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X-ray Studies on the Effects of Ba^{2+} Impurity in KCl

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Using the X-ray diffuse scattering technique, KCl crystals alloyed with 0·005 at.% barium were investigated. Possible distributions of Ba^{2+} impurities in the lattice of KCl, the formation of segregates in the form of additional planes parallel to the {100} and {130} planes of the matrix, are shown. On the basis of the analysis performed on the X-ray photographs the nature of distortions present in the alloyed lattice is ascertained. The influences of the impurities on the binding forces between matrix atoms in the ⟨100⟩ and ⟨130⟩ directions are shown.

Alloying is an important means of controlling the physical properties of materials. Introducing impurities into a crystal causes deformations and internal stresses (of various kinds); this causes crystal lattice defects (vacancies, interstitial atoms, dislocations) to appear which relieve the above internal stresses, and leads to changes in the acoustic wave spectrum and to a phase transition.

The reasons for the present study of the effects of barium alloying on the KCl lattice arise from the following. The Ba^{2+} ion radius is equal to the K^+ ion radius. Therefore, if Ba forms a solid solution, deformations that distort the crystal should be absent. However, there are anion vacancies in the neighbourhood of the divalent Ba and their presence leads to tetragonal lattice distortions spreading over several interplane distances.

If, however, the Ba atoms are clustered into 'minute' solid segregates the deformations distorting the crystal are due to the difference in morphology of crystalline $BaCl_2$ (rhombic) and KCl (cubic), and to the difference in their elastic properties. When Ba forms 'large' segregates that no longer have coherent coupling with the matrix then part of the elastic strain is relieved, owing to misfit dislocations appearing at the 'matrix–segregate' interface and to slide dislocations of the matrix and segregates. Thus the elastic distortion of the matrix lattice in this case is less than that in the case of coherent segregates.

Various physical techniques (investigations of resistivity, diffusion, and absorption in dielectrics) allow one to obtain important information about crystals alloyed with various additions. Apart from the techniques listed above there exists an X-ray method of investigating the early stages of aging. Using X-ray diffraction techniques (in particular, X-ray diffuse scattering) the presence of Guinier–Preston zones with dimensions from 10 to 100 Å may be established, as well as the type of coagulates being formed (*e.g.* rods or spiral trimer aggregates). A detailed analysis of numerous reciprocal-lattice points makes it possible to estimate not only the shape and dimensions of segregate particles but also their orientation with respect to the matrix. All this has made possible the use of X-ray diffuse scattering to investigate KCl alloyed with a small amount of divalent barium (0·005 at.%).

We have investigated annealed and hardened barium-alloyed KCl crystals and annealed 'pure' KCl crystals. The crystals were grown using the Kiropulos procedure; they were annealed for 8 h with subsequent slow cooling in a furnace (cooling rate $\sim 1{\cdot}5°\ min^{-1}$). The crystals were hardened in CCl_4 starting from 500 °C. The absence of thermal stresses during the hardening process was confirmed by polarized-light measurements.

The samples obtained were used to investigate the X-ray diffuse scattering. Transmitted Mo $K\alpha$ X-rays (monochromated by a LiF-based bent monochromator) from a Mo-tube URS-60, run at 25 kV and 20 mA, were detected photographically. The samples were oriented parallel to the [100] ray; during measurements, the samples were rotated around the [010] vertical axis from the 200 reflexion by ± 3, ± 5, ± 7, $\pm 10°$. The reflexions obtained on an individual X-ray pattern represent a view of the Ewald sphere cross section cut by the reciprocal lattice, and the entire set of X-ray patterns provides the total picture of the reciprocal-lattice intensity distribution. The vicinities of 14 reciprocal-lattice points were analysed in detail with regard to changes in intensity, shape and mutual position of the fourth-order sites for equatorial, upper and lower layer lines.

In order to determine the reflexion spread directions precisely, all the X-ray photographs obtained were processed on an MF-4 microdensitometer with the option of a logarithmic amplifier and automatic tape recording of the optical density variations. Then, by scanning the X-ray photographs layer-by-layer (Wooster, 1963) the optical density diagrams were plotted for all the reciprocal-lattice points. In such a

