Investigation of Off-Center Displacements in NaCl:OH⁻ by Nuclear Magnetic Double Resonance

Yoshinori Manmoto, Minaru Tei, Junichi Nogami
and Masakuni Furuyama

Department of Electronic Engineering,
Faculty of Engineering, Okayama University of Science,
Ridai-cho 1-1, Okayama 700-0005, Japan

Takashi Iwami

Technical Division, RSK,
Marunouti 2-1-3, Okayama 700-0823, Japan

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Abstract

The measurements of the quadrupole splittings of Na^+ ion in NaCl:OH⁻ crystal are performed by nuclear magnetic double resonance. The electric field gradients produced by lattice distortion at the Na nuclei in the vicinity of the substitutional OH⁻ impurity ion is obtained, and the displacement of Na^+ ions at (100) sites is decided. By analyzing the source of the Na^+ displacement, the off-center displacement of OH⁻ ion in NaCl crystal is determined, and the critical radius to produce the off-center defects is estimated.

1. Introduction

When a small impurity ion substitutes for a larger host ion in an alkali-halide crystal, such an impurity ion may adopt generally an off-center position displaced from a regular lattice site. Many experimental studies on such off-center defects have been performed by several methods such as the thermal conductivity measurement,[1] Raman scattering,[2] phonon spectroscopy,[3] microwave spectroscopy[4] and far-infrared spectroscopy.[5,6] In order to elucidate the mechanism of off-center, many theoretical investigations also have been reported.[7-9] The theoretical ideas are concerned with lattice distortion, lattice energy, polalization of impurity and host ions, and overlap of electron orbits between impurity and host ions. All smaller impurity ions in alkali-halide crystals do not always produce off-center. There may be the critical value of the ratio of radius of impurity ion to that of host ion for creating off-center. It is important to obtain the critical radius for elucidation of the mechanism of off-center.

Satoh *et al.*[10] obtained the electric field gradient (EFG) around various monovalent

impurity ions in several ionic crystals by nuclear magnetic double resonance (DNMR). They also calculated the lattice relaxation parameters in these crystals by means of energy minimization taking account of the Coulomb, overlap-repulsive and three-body potential energies.[11] Their samples contained smaller or larger impurity ions. Though in their calculation, the off-center defects were not considered, the theoretical values agree fairly well with the experimental ones without NaI:Cl⁻ crystal. In this crystal off-center may be created, since the ratio of ionic radius of impurity to that of the host ion is considerably small.

We have used the highly sensitive DNMR technique to study the off-center mechanism of OH⁻ ion in NaCl crystal. In this crystal the OH⁻ molecular ion substituted for a chlorine ion is located along the [100] off-center directions.[5,12] In perfect alkali-halide crystals, the EFG at any sites vanishes due to the cubic symmetry of the lattice. However, for nuclei in the vicinity of impurities the symmetry is lowered and the resutling EFG gives rise to quadrupole interactions. The smaller impurity ions than the critical radii create off-center which produces quadrupole interactions. The off-center displacement of the impurity ion can be decided by obtaining the quadrupole frequencies of the host ions surrounding the substitutional impurity ions. In our case, the magnitude of the off-center displacement of OH⁻ ion is estimated about 0.31 A.

2. Experimental Procedure

A double nuclear magnetic resonance technique was introduced by Hartman and Hahn,[13] and modified by Lurie and Slichter.[14] This method has a great advantage which enables us to observe a resonance too weak to detect by usual NMR, and is an epoch-making one for searching directly molecular and atomic motions in solids. In our sample, the number of Na⁺ host ions in the visinity of the doped OH⁻ impurity ions is few. The block diagram of our DNMR apparatus is shown in Fig.1. Free induction decay (FID) signal from the last stage of rf amplifier of the receiver is viewed directly on a digital oscilloscope, and is also fed into a workstation and several personal computers through the network in our laboratory for processing the experimental data.

