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H. Richtering, K. Becker, H. Hamann. DIFFUSION OF IMPURITIES IN IONIC CRYSTALS AS STUDIED BY NUCLEAR MAGNETIC RESONANCE TECHNIQUES. *Journal de Physique Colloques*, 1976, 37 (C7), pp.C7-373-C7-378. 10.1051/jphyscol:1976785 . jpa-00216945

HAL Id: jpa-00216945

<https://hal.science/jpa-00216945>

Submitted on 1 Jan 1976

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DIFFUSION OF IMPURITIES IN IONIC CRYSTALS AS STUDIED BY NUCLEAR MAGNETIC RESONANCE TECHNIQUES

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Résumé. — La méthode de l'investigation de la diffusion des défauts atomiques dans les cristaux ioniques cubiques par mesure de la relaxation nucléaire magnétique est très brièvement décrite. Des exemples sont donnés pour la relaxation longitudinale et transversale des noyaux ^{81}Br et ^{35}Cl dans le LiBr, TlBr, AgCl et AgBr.

Les coefficients d'autodiffusion obtenus pour Cu^+ et Ag^+ dans LiBr aux températures au-dessus de 350 °C sont

$$D(\text{Cu}^+) = 8 \exp(-1,0 \text{ eV}/kT) ; D(\text{Ag}^+) = 1 \exp(-1,0 \text{ eV}/kT) \text{ cm}^2 \text{ s}^{-1}.$$

Dans TlBr à 400 °C, les impuretés K^+ , Rb^+ et Cs^+ ont la même fréquence moyenne de saut. Cette fréquence est à peu près 3 fois plus grande que celle de Tl^+ est 3 fois plus petite que celle de Br^- . A 300 °C Ag^+ diffuse même 10 fois plus vite que Br^- .

Dans AgCl avec un dopage de CuCl la fréquence de formation d'un complexe de défaut ($\text{Cu}_i\text{V}_{\text{Ag}}$) est observée. Les sauts atomiques combinés avec la formation et la recombinaison de ce complexe ne contribuent pas sensiblement à la diffusion de traceur du cuivre.

Dans AgBr avec un dopage de CuBr et traité avec Br_2 les mesures de relaxation montrent que des ions Cu^{2+} sont formés. Les fréquences de saut du Cu^{2+} et du Cu^+ peuvent être déterminées l'une à côté de l'autre au voisinage de 200 °C.

Abstract. — The method to investigate the diffusion of atomic defects in cubic ionic crystals by measurements of nmr relaxation rates is described very briefly. Examples are given for longitudinal and transversal relaxation of ^{81}Br - and ^{35}Cl - nuclei in LiBr, TlBr, AgCl and AgBr.

Selfdiffusion coefficients obtained for Cu^+ and Ag^+ in LiBr at temperatures above 350 °C are $D(\text{Cu}^+) = 8 \exp(-1.0 \text{ eV}/kT) ; D(\text{Ag}^+) = 1 \exp(-1.0 \text{ eV}/kT) \text{ cm}^2 \text{ s}^{-1}$.

In TlBr at 400 °C the foreign ions K^+ , Rb^+ and Cs^+ have the same mean jump frequency. This frequency is about 3 times larger than that of Tl^+ and 3 times smaller than that of Br^- . Ag^+ diffuses at 300 °C, 10 times faster than even Br^- .

In AgCl doped with CuCl the frequency of formation of a defect pair ($\text{Cu}_i\text{V}_{\text{Ag}}$) is observed. The jump processes connected with formation and recombination of this pair do not contribute considerably to Cu tracer diffusion.

In AgBr doped with CuBr and treated with bromine the relaxation measurements show that Cu^{2+} - ions are formed. The jump frequency of Cu^{2+} can be determined besides that of Cu^+ at temperatures about 200 °C.

1. Introduction. — The diffusion of atomic defects in cubic crystals can be studied by nuclear magnetic resonance techniques provided the nuclei of a main constituent have an electric quadrupole moment. The most important quantity in this context is the correlation time τ of the relative diffusive motion between the defects (D) and the relevant main constituent (A) for which the nmr-signals are recorded. Pronounced peaks in nuclear magnetic relaxation rates can be observed in that temperature region, in which the reciprocal of the correlation time τ is of the same magnitude as the nuclear Larmor-frequency $\omega_L = 2\pi\nu_L$ in the applied magnetic field. Responsible for this type of relaxation is the interaction between the quadrupole moments of species A and the electric field gradients produced by the defects D. This interaction is fluctuating in time and intensity because

of the relative diffusive motion and thereby leads to nmr-relaxation.

