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DEFORMATION OF THE NaCl *LATTICE BY* Ag^+, Br^-, *AND* K^+ *IMPURITY IONS*

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The lattice constant and the intensity of the Na^{23} nuclear magnetic resonance absorption line were studied as functions of the impurity concentration in NaCl crystals containing AgCl, NaBr, and KCl impurities. A clear correlation was observed between decrease of the absorption line intensity and variation of the lattice constant. Both the intensity and the lattice constant are unique functions of n and c not depending on the kind of impurity. (c is the impurity concentration and n is the number of Na^{23} nuclei within the "critical" sphere.) The degree of elastic deformation of the lattice near an impurity ion is estimated. At distances of 8.9, 12.4, and 16.7 A from Ag^+, Br^-, and K^+ ions, respectively, the degree of deformation was approximately 10^{-3}.

1. INTRODUCTION

CRYSTAL lattices are deformed in the vicinity of impurity atoms and ions. However, very little is known regarding the nature and degree of this deformation. X-ray analysis shows that impurities change the average atomic separation (the lattice constant), but does not supply information regarding local deformations near impurity ions or atoms. The latter type of information can be obtained by means of nuclear magnetic resonance. The investigation of quadrupole effects in the nuclear magnetic resonance of impure crystals can be used to determine the character and degree of local lattice deformations. However, the results obtained by this method are still very incomplete.*[1,2]

Let us consider the method as applied to the simplest case of a cubic crystal. The high lattice symmetry of a pure and nearly perfect crystal makes the electric field gradient zero at all nuclei. Therefore the central line component (the transition $m = 1/2 \rightarrow m = -1/2$, where m is the magnetic quantum number) and satellites ($m \rightarrow m - 1$ transitions with $m \neq 1/2$) coincide in frequency, forming a single combined absorption line. The introduction of an impurity induces electric field gradients at the nuclei. These gradients can result both from the electric field of an impurity atom or ion and from elastic deformations, i.e., local changes of lattice symmetry. A charged impurity is accompanied by both effects, while only the second effect occurs in the case of a neutral impurity.

Satellite frequencies are shifted by an interaction between nuclear quadrupole moments and the electric field gradient. The maximum shift will obviously occur for nuclei in the immediate vicinity of an impurity ion, where the gradient is especially large; the shift will diminish with increasing distance between the nuclei and the impurity. We therefore introduce the concept of a critical sphere around an impurity ion. The radius of this sphere is defined as such that for all nuclei within the sphere the satellite frequency shift exceeds the half-width of the absorption line at its base, i.e., at the instrumental noise level. The satellites of these nuclei are smeared out within a broad frequency interval and are lost in the noise background, so that an apparent reduction of absorption line intensity is observed. The reduction of intensity becomes more marked as the impurity concentration increases and thus puts more nuclei within critical spheres.

At low concentrations, however, when there is only a small probability that critical spheres intersect, the contribution of satellites to the absorption line intensity is

$$J = J_0(1 - nc), \qquad (1)$$

where J_0 and J are the satellite intensity in a pure and impure crystal, respectively, n is the number of nuclei within a critical sphere, and c is the impurity concentration. The slope of the first segment of the curve of J/J_0 as a function of

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*This does not apply to Rowland's very thorough study[3] of impurities in copper, where it was shown that in this case charge effects, rather than lattice defomations, are responsible for the quadrupole interaction.

c can be used to determine n and thus also the radius R of the critical sphere.*

The critical radius determined in the foregoing manner is, of course, arbitrary since the width of the absorption line at its base depends on the noise level. However, this width can be used to determine the electric field gradient for nuclei at a distance R from an impurity ion, thus imparting a definite quantitative meaning to the concept of a critical sphere.

As a basis for a systematic study of the different impurities in NaCl crystals we had first determined the components of the tensor relating the electric field gradient at a Na^{23} nucleus to the elastic deformation of the NaCl lattice.[6] When these tensor components are known the degree of lattice deformation at the boundary of a critical surface can be computed.

