

Na Nuclear Magnetic Relaxation of NaCl Crystals Containing Divalent Impurity Ions¹⁾

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Na nuclear magnetic resonance was measured in NaCl crystals containing divalent impurity ions such as Ca^{++} , Cd^{++} and Mn^{++} . The spin-lattice relaxation in temperature range between 400°K and 650°K was found to be caused by the time dependent electric quadrupole interaction of Na nucleus due to the lattice diffusion of free Na-ion-vacancies. By analysing T_1 with the use of a modified Torrey's equation, the activation energy for vacancy jump is obtained to be 0.74 eV. The association energy of a vacancy and a divalent ion to form a complex was found to be almost zero for Ca^{++} , while that for Cd^{++} was estimated to be 0.4 eV. Above 650°K, other interactions, such as electric quadrupole interaction due to divalent ions, and that due to thermal vacancies contribute to T_1 . Also the motional narrowing of the dipolar width due to the diffusion of Na ion by vacancy jump was observed.

Nuclear magnetic resonance of Na nuclei was studied in NaCl crystals containing divalent impurity ions such as Ca^{++} , Cd^{++} , and Mn^{++} at 14 Mc/sec and in the temperature range between 10°C and 650°C by pulse method.

The spin-lattice relaxation time T_1 of Na nuclei in these crystals was found to come from several origins in different ranges of temperature:

(1) T_1 of Na nuclei in all the crystals from room temperature to about 450°K is mainly determined by the electric quadrupole relaxation arising from lattice vibrations. $1/T_1$ is nearly proportional to T^2 (see Figs. 1 and 2).
(2) In the temperature range from 450°K to 700°K, T_1 can be considered to be determined mainly by the relaxation due to the diffusion of the free Na ion vacancies.²⁾ A minimum in T_1 was observed at about 588°K for all samples containing impurity ions except Mn^{++} . At this temperature, the jumping frequency of the vacancy is expected to be equal about 1.66 times the Larmor frequency, according to Torrey's theory³⁾ applied to the case of quadrupole relaxation. T_1 in this temperature range depends upon the nature and the concentration of impurity ions. In the case of the crystal doped by Ca^{++} , $1/T_1$ is roughly proportional to the concentration of the

impurity ion and moreover the shape of temperature dependence is independent of the concentration (see Fig. 1). This means that almost all the vacancies exist in the isolated state, or, no complex is formed. This conclusion is based on the assumption that the electric quadrupole interaction coming from the isolated vacancy is considerably larger than that coming from the complex⁴⁾. Thus the association energy to form the complex should be very small for Ca^{++} ion.

On the other hand, in the case of the crystals doped by Cd^{++} , the absolute value of $1/T_1$ is not proportional to the concentration and the temperature variation of $1/T_1$ is steeper in the case of the higher impurity concentration than the lower one, in the temperature range between 450°K and 550°K (Fig. 2). This means that in this temperature range, considerable portion of the vacancies from the complex with Cd^{++} ions. By analysing these temperature dependence of T_1 , the association energy between a vacancy and a Cd^{++} ion was found to be about 0.4 eV⁵⁾. This value of the association energy coincides well with the value obtained by the ionic conductivity measurement.

(3) At still higher temperature, T_1 is shorter than the value expected by the vacancy diffusion alone (see Figs. 1, 2 and 3). Between 700°K and 900°K, the contribution of the diffusion of isolated divalent ions to the relax-

