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LOCAL DISTORTIONS OF A CRYSTAL LATTICE BY IMPURITY IONS

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The experimental data on the distortion of the sodium chloride lattice by Ag^+, K^+, Li^+, Br^-, I^-, and Rb^+ ions are compared with calculations based on the theory of elasticity of continuous media. It is shown that good agreement between the calculations and experimental data can be obtained if the inter-ionic distances of the corresponding crystal lattices are used as the characteristic dimensions.

In previous work[1] we used the method of nuclear magnetic resonance to investigate distortions of the sodium chloride lattice in the vicinity of various impurity ions. Through the use of the concept of the "critical sphere" described about the impurity ion (at the boundary of which the distortion has a given value) the dimensions of the distortion zones of the impurity ions Ag^+, Br^-, and K^+ were determined. An attempt to calculate the dimensions of the distortion zones for these ions on the basis of the tabulated values for their ionic radii, however, produced results that differed strongly from experiment.

The goal of the present work was to clarify the question of the theoretical estimation of distortion-zone dimensions. To do this it was necessary, first of all, to widen the range of the experimental data; in addition to the dimensions of the distortion zones for Ag^+, Br^-, and K^+ which were found earlier, the dimensions of the distortion zones around I^-, Li^+, and Rb^+ ions were also determined by the same method. A summary of the results for all six impurity ions is given below (n is the number of Na^{23} nuclei within the limits of a distortion zone and R is the radius of the zone in Angstroms).1)

Impurity ion:	Ag^+	Br^-	Li^+	K^+	I^-	Rb^+
n:	115	290	450	740	760	1020
R:	10	14	16	19	19.5	21

For what follows it is of importance that the ions considered enter into the sodium chloride lattice as substitutional impurities. Another important fact is that Ag, Li, K, and Rb with Cl as well as Br and I with Na form compounds that crystallize in the NaCl-type lattice. In this way, for example, one can speak either of K^+ replacing Na^+ or of a "molecule" consisting of a K^+ ion and its six Cl^- neighbors replacing the analogous "molecule" in the NaCl lattice. In the first case the distortion of the sodium chloride lattice is attributed to the difference in the ionic radii of K and Na, in the second case to the difference in the inter-ionic spacing in the NaCl and KCl lattices.

In both cases we shall make use of the solution of the elementary problem in the theory of elasticity concerning the deformation of an isotropic elastic medium with a spherical cavity of radius r_0 in which is inserted a sphere of radius r_n. Solution of this problem leads to the following expression for the deformation of the medium at a distance R from the center of the sphere:

$$\varepsilon = \varepsilon_0 r_0^3 / R^3, \tag{1}$$

where $\epsilon_0 = \alpha(r_n - r_0)/r_0$ is the deformation at the boundary of the sphere, and the coefficient α depends on the relation between the elastic properties of the inserted sphere and the medium. In case this sphere is absolutely rigid $\alpha \cong 1$, and in the other limiting case $\alpha = 0$; if the elastic constants of the inserted sphere and the medium are equal $\alpha \cong 1/2$.

If we take as the inserted sphere the "molecule" consisting of the impurity ion and its six neighboring ions of opposite sign, then we can set $\alpha \cong 1/2$, since the elastic properties of the crystals considered do not differ much from each other. Then, using the values for R given above and the data

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1)These figures are somewhat different from those given in [1]. The reason is that in previous work a natural crystal of rock salt from an unknown source was used as a standard. Later measurements showed that the intensity of the Na^{23} resonance was 10-15% higher in crystals of pure NaCl grown from the same salt and under the same conditions as the crystals containing the impurities, than in the natural crystal. Correction for this circumstance leads to somewhat greater dimensions for the distortion zones.

Impurity ion	Ag+	Br−	Li+	K+	I−	Rb+
r_n, Å	2.7745	2,9886	2.5698	3.1465	3.2365	3.2905
$\lvert \varepsilon_0 \rvert$	0,0081	0,03	0,0445	0,058	0,074	0,084
$\lvert \varepsilon \rvert \cdot 10^3$	0,18	0,24	0,24	0,19	0,23	0,20

for the inter-ionic separations r_n,[2] it is easy to calculate from Eq. (1) the deformation ϵ at the boundary of the distortion zone. The results obtained in this way are presented in the table; we have taken

$$r_0(\mathrm{NaCl}) = 2.8201 \text{ Å}.$$

The deformation at the boundary of the distortion zone should be constant, regardless of the kind of impurity.[1] As can be seen from the table, this is actually the case. On the other hand, the absolute value of the deformation calculated in this manner is found to be close to the value 10^{-3}—10^{-4} obtained experimentally.[1]

Thus, this method of calculation, in spite of the crudeness of the model, gives results in good agreement with experiment. It is interesting to note that the same results are given also by a microscopic calculation that takes into account the discrete structure of the lattice.[3]

In case we take as the inserted sphere the impurity ion itself, application of Eq. (1) does not produce agreement with experiment.[1] This is due both to the well-known uncertainty of the values for the ionic radii and to the dependence of the coefficient α in Eq. (1) on the kind of impurity ion. Actually, if one uses our experimental data and the tabulated values of the ionic radii,[4] it is possible to calculate relative values of the coefficient α from Eq. (1). For the impurity ions Ag^+, Li^+, K^+, Rb^+, Br^-, and I^- this coefficient is found to be equal respectively to 0.18, 0.65, 1.00, 0.98, 0.30, and 0.32, i.e., it differs significantly from ion to ion.

In conclusion we note that the method of estimating the magnitude of lattice distortions by impurities based on the change in the inter-ionic (interatomic) bond lengths applies, apparently, only in the case of impurities that crystallize in the same lattice as the host crystal. Some preliminary experiments we have carried out, for example, have shown that the impurity Cs^+ produces a greater distortion of the NaCl lattice than should be expected on the basis of Eq. (1).

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[1] M. I. Kornfel'd and V. V. Lemanov, JETP **41**, 1454 (1961), Soviet Phys. JETP **14**, 1038 (1962).

[2] Index to X Ray Powder Data File, ASTM, Philadelphia, 1959.

[3] I. S. Zhurkov and V. S. Oskotskiĭ, JETP **43**, 2261 (1962), this issue, p. 1597.

[4] Handbook of Chemistry and Physics, Chemical Rubber Publishing Co., Cleveland, 1955.

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