PHYSICAL REVIEW VOLUME 100, NUMBER 6 DECEMBER 15, 1955

Nuclear Magnetic Resonance Studies of Imperfect Ionic Crystals

F. Reif
Institute for the Study of Metals, University of Chicago, Chicago, Illinois

(Received September 2, 1955)

The method of nuclear magnetic resonance is applied to the study of ionic crystals containing point defects, i.e., vacancy, interstitial, or impurity ions. Experiments are described which show that the presence of such defects can have marked effects on the resonance line and can lead to a complicated temperature dependence of its width. A brief theoretical discussion is given of two effects important if the nucleus whose resonance is observed has a large electric quadrupole moment: (1) line width due to static second-order quadrupole interaction with defects, and (2) contribution to the nuclear relaxation time T_1 by quadrupole interaction with fluctuating electric fields caused by diffusing defects. Experimental results on the Br resonances in AgBr are analyzed in detail in terms of these effects. It is shown that the quadrupolar relaxation time due to diffusing defects in this salt can become sufficiently short to cause lifetime broadening of the resonance line, in particular that the motion of Ag vacancies seems to lead to a characteristic minimum of T_1 at about 0°C. The data also give some evidence for the association of defects in AgBr below 200°K. Cases of motional narrowing of the resonance line caused by the diffusion of defects are illustrated by experimental results on NaCl and LiBr. The existence of the various effects discussed in connection with these experiments indicates that nuclear resonance techniques can provide a means of studying the behavior of point defects in solids, their motion and in some cases their association, from a rather microscopic point of view. The desirability of careful relaxation time measurements is pointed out.

I. INTRODUCTION

THE method of nuclear magnetic resonance permits one to use the nucleus as a probe to explore the internal electromagnetic fields existing in solids and has thus proven itself useful in extending our knowledge of several aspects of solid-state physics. It seems of interest to apply nuclear resonance techniques also to the study of imperfect solids, in particular to the study of ionic crystals containing point imperfections, i.e., vacancy, interstitial, or impurity ions.[1] The defects in these relatively simple solids play an important role in the understanding of their properties. Accordingly such defects have been investigated extensively by more conventional methods, and some simple theoretical models are available to explain their behavior.[2]

The presence of point imperfections in a solid can affect the nuclear resonance in several ways, three of which will be of particular concern to us in the following pages. The first effect is specifically dependent on nuclei in the crystal lattice possessing electric quadrupole moments. Point imperfections in the lattice then destroy locally the cubic symmetry of the electrostatic field gradients at the positions of the nuclei and thus bring into play quadrupolar interactions which would not exist in a perfect crystal. Since the magnitude of the field gradient will vary from nucleus to nucleus one can expect a resultant broadening of the nuclear magnetic resonance line that depends on the configuration of defects in the solid. The other two effects we shall be interested in are connected with the diffusion of point defects through the lattice. First, the motion of defects may result in a rather short spin-lattice relaxation time for the nuclei, particularly if quadrupole interaction is involved. Second, the diffusion of defects may bring about a narrowing of the static width of the resonance line. In the present paper we give a simple theoretical discussion of some of these effects and present a number of experimental results which serve to illustrate them. Some of the more specifically theoretical points arising in connection with this work will form the subject of a subsequent paper by Cohen.[3]

II. EXPERIMENTAL ASPECTS

(a) Techniques

The radio-frequency spectrometer used in these experiments was of the Pound-Watkins type[4,5] and resonance lines were plotted on a recording meter by varying the frequency. A permanent magnet provided a magnetic field of about 5750 gauss in a gap 2 inches wide. The sample could be kept at any temperature between that of liquid nitrogen and +100°C by means of a cryostat containing a refrigerant reservoir and heater.[6] Alternatively a small water-cooled oven fitting into the magnet gap permitted one to maintain the sample at any temperature between 20°C and 500°C.

All the samples used in these experiments were polycrystalline. Introduction of impurities into the samples (doping) was achieved by melting a known amount of the pure salt to which had been added a known quantity of the impurity salt. Samples of smaller impurity ion concentration were then prepared by successive dilution with the pure salt of portions of the more highly

---

[1] For a preliminary report on this work see: M. H. Cohen and F. Reif, Proceedings of the Conference on Defects in Crystalline Solids, Bristol, 1954 (Physical Society, London, 1955), p. 44.

[2] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, New York, 1950).

[3] M. H. Cohen (to be published).

[4] R. V. Pound and W. D. Knight, Rev. Sci. Instr. **21**, 219 (1950).

[5] G. D. Watkins, thesis, Harvard University, 1952 (unpublished).

[6] The design of the cryostat was similar in conception to that described by Gutowsky, Meyer, and McClure, Rev. Sci. Instr. **24**, 644 (1953).

TABLE I. Nuclear properties of the Br isotopes: spin I, magnetic moment μ in units of the nuclear magneton, electric quardupole moment[a] Q in units of 10^{-24} cm^2.

Isotope	I	μ	Q	Abundance
Br^{79}	3/2	2.1058	0.335	50.6%
Br^{81}	3/2	2.2696	0.280	49.4%

[a] See reference 9.

doped specimens. Most samples were given the desired shape by compressing them in a hydraulic press into compact cylinders; they were then annealed at temperatures close to their melting point. Some care was taken to use as starting material salts of moderately high purity. For example, the reaction of $AgNO_3$ with HBr was the source of the AgBr used in the experiments; spectroscopic analysis showed this to contain a concentration less than 2.10^{-5} of metallic impurities.

