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MICROSCOPIC CALCULATION OF LATTICE DISTORTIONS DUE TO IMPURITIES

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The rigid-ion model is used to calculate distortions of the sodium chloride lattice due to the impurity ions Ag^+, Br^-, Li^+, K^+, I^-, Rb^+. The results are compared with the experimental data obtained by nuclear paramagnetic resonance and with the results of calculations based on the theory of elasticity.

KORNFEL'D and Lemanov[1] reported the results of investigations into distortions of the NaCl lattice caused by the substitutional impurity ions Ag^+, Br^-, Li^+, K^+, I^-, Rb^+, and gave a calculation of the magnitude of these distortions based on the theory of elasticity for a continuous medium. It was considered to be of interest to carry out a similar calculation allowing for the discrete nature of the lattice structure. Such a calculation was carried out by Hardy[2] for the NaCl crystal containing K^+ as an impurity. The results of this calculation can be generalized to other impurity ions.

Following Hardy we shall assume that in the lattice there is, apart from the electrostatic interaction, a central interaction due to the overlapping of electron shells having a potential of the form $A\exp(-r/\rho)$, where A and ρ are parameters determined from the compressibility and the condition of equilibrium of a crystal.[3] Displacements of the ions nearest to the impurity are found from the equation[2]

$$\xi \doteq 2.04\cdot 10^5\left[\frac{A}{\rho}\exp\left(-\frac{r_0+\xi}{\rho}\right)+\frac{A_0}{\rho_0}\left(\frac{\xi}{\rho_0}-1\right)\exp\left(-\frac{r_0}{\rho_0}\right)\right].$$

Here r_0 is the distance between nearest neighbors in the NaCl crystal, A_0 and ρ_0 refer to the NaCl crystal, and A and ρ refer either to a chloride crystal of the metal which acts as an impurity ion in NaCl or to a sodium salt of the halogen which is present as an ion impurity.

In calculating the distortions introduced by the silver impurity we must remember that the deformations in the AgCl crystal do not satisfy the Cauchy relationships, and consequently the noncentral interaction is important. However, when an ion of Na is replaced by an ion of Ag, the latter causes displacements of the neighboring Cl ions corresponding to uniform compression of the AgCl crystal, such that only the distance between the ions is altered. Introducing formally the central interaction potential for such deformations and determining its parameters A and ρ from the compressibility and the condition of equilibrium,[3] we obtain $A = 2.26\times10^{-9}$ erg and $\rho = 0.217\times10^{-8}$ cm.

In experiments on nuclear resonance[1] the number n of Na nuclei within the limits of a certain "critical sphere" around the impurity ion was determined. At the boundary of this sphere the lattice distortions due to the impurity have a certain form determined by the experimental conditions, and are independent of the nature of the impurity ion. Since the relative deformation of the lattice at a sufficient distance from the impurity is proportional to $\epsilon_0 r_0^3/R^3$, where $\epsilon_0 = \xi/r_0$ is the relative displacement of the ions nearest to the impurity, the volumes of the "critical spheres" and the numbers n of Na nuclei inside such spheres for various impurity ions should be in the same ratios as the corresponding ϵ_0.

The experimental values of n[1] and the calculated values of ξ and ϵ_0 are listed in the adjoining table, which shows that the ratio n/ϵ_0 is the same, within the experimental error, for all impurity ions, in agreement with theory.

We now estimate the magnitude of the deformation at the boundary of the "critical sphere," which is really a very complex surface. It follows from Hardy's work[2] that the relative radial deformations in units of $\epsilon_0 r_0^3/R^3$ are 1.74 for the [100] axis, 1.25 for the [110] axis and 0.73 for the [111] axis.

We assume that the "critical sphere" has the radius given by Kornfel'd and Lemanov[1] and that at its boundary the mean radial deformation is $\epsilon = 1.25\,\epsilon_0 r_0^3/R^3$. The values of ϵ calculated in this way are listed in the table. They are approximately the same for all impurities, in agreement

Impurity ion	Ag^+	Br^-	Li^+	K^+	I^-	Rb^+
n	115	290	450	740	760	1020
ξ, Å	—0.03	0.072	—0.088	0.15	0.176	0.208
$\lvert\varepsilon_0\rvert$	0.011	0.025	0.031	0.053	0.062	0.74
$n/\lvert\varepsilon_0\rvert$, rel. units	0.75	0.83	1.04	1	0.88	0.99
$\lvert\varepsilon\rvert\cdot 10^3$	0.3	0.2	0.21	0.22	0.24	0.22

with experiment. Such a calculation is, of course, purely qualitative. Its results are almost identical with those calculated by Kornfel'd and Lemanov using the theory of elasticity. This is not surprising, since the surface of the "critical sphere" lies at such a distance from the impurity that we can use the theory of elasticity.

The greatest divergence between the theory and experiment occurs, as shown in the table, in the case of Ag, which is obviously due to the poor applicability of the central-force model to AgCl.

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[1] M. I. Kornfel'd and V. V. Lemanov, JETP **43**, 2021 (1962), this issue p. 1427.

[2] J. R. Hardy, J. Phys. Chem. Solids **15**, 39 (1960).

[3] M. Born and K. Huang, Dynamical Theory of Crystal Lattices, Oxford, Clarendon Press, 1954.

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