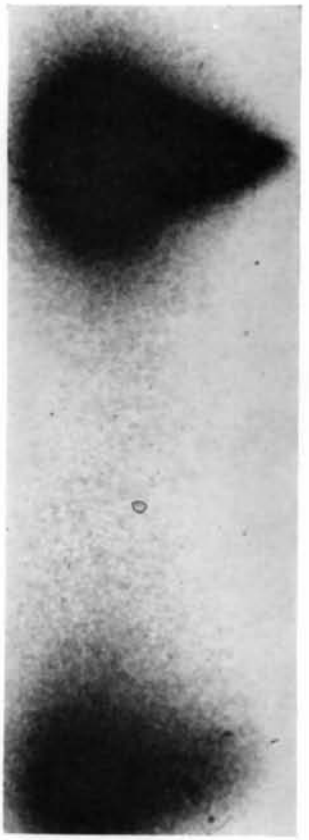

Fig. 1. Cone-like elongations of diffuse spots along the ⟨001⟩ directions (upper reflexion: $\bar{4}00$, lower reflexion $\bar{4}\bar{2}0$, rotation by $+5°$) for Ba^{2+}-alloyed KCl crystals.

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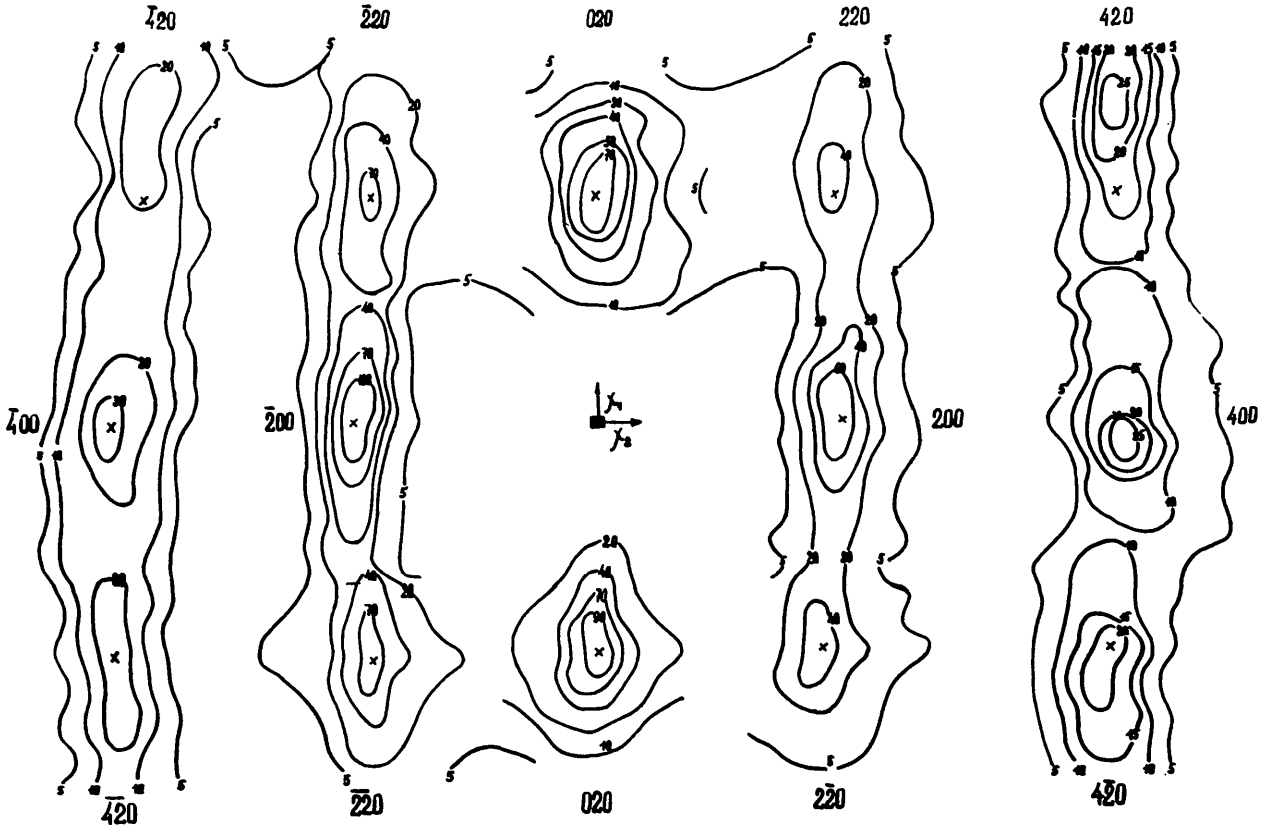
way the intensity distribution (iso-intensity curve) was measured for 'pure' KCl as well as for annealed and hardened KCl crystals with Ba^{2+} impurities.