In the present paper, the abundant Na nuclei far away from the impurity ions are denoted by I, while the rare quadrupole-affected Na nuclei near the doped impuriry ions are denoted by S. The measurements were performed as following processes. First the rf pulse is applied only to the I spin system at the resonance frequency, then the magnitude of the FID, we called M_0, is measured. Next in addition the heating rf pulse is applied simultaneously to the S spin system at an appropriate frequency, then the FID is measured, whose magnitude is denoted by M. One cycle of the experiment is performed by measuring M_0 and M, varying the frequency of the heating pulse to the S spin system. In these procedure, the angle θ between the [001] crystal axis and the applied static magnetic field H_0 is fixed at an appropriate value. The sample used in the experiments is a NaCl crystal containing 0.125 mole% OH⁻ impurity ions. All experiments were performed at liquid nitrogen temperature.
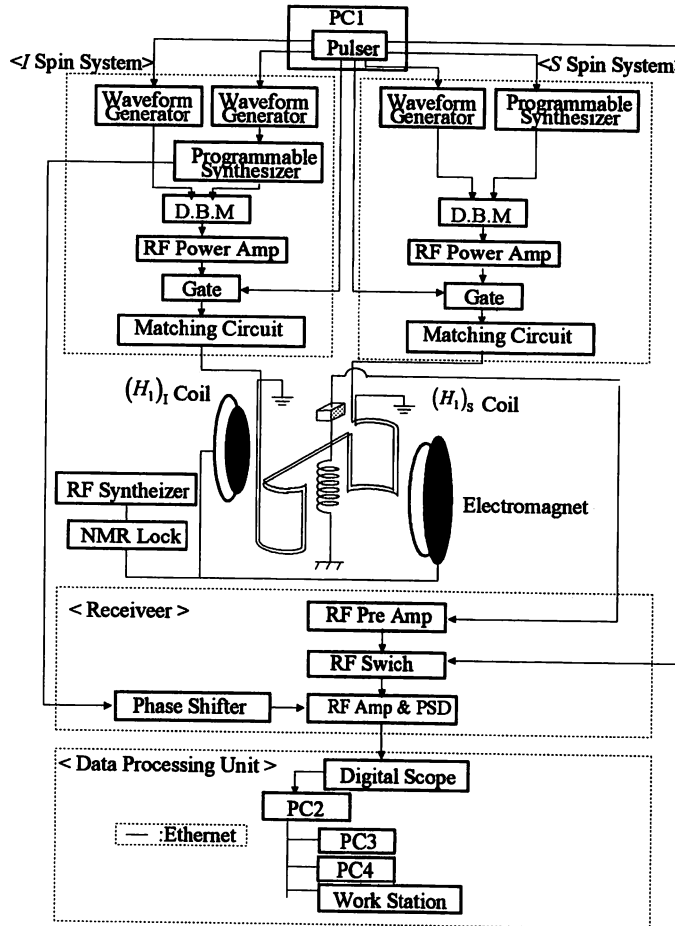
Fig. 1   Block diagram of DNMR spectrometer.

3. Experimental Results and Discussion

An example of DNMR spectra is shown in Fig.2. M_0 and M express the FID amplitudes of I spins at the end of measuring periods with and without, respectively, heating rf pulses. $\triangle \nu = \nu_m - \nu_L$ represents the difference between the satellite $\nu_m (m = 3/2$ or $-3/2)$ and the Larmor frequency ν_L for the S spin system, and $\theta = 5.8°$. The lines labeled as A and C are considered to be due to (001) and (100) Na^+ ions, respectivery, with respect to the substitutional impurity ion at (000). The B corresponds to the signal from (010) Na^+ could not be observed, scince the signal was masked under the spread of the central line. Such an identification of the signals with the lattice sites of the reference ions surrounding impurity ion is made by obtaining the rotation pattern of the resonance line of the nucleus under study.