A theory connecting nmr quadrupole relaxation rates with jump frequencies of defects in solids has been given by Cohen and Reif as early as 1954 [1, 2, 3]. The formulae which are used in this paper are given in section 2. Hints to their derivation can be found in [4].

Various authors have studied the diffusion of vacancies in doped ionic crystals by this method [5, 6 (LiBr) ; 7 (NaF) ; 8, 9 (NaCl) ; 2, 10 (AgBr)]. Our main interest has been the diffusion of foreign ions [11, 12]. We have also checked the theory for longitudinal and transversal relaxation in respect to the dependence on Larmor-frequency and on concentration of foreign ions [4]. Of special importance is the comparison of diffusion coefficients obtained by the

nmr-method with tracer results. The agreement in some cases is excellent. There are, however, cases, in which large deviations occur (see section 5). The purpose of this paper is to give some examples which demonstrate the possibilities of the method.

2. Basic formulae and experimental procedure. —

For the correlation time τ of the relative diffusive motion between the defects D and the nuclei of species A the following relation holds

$$\frac{1}{\tau} = \nu(D) + \nu(A) \quad (1)$$

$\nu(D)$ and $\nu(A)$ are mean jump frequencies of D and A respectively. In most cases which have been investigated, $\nu(A)$ is much smaller than $\nu(D)$ and can therefore be neglected.

For nuclei A with spin quantum number $I = 3/2$ Hubbard [13] has derived the following result for quadrupole relaxation of nuclear magnetization in the direction of the external field (longitudinal relaxation; M_z^0 : magnetization in thermal equilibrium)

$$M_z^0 - M_z(t) = 2 M_z^0 \left\{ \frac{1}{5} \exp(-2(w_1 + w_g)t) + \frac{4}{5} \exp(-2(w_2 + w_g)t) \right\} \quad (2)$$

w_1 and w_2 contain the contribution of diffusion to quadrupole relaxation, w_g represents the contribution of lattice vibrations. w_g can be determined separately by measurements with pure samples.

Experimentally $M_z(t)$ was followed by standard pulse techniques with a Bruker nmr-spectrometer (BKR 321 s). In addition to an electromagnet with iron core a kryomagnet has been used which allowed magnetic fields up to 6.3×10^4 G. Experimental details are described elsewhere [4, 14]. From measurements on a doped and the corresponding pure sample w_1 and w_2 can be obtained as function of temperature T . Since the determination of w_2 always was more reliable, all the results for longitudinal relaxation are plotted as $w_2(T)$.

With a simple exponential correlation function for the diffusive motion, w_1 and w_2 are related to τ in the following manner

$$w_1 = \text{Const.} \frac{x_d \cdot \tau}{1 + \omega_L^2 \tau^2}; \quad (3)$$

$$w_2 = \text{Const.} \frac{x_d \cdot \tau}{1 + 4 \omega_L^2 \tau^2}$$

$\omega_L = 2 \pi \nu_L$ is the Larmor frequency, x_d is the mole fraction of defects produced by doping. It is assumed that only one type of defect is responsible for relaxation in a certain temperature range. For a given

concentration x_d the maximum of w_2 as function of temperature shows up for

$$\frac{1}{\tau^*} = 2 \omega_L \quad (4)$$

$$w_2^* \sim \frac{x_d}{\omega_L} \quad (5)$$

(All quantities at the relaxation maximum are marked by an asterisk in this article.) By means of (3) and (4) the correlation time τ can be calculated as function of temperature from the experimentally determined $w_2(T)$.

For relaxation of nuclear magnetization perpendicular to the external field (transversal relaxation) Hubbards result is [13, 4]:

$$M_x(t) = 0.4 M_z^0 \exp(-(w_1 + w_2)t) \quad (6)$$

This relation holds under the assumption that only the two central Zeeman levels contribute to the detected signal. This assumption is justified for the nuclei ^{81}Br and ^{35}Cl , for which results are given in this article. The reason is that static quadrupole interactions in the samples shift the outer levels. Their contribution to the signal is therefore wiped out [2, 15].