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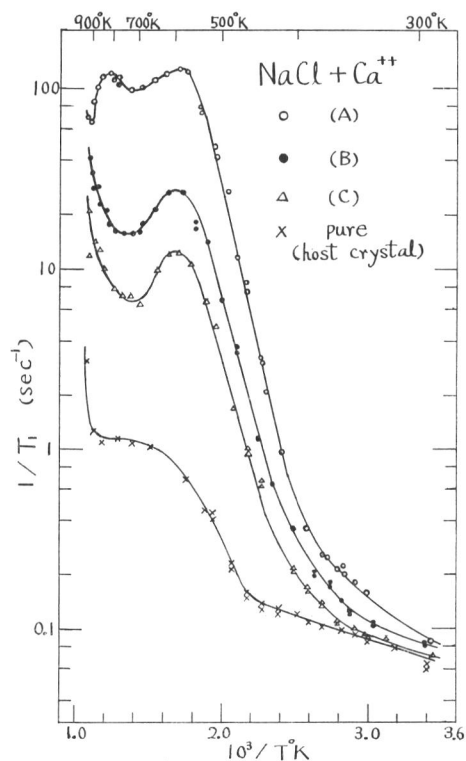


Fig. 1 Spin lattice relaxation rate $1/T_1$ of Na in $\text{NaCl} + \text{Ca}^{++}$ versus inverse absolute temperature.

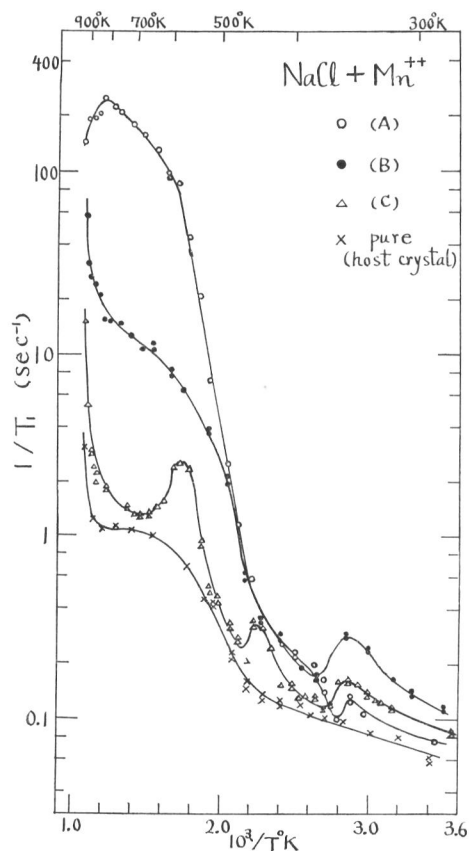


Fig. 3 Spin lattice relaxation rate $1/T_1$ of Na in $\text{NaCl} + \text{Mn}^{++}$ versus inverse absolute temperature.

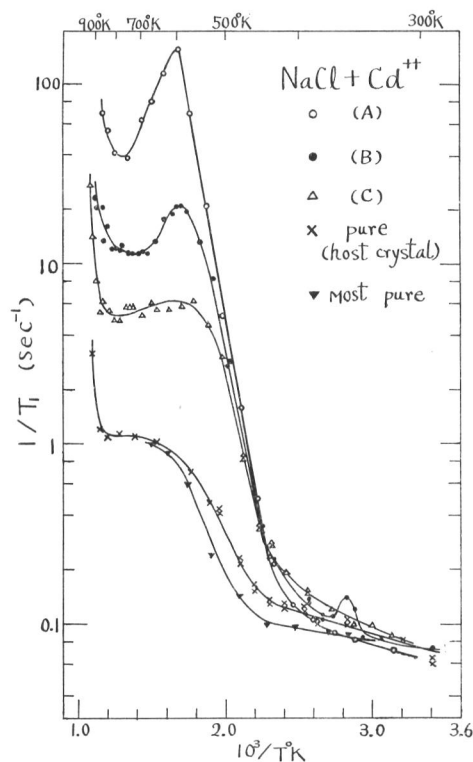


Fig. 2 Spin lattice relaxation rate $1/T_1$ of Na in $\text{NaCl} + \text{Cd}^{++}$ versus inverse absolute temperature.