The angular dependence of the quadrupole spectra is obtained by rotating the static magnetic field H_0 about [100] crystal axis. The rotation patterns of the A and C sites are presented in Fig.3. We calculated the angular variations of the quadrupole split- tings corresponding to the ions at the nearest neighbour sites of the impurity by the
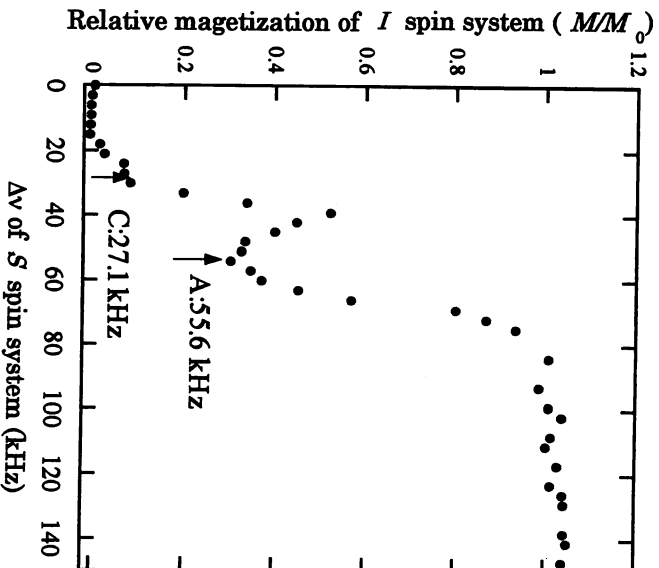
Fig. 2   DNMR spectrum ascribed to Na$^+$ ions at (001) and (100) sites around OH$^-$ impurity ions in NaCl:OH$^-$ crystal at $\theta = 5.8°$.

first order perturbation, as well as other workers. The quadrupole splittings for each site are given by

$$\Delta\nu \text{ (A)} = \pm \nu_Q (1 + 3 \cos 2\theta)/4, \tag{1}$$

$$\Delta\nu \text{ (B)} = \pm \nu_Q (1 - 3 \cos 2\theta)/4, \tag{2}$$

$$\Delta\nu \text{ (C)} = \pm \nu_Q /2, \tag{3}$$

where $\nu_Q = e^2 q Q/2h$ is the quadrupole frequency. eq is the principal value of EFG at the nucleus in question, Q is the quadrupole moment of nucleus under study, h is the Planck's constant. In this figure, the solid lines are calculated from Eqs. (1) and (3), assuming that $\nu_Q = 53.8$ kHz and 54.2 kHz, respectively, for fitting the theoretical curves with the experimental points. It is concluded that adopting the average of these two values, the quadrupole frequency is 54.0 kHz, and then using $Q = 0.101 \times 10^{-24}$ cm^2, the principal value of EFG at the first neighbour Na$^+$ around the impurity ion is given by 15.0×10^{12} esu/cm^3.

Satoh *et al.* obtained the EFG at the various sites in the vicinity of substitutional impurity ions in several ionic crystals by DNMR method. They also calculated the lattice energy in these crystals, and then obtained the magnitudes of the displacements of the host ions, α, corresponding to the values of the EFG. The magnitudes of the EFG and displacement of (100) Na$^+$ obtained by them and us are shown by the solid circles and the tetragon, respectively, in Fig.4. The lines are drawn by the least squares method in agreement with the points except one of NaI:Cl$^-$. By fitting $eq = -15.0 \times 10^{12}$
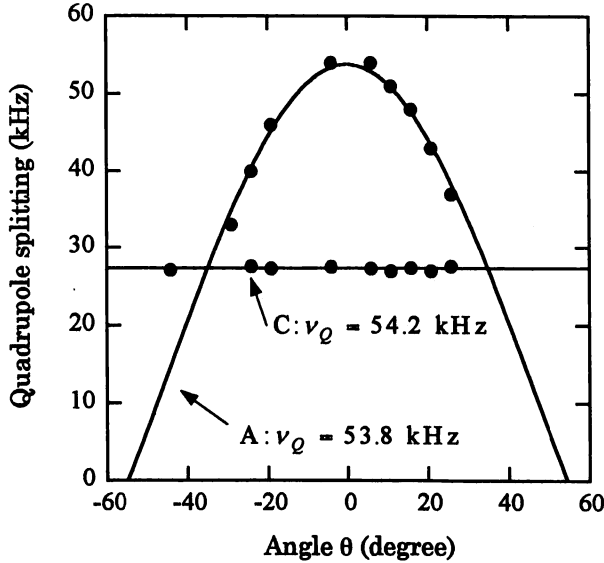
Fig. 3   Angular variation of the quadrupole spectra ascribed to Na⁺ ions at the same sites in Fig. 2. The solid lines are drawn by Eqs. (1) and (3).

