

## CHARGE TRANSPORT MECHANISM IN $\text{KCl}:\text{BiCl}_3$ CRYSTALS

МЕХАНИЗМ ПЕРЕНОСА ЗАРЯДА В КРИСТАЛЛАХ  $\text{KCl}:\text{BiCl}_3$

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There exist only a few data concerning the influence of trivalent cations on alkaline halides [1—6]. Most works deal with crystals doped by divalent cations [7]. The investigation of transport properties of alkali halides doped by trivalent cations appears, however, to be interesting from the viewpoint of electrical neutrality (each trivalent cation should be substitutionally incorporated accompanied by two vacancies or three vacancies for an interstitial cation, respectively) as well as from the viewpoint of net impurity charge, which should influence the energies of impurity association, solubility and migration. The method of the measurement of electrical conductivity with varying temperature and concentration of trivalent bismuth in NaCl single crystals was used.

Single crystals of various concentrations were prepared by the Stockbarger method. The basic material — potassium chloride — was purified by extraction [8, 9]. The KCl crystal with  $\text{BiCl}_3$  impurity was prepared from the melt by one hour gurgling  $\text{Si}_2\text{Cl}_6$  vapour [10, 11]. In a neighbouring pipe bismuth chloride was prepared by burning the metal in a flow of chlorine saturated by tetraethylorin methane vapour. Under a continual flow of protective atmosphere it was poured into the potassium chloride melt in the growth ampoule. The size of samples used for the electrical conductivity measurement (0.001, 0.01 and 0.1 of  $\text{BiCl}_3$  in melt) was approximately  $0.6 \times 0.6 \times 0.1 \text{ cm}^3$ . The surfaces were graphitized by electrodes. The measurements were performed in the temperature range 25 ° to 650 °C by methods described in [12, 13].

In various samples electrical conductivity of pure and doped crystals was measured as a function of temperature (Fig. 1). In the course of own measurements, impurity and precipitation ranges can be observed. Moreover, one can see that the solubility of bismuth in KCl is low.

The energy of  $\text{Bi}^{3+}$  migration in KCl equals 0.61 eV, which is a value lower than for divalent cations [14] and that of the host potassium ions self-diffusion (0.71 eV to 0.84 eV) [15]. This low value can be explained by realizing the interstitial mechanism of the  $\text{Bi}^{3+}$  diffusion. This mechanism is highly probable, due to small repulsive forces applied to an interstitial ion with a small radius, for  $\text{Bi}^{3+}$  (0.081 nm) in alkali halides and especially in KCl ( $K^+ - 0.133 \text{ nm}$ ).

Tharmalingham [16] computed interstitial anion and cation migration in NaCl, KCl and KBr. Using the BMW potential he obtained for the  $K^+$  interstitials activation energy values 1.31 eV for the diffusion in the direction (100) and 0.87 eV for the diffusion in the (111) direction. In the case of bismuth, the activation energy for interstitial diffusion is much lower than that of  $K^+$ . In the case of bismuth the charge transport can be considered as follows: each trivalent interstitial bismuth atom should be accompanied by three cation vacancies in order to preserve the electrical neutrality of the crystal. In the eight corners of a cube with a bismuth atom in the center (Fig. 2) there should be four tetrahedrally coordinated chlorine ions around the bismuth ion and furthermore, a potassium cation and three cation vacancies (two of them shared with the the neighbouring cube). The four chlorine ions

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will move off the lattice, thus the original lattice will get deformed. Because of this deformation and the existence of the shared vacancies, the energy required for the jumping of a bismuth ion from the centre of one cube to another is negligible, thus yielding an oscillation of the bismuth ion between two neighbouring cubes. For direct motion of a bismuth ion a vacancy must simultaneously move by two consequent jumps with the probability  $w_1$  from the corner behind the bismuth ion to that in front (in the direction of the diffusion) so that a new interstitial position is formed. In this manner the interstitial diffusion will be determined by the jumps of vacancies around bismuth, thus the measured activation energy (0.61 eV) is due to the  $w_2$  jumps.

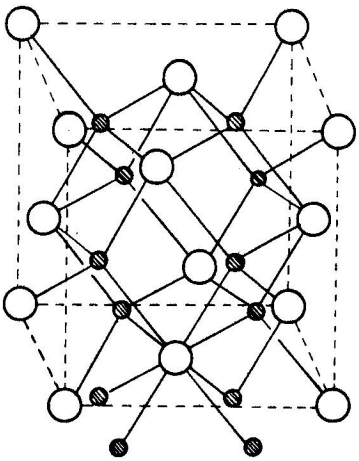


Fig. 1.

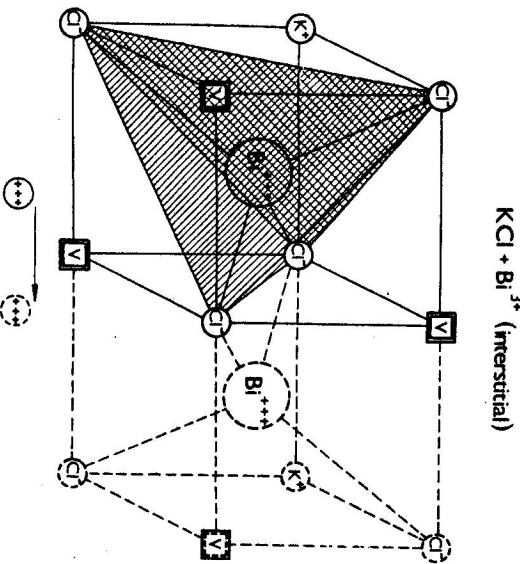


Fig. 2.

These considerations can be generally applied to other polyvalent impurities with jumping energies lower than those for self-diffusion for both divalent and trivalent cations. In the case of divalent impurities the cube corners will possess only two vacancies. According to an estimate, the impurity association energy equals 0.56 eV. From the charge viewpoint there are three possible interstitially built-in impurity-vacancy complexes:  $\text{Bi}^{3+}$  (net charge  $+3e$ ) + 1 vacancy (net charge  $-e$ ),  $\text{Bi}^{3+}$  + 2 built-in impurity-vacancy complexes:  $\text{Bi}^{3+}$  (net charge  $+3e$ ) + 1 vacancy (net charge  $-e$ ),  $\text{Bi}^{3+}$  + 2 cation vacancies and  $\text{Bi}^{3+}$  + 3 cation vacancies. Owing to low solubility it is difficult to consider influences of individual complexes (i.e. their contribution) on the electrical conductivity  $\sigma$ . The experimental results regarding impurity diffusion [1, 5] have shown that the charged complex is much less movable than the free vacancy so that this contribution can be neglected. At higher solubilities the complex structure could be determined by some relaxation measurements.

The value of the Coulomb energy calculated for the  $\text{Bi}^{3+}$  ion in an interstitial location and one (two, three) cation vacancy (ies) in n.n. positions according to the  $\text{Bi}^{3+}$  ion, together with a comparison of the obtained value of the experimentally determined association energy 0.56 eV suggest that most complexes are formed by a  $\text{Bi}^{3+}$  ion with three vacancies in the nearest neighbouring positions.

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