By conventional cw-detection of the nmr absorption signal in a wide-line spectrometer (Varian, DP 60) the Fourier transform of $M_x(t)$ is obtained. The contribution to the linewidth by quadrupole relaxation is given by

$$\gamma \cdot \Delta H_q = 1.15(w_1 + w_2) \quad (7)$$

γ is the gyromagnetic ratio, ΔH_q is the linewidth between the inflection points of the absorption signal. From ΔH as determined from the registration curve, a contribution of the static dipolar linewidth must be subtracted to get ΔH_q as function of temperature. Measurements with the pure sample again serve for this purpose. At the linewidth-maximum which corresponds to the maximum in transversal relaxation, the following relations are valid [4]

$$\frac{1}{\tau^*} = 1.23 \omega_L \quad (8)$$

$$\gamma \Delta H_q^* \sim \frac{x_d}{\omega_L} \quad (9)$$

In respect to simplifications which were made in the derivation of the formulae above, some comments seem to be in order:

1) In equation (1) each of the two jump frequencies should be multiplied by a correlation factor f_i^{nmr} . Such factors originate from the influence of the correlation between successive jumps on the nmr-measurements [16, 17]. They are smaller than one but of the order of one. For jumps on nearest neighbour sites in a face centered cubic lattice for example $f_A^{\text{nmr}} \approx 0.7$ [17]. The correla-

tion factor f_A^{tr} connecting tracer diffusion and ionic conductivity in the same case is 0.78 [see e. g. 18]. f^{nmr} always seems to be somewhat smaller than f^{tr} .

2) A simple exponential is not the correct correlation function for lattice diffusion with random walk on a specified lattice. An improvement has been given by Torrey [19].

More recent work by Wolf [17, 20] includes both factors. The calculations for any specified jump mechanism on a given lattice are rather complex. In most of our examples, however, the diffusion mechanism is unknown and different jump processes for the same defect may contribute to relaxation. We therefore decided to use a simple exponential correlation function together with $f^{\text{nmr}} = 1$ as standard procedure in calculating jump frequencies from our measurements. This may be justified because we are often interested in comparison between various foreign ions and in large differences in the jump frequencies. In addition, an example given by Wolf shows that there is a chance of cancellation of errors from the two simplifications.

3. **Diffusion of Cu^+ and Ag^+ in LiBr.** — For the ^{81}Br resonance we have measured both the linewidth and the longitudinal relaxation up to the melting point (550 °C). Results for ΔH and w_2 are shown in figure 1. For the pure substance two regions of motional

FIG. 1. — Linewidth ΔH and longitudinal relaxation rate constant w_2 of ^{81}Br in LiBr with additions of CuBr and AgBr. Experimental points are shown only for LiBr doped with CuBr.

narrowing of the linewidth can be observed (lower part of Fig. 1). The first decrease at 120 °C is caused by the motion of Li^+ -ions. The reason for the second decrease at 330 °C is the motion of Br^- -ions. It can be concluded that $\nu(\text{Br}^-)$ is of the order of 10^4 s^{-1} at 330 °C.

If CuBr or AgBr is added, a pronounced maximum in the temperature dependence of the linewidth shows up at 350 or 450 °C respectively. This maximum is due to transversal relaxation by quadrupole interaction between the diffusing foreign cations and the ^{81}Br -nuclei. The jump frequency $\nu(\text{Br}^-)$ in equation (1) can be neglected in this case. In the upper part of figure 1 results for the contribution of diffusion to longitudinal relaxation are shown (w_2). The concentrations of the foreign ions are considerably lower than in the linewidth measurements. The maxima for w_2 appear at a somewhat higher temperature than in the lower part of figure 1. The reason is mainly that the Larmor-frequency used in the pulse experiments is higher by a factor of 3.75 than in the linewidth determinations.

The mean jump frequencies of Cu^+ and Ag^+ derived from the measurements are

$$\nu(\text{Cu}^+) = 1.5 \times 10^{16} \exp(-1.0 \text{ eV}/kT) \text{ s}^{-1}$$

and

$$\nu(\text{Ag}^+) = 2 \times 10^{15} \exp(-1.0 \text{ eV}/kT) \text{ s}^{-1}.$$

These frequencies are valid for temperatures above 350 °C. From determinations of longitudinal relaxation rates of ^7Li in the same substance [14] it can be concluded that Cu^+ and Ag^+ are both incorporated substitutionally in LiBr and that Cu^+ diffuses considerably faster than Li^+ whereas Ag^+ has approximately the same jump frequency as Li^+ at 450 °C. For the corresponding diffusion coefficients of Cu^+ and Ag^+ in LiBr the preexponential factors D_0 are $D_0(\text{Cu}^+) = 8$ and $D_0(\text{Ag}^+) = 1 \text{ cm}^2 \text{ s}^{-1}$. These values have been calculated under the assumption of diffusion by cation vacancies in nearest neighbour position.