In the present work we investigated NaCl crystals with neutral impurities containing Ag^+, Br^-, and K^+. The dependence of the Na^{23} absorption line intensity on impurity concentration was measured along with x-ray measurements of the lattice constant.

2. PREPARATION OF SAMPLES

Pure NaCl crystals and crystals doped with AgCl, NaBr, or KCl were grown by the Kyropoulos method from a melt containing chemically pure materials. The impurity content was determined by chemical analysis—by weighing in the case of Ag, by the iodometric method in the case of Br, and by the cobaltinitrite method in the case of K.†

The largest concentrations of AgCl, NaBr, and KCl in the crystals were 4, 11, and 3% mole, respectively. All crystals grew well within these limits. An attempt to grow NaCl-AgCl crystals containing above 5% AgCl was unsuccessful; the growth rate decreased sharply and the crystals were unsatisfactory.

It should be noted that the impurity concentration in the NaCl-NaBr system was almost identical with the concentration in the melt, but that there were considerable differences in the other two systems.

Samples for both x-ray structural measurements and nuclear magnetic resonance measurements were cut from single crystals grown to a diameter of about 50 mm and height of 30 mm. The average dimensions of the samples were 5 × 5 × 10 mm and 9 × 9 × 20 mm, respectively. Samples for chemical analysis were taken from the same portions of the respective crystals. In order to allow for a possible nonuniform impurity distribution many samples were analyzed chemically following the completion of the other measurements. It was found that the nonuniformity of impurity distribution within a sample did not exceed 10% of the mean concentration. In most instances the nonuniformity was at a satisfactory level of about 5%.

It is known from the literature that some mixed alkali halide crystals contain a large number of vacancies (see[7], for example). To determine the vacancy concentration, the density of our samples was measured by flotation, and the results were compared with the densities calculated from x-ray data. The discrepancy found in the case of NaCl crystals containing NaBr indicates that one vacancy exists for every seven Br^- ions. In the case of crystals doped with AgCl and KCl the disagreement between the computed and measured densities did not exceed the experimental error limit. On the basis of the measurements we conclude that not more than one vacancy exists for every 15 Ag^- ions or every 25 K^+ ions.

We have thus found that crystals containing NaBr have the largest number of vacancies, while those containing KCl have the smallest number. Our results will show that vacancies do not appreciably influence the intensity reduction of the nuclear magnetic resonance line.

3. MEASUREMENT OF THE LATTICE CONSTANT

The lattice constants were measured by A. I. Zaslavskii and T. B. Zhukova, using K_α emission from copper in a RKU-114 camera. Preliminary adjustment of the samples was performed in a RKSO camera. The lattice constant was determined to within $\pm 3 \times 10^{-4}$ A from the distance between reflections from (640) planes. The results are seen in Fig. 1, which also gives the relative change $\Delta a/a_0$ of the lattice constant as a function of impurity concentration for each of the three systems. $\Delta a/a_0$ is seen to be a linear function of concentration within the given limits. The lattice constant changes most markedly in NaCl-KCl crystals. Changes in the NaCl-AgCl system are small, and the NaCl-NaBr system occupies an intermediate position.

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*In earlier work[4,5] we determined the number of atoms in a critical sphere from the expression $J/J_0 = (1-c)^n$, which was derived from probability considerations.[1] It is easily seen that at low concentrations this expression is equivalent to the simpler formula (1).

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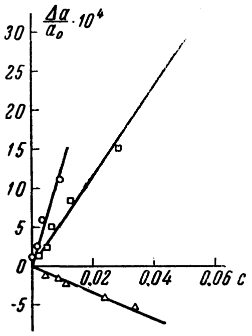

FIG. 1. Relative variation of lattice constant as a function of impurity concentration. Δ – Ag^+, □ – Br^-, ○ – K^+.