To determine the diffuse-spot orientation in reciprocal space it was necessary to know precisely the location of the main crystalline axes. Calculations using the formula of Bagaryatsky (1958) performed on an M-222 computer yielded the positions of these axes. In processing the experimental data we discovered a number of interesting properties of the alloyed crystals.

The measurements revealed the following peculiarities on the X-ray photographs obtained from $KCl.Ba^{2+}$: extremely sharp changes in the shape of diffuse spots were clearly observed; reflexions were elongated, and grew in intensity and area, the intensity distribution within a spot becoming asymmetric. Let us consider each of these observations separately.

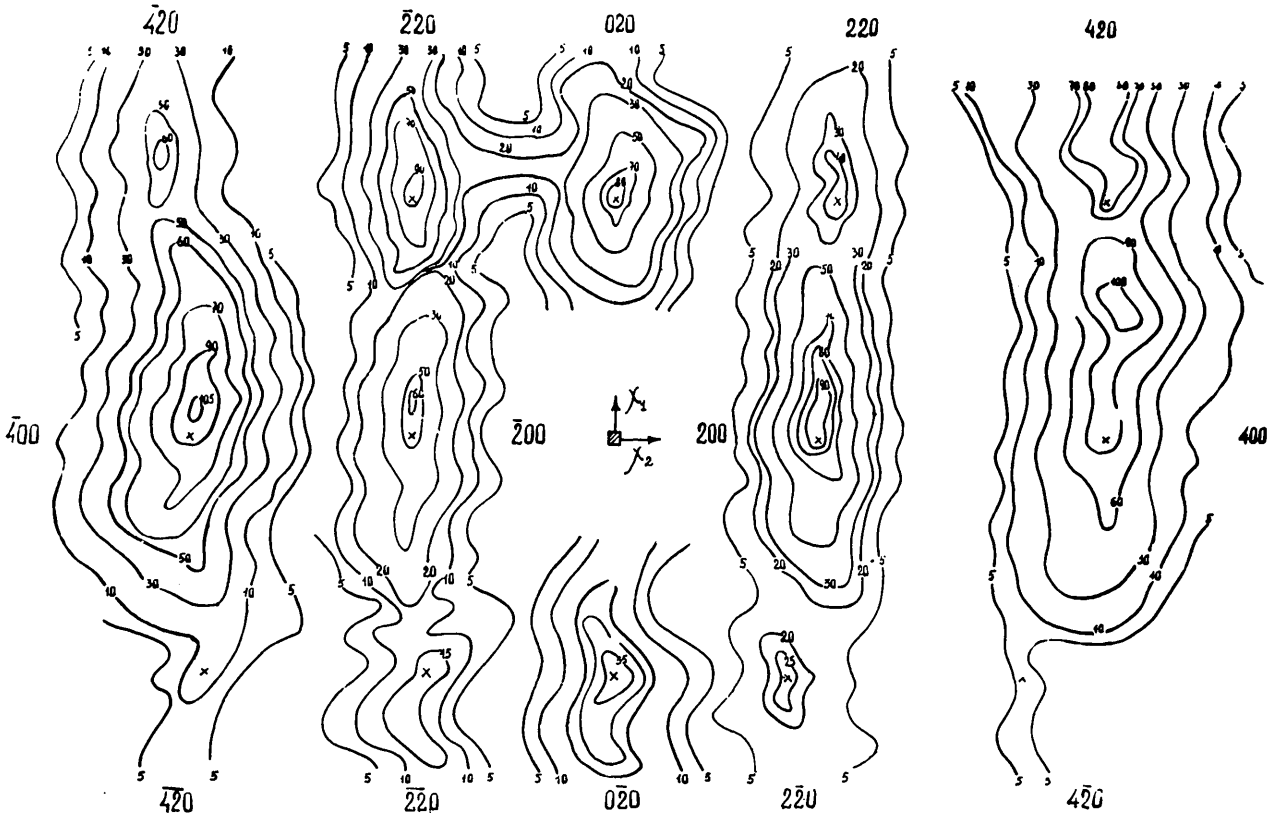
On the diffuse spots of the X-ray photographs investigated, regions of higher intensity appear which are comparable in length with the diffuse spots themselves, and elongated along the ⟨001⟩ direction (Fig. 1). These elongations in the vicinity of the diffuse maxima are also noticeable on the X-ray photographs at rotation angles of +3, +5 and +7°. The appearance of the increased intensity areas elongated along the ⟨100⟩ direction [*i.e.* the presence of the cone-like spot elongation (CSE) of the intensity in reciprocal space] indicates that the number of spaced crystalline planes increases. The planes make up zones. Suppose that the number of planes in these zones is inversely proportional to the CSE length (the dimension of the reciprocal-lattice cubic cell is a unit of the measured CSE). Then the CSE along the ⟨001⟩ direction found by the experiment corresponds to a distortion involving one plane. Taking into account the accuracy of this experiment (0·1 mm on the film corresponds to 0·009 $Å^{-1}$), it can be shown that a zone contains not more than 20 planes.