4. **Diffusion of K^+ , Rb^+ , Cs^+ and Ag^+ in TlBr.** — Results for the temperature dependence of the ^{81}Br linewidth in TlBr are shown in figure 2. For the pure material (Serva; 99.998 %) motional narrowing occurs between 100 and 200 °C. Additions of K^+ ,

FIG. 2. — Linewidth ΔH of ^{81}Br in TlBr with additions of foreign cations ($\nu_L = 16 \text{ MHz}$). Experimental points are shown only for pure TlBr and TlBr doped with CsBr.

Rb⁺, Cs⁺ and Ag⁺ do not change the motional narrowing but in each case a maximum of transversal relaxation is observed. (For Li⁺ and Na⁺ the solubility at 400 °C seems to be smaller than 10⁻³; for Cu⁺ no relaxation maximum could be obtained.) For K⁺, Rb⁺ and Cs⁺ the temperatures T^* at the relaxation peaks coincide ($T^* = 400$ °C); for Ag⁺ the corresponding temperature is $T^* = 300$ °C.

The observed relaxation maxima are again due to quadrupole relaxation by the relative diffusive motion between the foreign cations (which produce the electric field gradient) and the ⁸¹Br-nuclei. For TlBr, however, the jump frequency of the Br⁻-ions cannot be neglected in comparison to that of the foreign ions as in the case of LiBr. From earlier measurements of electrical conductivity, transference number and Tl-self-diffusion [21, 22] it can be concluded, that the anions are much more mobile than the cations in TlBr. (For the anions and cations in TlCl the ratio between the mobilities has been quantitatively determined [23], at 400 °C this ratio is 15). The jump frequency $\nu(D) \equiv \nu(M^+)$ of the foreign cations can be evaluated from the measured correlation time τ only if $\nu(\text{Br}^-)$ can be obtained separately. In the present case $\nu(\text{Br}^-)$ can be calculated from measurements of ionic conductivity [21] and Tl tracer-diffusion [22]. The Tl-ions at this temperature contribute only 10 % to the total conductivity. The result is

$$\nu(\text{Br}^-) = (7.8 \pm 2) 10^7 \text{ and } \nu(\text{Tl}^+) = 1 \times 10^7 \text{ s}^{-1}$$

for a jump process via vacancies in nearest neighbour positions. For the foreign ions K⁺, Rb⁺ and Cs⁺ the jump frequencies are therefore

$$\nu(M^+) = (4.5 \pm 2) 10^7 \text{ s}^{-1} \text{ at } 400 \text{ °C.}$$

In the case of Ag⁺, $\nu(\text{Br}^-)$ can be neglected in comparison to $1/\tau$ and one directly obtains

$$\nu(\text{Ag}^+) = 12 \times 10^7 \text{ s}^{-1} \text{ at } 300 \text{ °C.}$$

The conclusion is, that the diffusion of K⁺, Rb⁺ and Cs⁺ in TlBr at 400 °C is appreciably faster than the Tl⁺-diffusion but slower than the diffusion of the Br⁻-ions. The diffusion of Ag⁺, however, is at 300 °C more than ten times faster than the anion-diffusion. In the latter case probably the diffusion mechanism is different.

Figure 2 also contains some results for TlBr doped with Pb²⁺. In this case motional narrowing occurs at temperatures which are about 50 K higher than in the pure substance. This can easily be understood by Schottky-disorder in TlBr: The concentration of anion-vacancies is lowered by the addition of divalent cations. At temperatures above 300 °C the linewidth shows a steep increase. This again results from quadrupole relaxation by relative diffusive motion of Pb²⁺ and Br⁻.