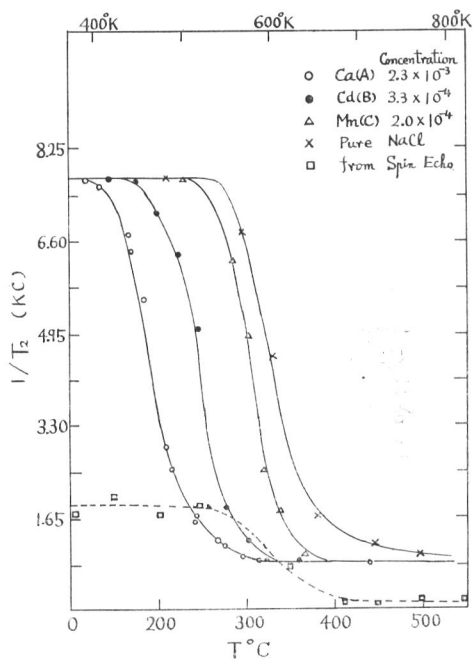


Fig. 4 Temperature dependence of $1/T_2$ of Na.

ation may take the main part. Above 900°K, T_1 in all samples decreases very rapidly, which may come from the diffusion of thermal Cl^- vacancy or that of the thermal vacancy-pairs⁶⁾.

Next, the temperature dependence of the spin-spin relaxation time T_2 was measured (Fig. 4). In all cases, $1/T_2$ decreases and coincides with $1/T_1$ as the temperature rises, which can be well accounted for by the motional narrowing of the dipolar interaction due to the diffusion of Na^+ ion via vacancy. The temperature of the motional narrowing becomes higher for the lower concentration

of the impurity ions.

References

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DISCUSSION

Nowick, A.S.: The conclusion that Ca^{++} has a weak binding to a cation vacancy is very surprising in view of other experimental results. First, several workers have observed dielectric relaxation due to impurity-vacancy dipoles in Ca-doped crystals as well as in Cd-doped samples, involving almost complete association at low temperatures (near room temperature). Furthermore, recent work on ionic conductivity by Dreyfus and Nowick (Phys. Rev., May 15, 1962) shows that the slope of the $\log \sigma T$ vs. $1/T$ curves in the low temperature range for various divalent solutes in NaCl is quite consistent with binding energies ~ 0.4 eV. In all these electrical experiments Ca-doped crystals are not different from Cd-doped crystals.

Itoh, J.: Our experiments results for Ca-doped crystal and Cd-doped crystals are not the same. This difference is outside of our experimental inaccuracy. We know the experiments which you refer and our results seem to be in contradiction with these experiments. However, the explanation which I gave in my report seems to be the most naive one to interpret our experimental result. If the binding energy of Ca-complex were 0.4 eV, how can we interpret the difference which we obtained for Ca-doped and Cd-doped crystal? Some dynamical properties of the complex might have important effect on the nuclear spin relaxation.

Lidiard, A.B.: Your conclusion that pairs of calcium ions with vacancies do not form is derived from the proportionality of T_1^{-1} to total calcium concentration. Previously this same inference was made by Bean from ionic conductivity measurements. Nevertheless, dielectric relaxation experiments such as those by Haven, Dryden and Dreyfus and Nowick show quite clearly that these pairs do form. Now it has been shown recently by Etzel, Lüty and others that calcium ions have strong affinity for OH^- ions in NaCl. These ions are known to be present in air-grown crystals and to compensate partially for the calcium in the sense that they effectively remove some of the calcium and thus some of the positive ion vacancies. This has been demonstrated by Lüty and co-workers by experiments on crystals with both calcium and hydrogen additions. I suggest that it is possible that the incidental presence of OH^- in your crystals may so change the relation between the free vacancy as to lead to the apparent absence of association which you see.

Itoh, J.: We did not measure the concentration of OH^- in our crystals. We made the crystals in air, but the NMR experiments were done in N_2 atmosphere and after the temperature of the crystal was raised up to 900°K, the experimental values of T_1 were just the same as before. They were quite reproducible. So, we wonder if the possible existence of OH^- is the origin of our experimental results which indicate a small value for the binding energy of Ca-complex. Some particular dynamical properties of Ca-complex might have a predominant effect on nuclear magnetic relaxation.