Apart from the bright ⟨001⟩ CSE on the X-ray photographs, additional elongations along the ⟨130⟩ direction on the isointensity plots were discovered. They can be seen most distinctly when the crystal is rotated at +5 and +7° [Fig. 2(*b*)]. These CSE directions may correspond to two types of plane parallel to the ⟨100⟩ and ⟨130⟩ planes of the matrix. The length of the diffuse regions in the directions of these additional elongations along ⟨130⟩ is shorter by a factor of two or three than that for CSE along ⟨001⟩. Therefore the number of planes containing lattice distortions along ⟨130⟩ exceeds that of those along ⟨001⟩. Ac-



(*a*)

Fig. 2. The isointensity plots of the thermal diffuse scattering for (*a*) 'pure' KCl crystals. (1 mm on the film corresponds to 3 mm on the graph.)



(*b*)

Fig. 2 (*cont.*) (*b*) KCl.Ba^{2+}.

cording to the calculations performed, the number of such planes varies from one to three.

With 'pure' KCl crystals there are not the described peculiarities on the X-ray photographs, and only elliptical diffuse maxima are observed on the iso-intensity plots, the major ellipse axis being oriented along ⟨010⟩ [Fig. 2(*a*)].

The analysis of the isointensity plots has shown that the direction of the elongation changes on changing the angle of crystal rotation (from ± 3 to $\pm 10°$): this is an indication of anisotropic distortion of the reciprocal-lattice points.

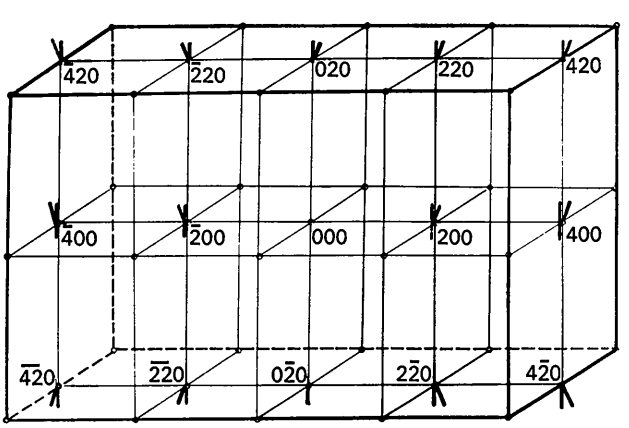


Fig. 3. Diffuse scattering intensity distribution in reciprocal space for KCl.Ba^{2+}.

The experimentally determined anisotropic intensity distribution in reciprocal space is shown in Fig. 3. This distribution has the following peculiarities: CSE's go through the reciprocal-lattice points along the ⟨130⟩ and ⟨001⟩ directions for the points of the upper and lower layer lines and along the ⟨130⟩, ⟨001⟩ and ⟨00$\bar{1}$⟩ directions for the points of the equatorial layer line. As seen from Fig. 3, the diffuse scattering areas are not centrally symmetric as they should be according to the classical Laue (1936) theory. Moreover, the asymmetry of the diffuse scattering areas is different for different reciprocal-lattice points; there are three CSE's for $n,0,0$ points and two for $n,n,0$ points (excluding the point $0,\bar{2},0$). The asymmetrical intensity distribution discovered experimentally testifies to the existence of distortions caused by alloying KCl with Ba^{2+}. As has been shown experimentally, introducing Ba^{2+} into KCl makes additional planes appear containing Ba^{2+}, K^+, Cl^- ions and vacancies. These planes cluster into zones. Atoms within these planes are not displaced whereas matrix atoms are displaced at both sides of the zone along one of the ⟨100⟩ directions perpendicular to the

plane of the zone. This may be considered to be a cause of tensile stresses bringing about tetragonal distortions of the lattice.

Similar effects can also be observed in the ⟨130⟩ direction, the latter being oriented at an angle of 70° relative to ⟨100⟩. This may be attributed either to the initial stage of the flaw-forming process (as due to the formation of the zones in these directions) or to vector summing of the distortions corresponding to all the ⟨100⟩ directions. This may also testify to the formation of zones in the ⟨130⟩ directions similar to those in ⟨100⟩.