5. Diffusion of copper-ions in AgCl and AgBr. — In AgCl and AgBr the diffusion of numerous foreign

ions has been studied [see e. g. 24-25]. For Cd²⁺- and Mn²⁺-ions in AgBr the diffusion coefficients have been determined both by the tracer method and by nuclear magnetic relaxation via quadrupole interaction [26, 27, 11, 28]. The difference at 350-400 °C between the results of the two methods is less than 20 % in both cases (calculation of D according to $D(M^{2+}) = l^2/(6\tau)$; with l : distance between nearest neighbours in the cation lattice). Among all foreign ions investigated by the tracer method Cu⁺ shows the highest diffusion coefficient. The numerical value at 200 °C in AgCl is

$$D^{\text{tr}}(\text{Cu}^+) = 5 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$$

($D^{\text{tr}}(\text{Ag}^+)$ at the same temperature is $5.5 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ only [29]).

Results for our ³⁵Cl nmr-relaxation measurements in AgCl are shown in figure 3. When Cu⁺ is added,

FIG. 3. — Linewidth ΔH and longitudinal relaxation rate constant w_2 of ³⁵Cl in AgCl with additions of CuCl and CdCl₂.

a maximum in the linewidth is observed at 200 °C approximately. The signal to noise ratio in these cw-experiments is rather poor. Much better is the precision in the determination of the longitudinal relaxation (w_2) from measurements with doped and pure samples. In the upper part of figure 3 w_2 is plotted against temperature. For a sample AgCl + 6×10^{-4} CuCl and a Larmor frequency of $\nu_L = 4.5 \times 10^6 \text{ s}^{-1}$ the main relaxation maximum is observed at 205 °C (full curve in figure 3). A second maximum, which is much weaker, shows up at -20 °C with the same sample.

For the main relaxation maximum figure 3 shows some results for the influence of Larmor-frequency ν_L and concentration of the added ion x_d (dashed curves). The proportionality of the peak height w_2^* to x_d/ω_L is observed as expected from equation (5). In addition the peak temperature T^* is shifted with frequency

as expected from (4). Calculation of a jump frequency $\nu(D)$ with the aid of equations (1)–(5) leads to

$$\nu(D) = 1.4 \times 10^{15} \exp(-0.7 \text{ eV}/kT) \text{ s}^{-1}.$$

With a mean jump length $l = d/\sqrt{2}$ (d : lattice constant) at 205 °C a diffusion coefficient of

$$D^{\text{nmr}}(\text{Cu}) = 5 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$$

results. Using ^{64}Cu as tracer Süptitz [30] obtained at the same temperature $D^{\text{tr}}(\text{Cu}) = 5.6 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ with an activation energy of 0.4 eV. The large ratio $D^{\text{tr}}(\text{Cu}^+)/D^{\text{nmr}}(\text{Cu}^+) \approx 100$ at 205 °C and the difference in activation energy can only be accounted for if in both cases a different diffusion mechanism is decisive (with $l = d/2$ as for interstitial diffusion the factor is still 50). This has already been discussed in connection with the diffusion of Cu^+ in AgBr [10, 11, 31]. In AgBr the corresponding ratio $D^{\text{tr}}/D^{\text{nmr}}$ is approximately 10, the activation energy from the nmr data, however, is only 10 % larger than for tracer diffusion. What is most probably observed in nmr-relaxation is the mean frequency with which a Cu^+ -ion jumps from normal lattice site to a neighbouring interstitial position. The complex of the interstitial ion and the vacancy formed by this process contributes to tracer diffusion since the defect pair can make a considerable number of jumps before recombination takes place. On the other hand dissociation of the complex may occur and fast diffusion of the free interstitial Cu^+ -ion can be decisive for tracer diffusion. Süptitz [30] has concluded from the concentration dependence of $D^{\text{tr}}(\text{Cu}^+)$ that this is the case in AgCl and AgBr. Conductivity measurements for AgCl with increasing concentration of CuCl lead to the same conclusion [32].

The second relaxation maximum at -20 °C originates from the diffusion of cation vacancies. This can be seen by comparison with results for longitudinal relaxation in AgCl with small additions of CdCl_2 (dotted curve in Fig. 3). It also can be concluded by analogy from nmr-measurements on AgBr doped with CdBr_2 [2, 10, 11]. The calculation of the jump frequency of cation vacancies $\nu(V)$ in AgCl from conductivity data [33] leads to $\nu(V) = 10^8 \text{ s}^{-1}$ at -20 °C which is in reasonable agreement with $1/\tau^* = 5.6 \times 10^7 \text{ s}^{-1}$ (for $\nu_L = 4.5 \times 10^6 \text{ s}^{-1}$). Thus it follows from the observation of the second maximum at -20 °C that some vacancies are formed when CuCl is added to AgCl. Consequently some Cu^+ -ions are incorporated at interstitial positions. This has also been found with AgBr [4] and has been concluded from conductivity data and tracer results [34, 32, 30]. The difference in w_2^* at the second maximum for Cu^+ - and Cd^{2+} -addition shows that the fraction of Cu^+ on interstitial position is small.