4. MEASUREMENT OF NUCLEAR MAGNETIC RESONANCE

The Na^{23} absorption line in pure and impure NaCl crystals was measured with the apparatus described in[8], using both a Franklin oscillator and one of the type described by Gutowsky et al. in in[9]. The latter differed from the original design in that prior to detection the signal was amplified at high frequency, thus somewhat improving the signal-to-noise ratio. In order to avoid saturation of the absorption line, measurements were performed at low voltages of the order 0.03 and 0.01 volt, respectively, in the Franklin and Gutkowsky oscillator circuits. For all measurements the magnetic field strength was 45 oe with 0.5 oe modulation amplitude.

The measurements showed that with increasing impurity concentration the absorption line intensity is reduced, approaching that of the central component, which in the case of Na^{23} with spin $^3/_2$ is four-tenths of the total intensity.[10] With further increase of the impurity concentration a reduction of central line intensity is observed; this corresponds to a second-order quadrupole effect.[10] The concentration at which this reduction begins is 3% mole in KCl and 10% mole in NaBr. Reduced central line intensity was not observed for crystals containing AgCl since, as already mentioned, crystals could not be grown with a sufficient AgCl content.

Figure 2 shows the relative intensity of satellites as a function of impurity concentration. Satellite intensity was taken as the difference between the measured intensity and that of the central component. The steepest reduction of satellite intensity is seen to occur for NaCl-KCl, where the intensity is reduced to approximately one-fifth for 1% mole KCl. The NaCl-AgCl system exhibits the smallest intensity reduction, while NaCl-NaBr occupies an intermediate position.

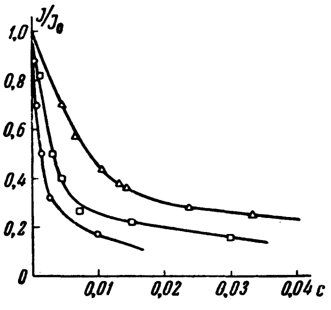

FIG. 2. Relative intensity of satellites as a function of impurity concentration. (Notation as in Fig. 1).

It should be noted here that the measure of satellite intensity in Fig. 2 is the amplitude of the derivative of the absorption line, since no changes of line width and shape were observed within experimental error limits. However, the absorption line area was calculated for individual samples, as a check. The intensities obtained in this way showed that the amplitude of the derivative is an exact measure of intensity only at low impurity concentration, but gives slightly overestimated intensities at high concentrations, when the satellite intensity approaches zero. This can account for some narrowing of the central line as the satellites are smeared out.[10] However, since the general character of the dependence of intensity on impurity concentration does not vary and only low concentrations are important for our quantitative purposes, the amplitudes of the derivative of the absorption line have been used as a measure of intensity for all points in Fig. 2.

It is seen from Fig. 2 that the first portion of the satellite intensity vs impurity concentration curve is a straight line for each of the three systems. The slope of each line gives the number n of Na^+ ions within the critical sphere and thus the radius R of the critical sphere. The values of n and R obtained in this manner are shown in the table.

Impurity ion	n	R, A
Ag^+	76	8.9
Br^-	200	12,4
K^+	460	16,7

5. DISCUSSION OF RESULTS

1. From the determination of the critical sphere in accordance with Eq. (1) it follows that at low impurity concentrations the satellite intensity is a unique function of the total volume nc of critical spheres, independently of the kind of impurity. Experiment shows (Fig. 3) that this also occurs at high concentrations, when the critical spheres must intersect. This intersection only causes the given dependence to depart from linearity, beginning at nc ≈ 1, as was to be expected.

Another interesting result is that the absolute value $|\Delta a|/a_0$ of the relative change of the lattice

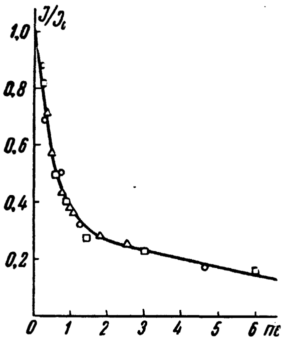

FIG. 3. Satellite intensity vs. total volume of critical spheres. (Notation as in Fig. 1).