A model of similar segregates for metallic solid solutions has been proposed by Dobromyslov (1971) has proved to be most suitable for qualitatively describing processes occurring in supersaturated solid solutions. Such a scheme seems to be valid for alloyed alkali–halogen crystals.

In addition to the changes in the shape of diffuse spots there are another two peculiarities of the substitution disorder. (*a*) The intensity around the zeroth point is enhanced. (*b*) The diffuse scattering is localized around the points of the reciprocal lattice. This suggests that disordering of the atomic arrangement is mainly due to the substitution disorder [according to Guinier's (1962) classification].

Foreign cation impurities are known to interact with positively charged vacancies and to form dipole-like impurities. In its turn, this phenomenon causes heavy local distortions of the crystal lattice, *i.e.* brings about the displacement disorder.

From experimental X-ray photographs it is seen that in addition to the substitution disorder in the alloyed crystals under study there are clear indications of the presence of displacement disorder: spot intensities increase for higher reflexion orders (from 200 to 600). This is due to the lattice distortion caused by an added impurity (Krivoglaz, 1969). The effect of the displacement is also confirmed experimentally by the asymmetry of the diffuse scattering points on the X-ray photographs.

To check that the lattice distortions are caused by impurities we investigated hardened $KCl.Ba^{2+}$ crystals. It was found that hardening entirely obliterates the CSE's elongated in the ⟨100⟩ and ⟨130⟩ directions. This is substantiated by the fact that the lattice distortions producing CSE's are associated with the segregates present, since their absence causes the CSE's to disappear. Thus the increase of the crystal's yield limit observed during aging (Novikova & Lubenets, 1970) should be attributed only to the distortions associated with segregates and not to the distortions due to isolated dipole pairs, *e.g.* impurity cation – positive vacancy.

Trimer conglomerates are assumed to separate into small dipoles during the hardening process. It is not unlikely that in this experiment hardening starting from 500 °C caused significant stresses and an increase in dislocation density. It has been shown (Lubenets & Startsev, 1968) that the yield limit of such crystals does not differ appreciably from the initial value.

The last and most interesting peculiarity common to all the X-ray photographs obtained (for all rotation angles referred to the Bragg angle) is that it has been found that the spacings between diffuse maxima decrease with simultaneous increase in their area (Fig. 2). The latter feature suggests the presence of static distortions caused by Ba^{2+} impurities.

The decrease in the distance between diffuse maxima implies that they are shifted towards the centre of the reciprocal lattice with respect to corresponding selected reflexions. It may be suggested that the binding forces along the ⟨100⟩ directions (along which the diffuse spots are shifted towards the centre of an X-ray photograph) between atoms in the planes perpendicular to these directions, decrease because of Ba^{2+} impurities.

The results of this work may be summarized as follows.

(1) Diffuse scattering enables us to detect the presence of impurity concentrations as low as 0·005 at.%.

(2) The possibility of zones being formed parallel to the {100} and {130} planes of the matrix has been shown.

(3) The observed asymmetric diffuse spots at reciprocal-lattice points suggest an anisotropy of matrix elastic distortions around plate-like segregates.

(4) The nature of local impurity centres in crystals of $KCl.Ba^{2+}$ has been ascertained, and the diffraction effects caused by static distortions generating lattice defects have been studied.

In conclusion it is a welcome duty to express our gratitude to Dr V. Z. Bengus and Dr S. V. Lubenets for their advice and discussions.

References

BAGARYATSKY, YU. A. (1958). *Kristallografiya*, **3** 570–577.

DOBROMYSLOV, A. V. (1971). *Fiz. Met. Metalloved.* **32**, 780–785.

GUINIER, A. (1962). *Heterogeneities in Metallic Solid Solutions*. Russian translation by TYAPKIN, YU. D., edited by YU. A. BAGARYATSKY. Moscow: Mir.

KRIVOGLAZ, M. A. (1969). *The Theory of X-ray and Thermal Neutron Scattering by Real Crystals*. New York: Plenum.

LAUE, M. VON. (1936). *Ann. Phys. Leipzig*, **26**, 55–59.

LUBENETS, S. V. & STARTSEV, V. I. (1968). *Fiz. Tverd. Tela*, **10**, 22–29.

NOVIKOVA, I. G. & LUBENETS, S. V. (1970). *Metallofizika, Kiev*, **30**, 75–81.

WOOSTER, W. (1963). *Diffuse X-ray Reflections from Crystals*. Russian translation by L. I. MIRKIN, edited by G. S. ZHDANOV. Moscow: Mir.