In AgBr containing 10^{-2} CuBr we have tried to produce some Cu^{2+} by treatment with gaseous bromine. The sample was exposed to a given partial

pressure $P(\text{Br}_2)$ at a temperature slightly above the melting point and sealed afterwards. Results for the ^{81}Br -linewidth as function of temperature are shown in figure 4. Without bromine the Cu^+ -maximum is

FIG. 4. — Linewidth ΔH of ^{81}Br in AgBr + 10^{-2} CuBr treated with bromine. — : pure AgBr.

observed in this case at 145 °C for $\nu_L = 16 \times 10^6 \text{ s}^{-1}$. Under the influence of bromine a second relaxation maximum develops. This maximum at 200 °C is with high probability due to diffusion of Cu^{2+} -ions. Since the peak temperature T^* for Cu^{2+} is higher than for Cu^+ , the jump frequency of Cu^{2+} at a given temperature is lower than the frequency of the Cu^+ -process described above in the case of AgCl. The height of the Cu^{2+} -maximum is obviously much greater than in the case of Cu^+ for a given concentration. The Cu^{2+} -concentration is unknown. It is certainly small since the concentration of Cu^+ is not decreased to a considerable extent by the formation of Cu^{2+} . The dependence of the Cu^{2+} -concentration on $P(\text{Br}_2)$ can roughly be estimated: it is proportional to $P^{1/n}$ with $n = 4 \pm 1$ [35].

6. Conclusion. — The examples show that with the method described not only the diffusion of atomic defects with an excess charge (aliovalent ions, interstitials, vacancies) can be investigated. Small concentrations of substitutionally incorporated foreign ions with the same valency as the ions of the matrix crystal obviously give rise to an electric field gradient which is so large that the nuclear magnetic relaxation rate is mainly determined by diffusion and quadrupole interaction in the appropriate temperature range. This considerably extends the applicability of the method. It offers the opportunity to investigate and compare the diffusion of a wide variety of foreign ions in the same crystal. No single crystals are necessary for the measurements. The formulae given in section 2 apply to crystal powders only.

If more than one defect is produced by one impurity,

these defects may be separately detected if the difference in their jump frequency is large enough. The same holds true for the case of doping with two foreign ions. In certain cases jump processes may be detected, which do not show up in tracer diffusion and ionic conductivity.

Among the elements for which (as main crystal constituents) such relaxation measurements can be made (in natural isotopic composition) are Cl, Br, I, Li, Na, Rb, Cs, Be, Al and Cu. The strength of quadrupole interaction is, however, quite different in different cases. For a hypothetical given defect at given concentration for instance ^{81}Br is more than 1 000 times more sensitive than ^{23}Na for quadrupole relaxation. Thus for ^{81}Br very small additions and

transversal relaxation are favorite whereas with ^{23}Na a higher concentration range and longitudinal relaxation may be preferable.

Difficulties in the interpretation of the measurements can arise from a number of reasons. Among these are contributions of other interactions to relaxation, influences of static quadrupole interactions other than those mentioned in section 2, contribution of several jump processes to relaxation at the same temperature, association between defects, difficulties of theory (especially for $I > 3/2$). If a relaxation maximum is obtained with addition of an impurity, however, some valuable information is obtained in almost any case for the temperature of the relaxation maximum and comparison with other ions is possible.

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DISCUSSION

R. J. FRIAUF. — How does it happen in AgCl with Cu that you do not see the jumps of the interstitial copper ions ?

H. RICHTERING. — For interstitial Cu^+ -ions the main contribution to relaxation is to be expected at temperatures considerably below 200 °C. It is possible that this contribution is already contained in the solid

curve in figure 3 and simply cannot be resolved. It is also possible that this contribution occurs at even lower temperatures than — 60 °C. Alternatively, the second maximum at — 20 °C may be due to jumps of a vacancy in the complex $(\text{Cu}_i^+ \text{V}_{\text{Ag}}')$ and the concentrations of free vacancies and interstitial Cu^+ -ions are too small to be detected.