esu/cm³ obtained in our experiments to the line, we obtain $\alpha = -7.8 \times 10^{-3}$% for the magnitude of the displacement of (100) site Na⁺ around OH⁻ impurity ion. The magnitude of the displacement of the host ions is due to the radius of the substitutional impurity. We denote the ratio of the radius of the substitutional ion to that of the host ion by R, where the radius of free ion are adopted for all ions.

Fig.5 represents the relation between the relative ionic radius R and the displacement α of these crystals. As is obvious from this figure, there is the linearity between these two quantities. Using $\alpha = -7.8 \times 10^{-3}$% for the displacement of (100) Na⁺, we have $R = 0.97$ for the relative radius of OH⁻ impurity ion. If we adopt the free ion radius 1.81Å for the radius of Cl⁻ ion, we have 1.76Å for the radius of OH⁻ ion. Since the radius of free ion OH⁻ is 1.45Å, it is natural to consider that the difference between this value and our result is due to the off-center displacement, whose magnitude is 0.31Å. This value disagrees with the experimental results and the expected values by calculations by other workers.[6,9] Scince our experiments were performed at 77K, the off-center ion moves among six equivalent positions which are potential minima along [100] crystal direction, through tunneling motion.

Fig.6 represents the relation between the relative ionic radius and the EFG for several ionic crystals containing larger impurity ion than the host ion. The solid line is drawn by the method of least squares. It is found that individual points plotted are on this line, and then the EFG varies in proportion to the R.

On the other hand, the relation between the R and EFG for the case of containing smaller impurity ions is given in Fig.7. The line is drawn by the least squares method using the data of NaBr:Cl⁻ and NaI:Br⁻. The points of NaI:Cl⁻ and NaCl:OH⁻ obtained in our experiments are enormously out of the line. The cause may be due to the
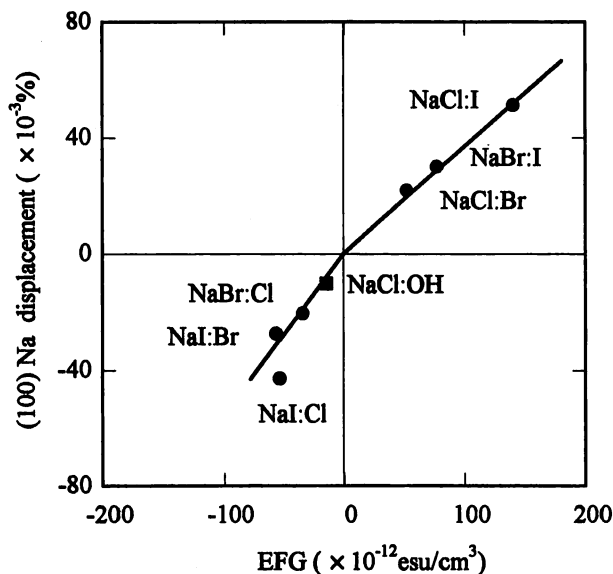
Fig. 4   The EFG and the displacement of Na^+ ions at (100) site in the vicinity of impurity ion in several ionic crystals. The solid circle and tetragon represent the data obtained by Satoh *et al.* and us, respectively.
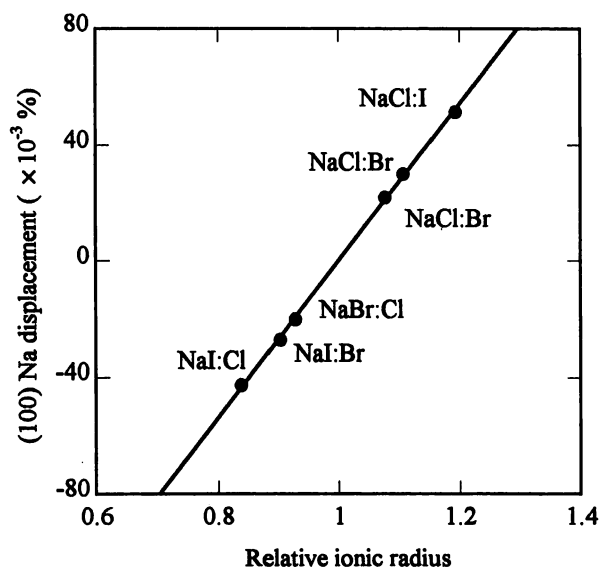