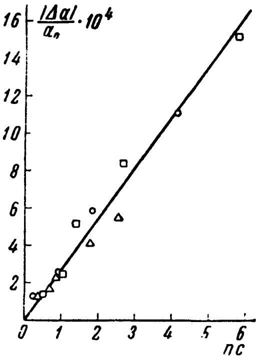

FIG. 4. Relative change of lattice constant vs. total volume of critical spheres. (Notation as in Fig. 1).

constant is also a unique function of nc, independently of the kind of impurity (Fig. 4).

A clear correlation, independent of the kind of impurity, therefore exists between the change of atomic separation determined by x-ray analysis and the departure from cubic symmetry detected by means of nuclear magnetic resonance.

2. We now compute the plastic deformation of the NaCl lattice caused by impurity ions. For this purpose we use the previously[6] determined components of the tensor S ($S_{11} = 2 \times 10^{15}$ and $S_{44} = 0.5 \times 10^{15}$ in cgs electrostatic units) which relate the electric field gradient at a nucleus to the elastic deformation of the lattice. When the field gradient at the nucleus is known the degree of deformation can be evaluated from a knowledge of these tensor components.

By perturbation theory the satellite frequency shift associated with quadrupole interaction is given by[10]

$$\Delta\nu = \frac{3eQ\,(2m-1)}{4I\,(2I-1)\,h}\,\varphi_{HH}, \tag{2}$$

where I is the nuclear spin, Q is the nuclear quadrupole moment, and φ_{HH} is the component of the gradient along the magnetic field.

Equation (2) enables us to determine the gradient φ_{HH} for nuclei located at the critical sphere boundary. As already stated, the critical sphere is defined in such a manner that for nuclei situated at the critical radial distance from impurity ions the frequency shift $\Delta\nu$ equals one-half the experimental line width at its base. Equating the right-hand side of (2) to the half-width, which in our case is ~ 5 kc, we determine the gradient at the critical sphere boundary. Our result, $\varphi_{HH} \approx 10^{12}$ cgs esu, leads to a deformation of the order 10^{-3} at the critical sphere boundary.

This deformation occurs at distances of 8.9, 12.4, and 16.7 A from Ag^+, Br^-, and K^+ ions, respectively. This large deformation at such large distances from impurity ions shows how strongly the lattice is deformed by impurities. Even at low impurity concentrations a cubic crystal is actually cubic only "on the average" and departs from cubic symmetry at every individual point.

3. The theory of elasticity for an isotropic continuum is conventionally used to determine lattice deformations induced by impurities. The relative deformation ε at a distance r from an impurity ion is taken to be

$$\varepsilon = (a_n - a_0)\,a_0^2 r^{-3}, \tag{3}$$

where a_0 and a_n are the radius of the host ion and impurity ion, respectively. It is interesting to check the consistency of this formula with our experimental data.

It follows from the definition of the critical sphere that the relative deformation ε_{cr} at the critical sphere boundary should be a constant that is independent of the kind of impurity. We obtained the following values of $\varepsilon_{cr} = (a_n - a_0)\cdot a_0^2 R^{-3}$ for each of the impurities:

	Ag^+	Br^-	K^+
$\varepsilon_{cr}\cdot 10^4 =$	3,95	2,40	0,73.

Pauling's values of the ionic radii have been used: Na^+ – 0.95, Cl^- – 1.81, Ag^+ – 1.26, Br^- – 1.95, and K^+ – 1.33 A.

Very different values of ε_{cr} are therefore associated with the different ions. This result probably ensues mainly from the fact that ions do not actually resemble solid spheres with well defined radii, as was assumed in deriving (3).

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