Kheiker, A. N. Popov, V. I. Simonov, Yu. S. Anisimov, S. P. Chernenko, A. B. Ivanov, S. A. Movchan, V. D. Peshekhonov, and Yu. V. Zanevsky, *J. Appl. Cryst.* **15**, 626 (1982).