Fig. 5   The relative ionic radius and the displacement of (100) Na^+ ions. The points plotted are the same as those used in Fig. 4.

formation of off-center in these crystals. In these two crystals the radius of the impurity ion is very smaller than that of the host ion. It is considered that the critical relative radius to produce off-center is between 0.85 and 0.90 in these crystals. The crystals studied by Satoh *et al.* contained only monovalent impurity ions. However,
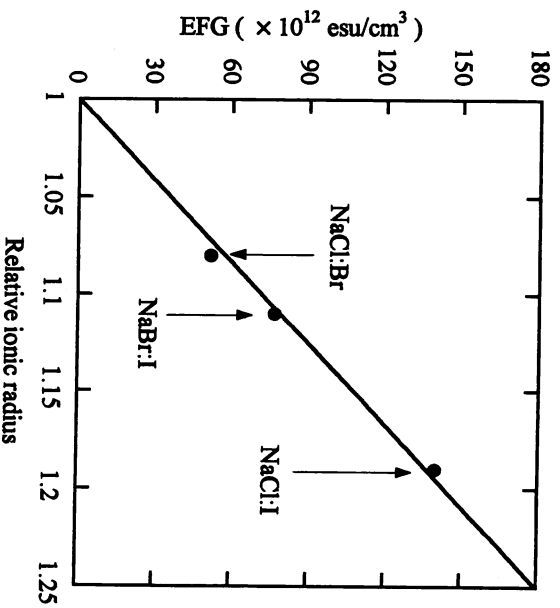
Fig. 6 The relative ionic radius and the EFG at (100) Na⁺ ions. The points plotted represent the data obtained in the crystals containing larger impurity ions.
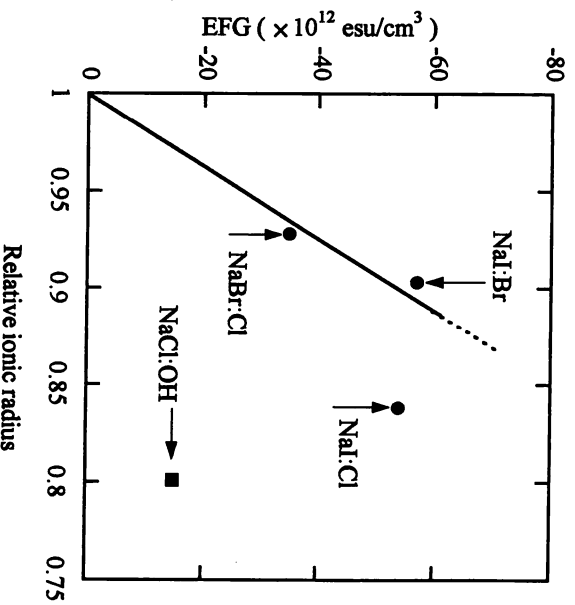

Fig. 7 The relative ionic radius and the EFG at (100) Na⁺ ions in the case of smaller impurity ions.

OH⁻ impurity in our case is a polar molecule and has a great dipole moment, besides a pair of the off-center impurity ions may be produced by the dipole-dipole interaction. It is necessary to consider the effects of the dipole moment on the electric field gradient at the nuclei in the vicinity of substitutional impurity.

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