(b) Experimental Results: AgBr

The substance most extensively studied in these experiments was AgBr. This salt is readily doped with $CdBr_2$, and the properties of the defects in its lattice have been thoroughly investigated by electrical conductivity measurements.[7,8] Furthermore the temperature range of interest is not excessively high for nuclear resonance experiments, even near the melting point of 434°C. The nuclear moments of the two bromine isotopes are shown in Table I.[9] Since the isotope with the larger magnetic moment has the smaller quadrupole moment, it should be experimentally possible to distinguish the effects of magnetic or electric interactions by comparison of the resonance lines of the two isotopes.

A few representative data on AgBr will serve to show that the presence of point imperfections in the lattice may have marked effects on the nuclear resonance line and may result in a rather complicated temperature dependence of this line. Doping of AgBr with $CdBr_2$ results in divalent Cd^{++} ions entering the lattice substitutionally.[7] To preserve the electrical neutrality of the crystal, an equal number of vacancies are formed on the Ag sublattice. Figure 1 shows the effect on the Br resonance line at room temperature of increasing the Cd^{++} ion concentration in AgBr. There is a rapid increase in width and consequent reduction in intensity of the line, the effect being more pronounced for the isotope with the larger quadrupole moment. The second moment of the resonance line[10] is in these experiments a poor and inaccurate measure of the line width since the line has extensive wings, partially submerged in noise, which contribute heavily to the value of the second moment. The most sensitive indication of the effects observed is D, the peak-to-peak intensity of the derivative of the resonance line. It is this derivative which is experimentally plotted directly on the recording meter, and use of the calibrating circuit[5] in the rf spectrometer makes reproducible measurements of D readily possible. D is a rough measure of the reciprocal of the square of the line width; if T denotes the absolute temperature, the quantity TD should be a constant independent of T if there is no change in line shape.

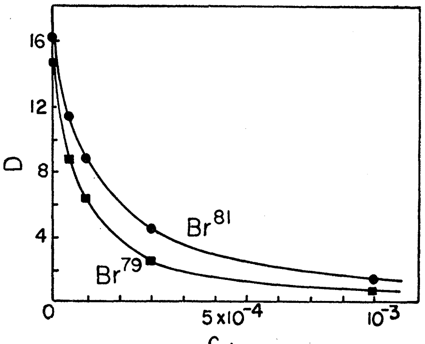

FIG. 1. Dependence of Br resonance line intensity D on the molar concentration c_d of Cd^{++} ions in AgBr at room temperature. (Note: for the same line shape, the small differences in magnetic moment and abundance should hake the Br^{79} line about 20% less intense than the Br^{81} line.)

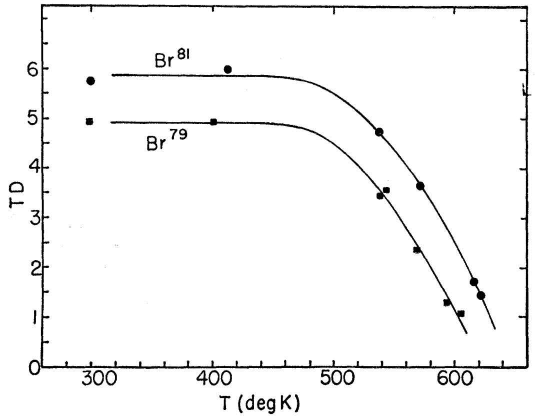

FIG. 2. Behavior of the Br resonance line intensity D in a pure sample of AgBr at high temperatures.

A second way of introducing point defects in a crystal is by raising its temperature sufficiently to create such defects in thermal equilibrium with the crystal lattice. In AgBr the imperfections thus produced are Frenkel defects,[7] i.e., Ag^+ vacancies and Ag^+ interstitial ions. The effect on the nuclear resonance line of heating a sample of pure AgBr is shown in Fig. 2. It is seen that beyond about 500°K there is a rapid decrease in intensity of the line suggestive of an exponential increase of the number of defects in the salt. Doped samples exhibit similar behavior at high temperatures. Finally, Fig. 3 shows the complicated temperature dependence of the intensity of the resonance line in some repre-

---

[7] J. Teltow, Ann. Physik 5, 63-88 (1950).

[8] S. W. Kurnick, J. Chem. Phys. 20, 218 (1952).

[9] The quadrupole moments are those given by J. G. King and V. Jaccarino, Phys. Rev. 94, 1610 (1954).

[10] J. H. Van Vleck, Phys. Rev. 74, 1168 (1948).

sentative samples of AgBr containing Cd^{++} impurity ions. Below 200°K the product TD remains constant for each sample and there is only a slight dependence of the intensity on the impurity concentration, amounting to less than 20% in going from the pure sample to one containing 10^{-3} atomic fraction of $CdBr_2$. There is a rapid decrease in intensity beginning at the same temperature of about 200°K for the resonance lines of both isotopes in all the doped samples. The intensity then reaches a minimum (and correspondingly the line width a maximum) the magnitude of which depends on the Cd^{++} ion concentration, but the position of which occurs at the well-defined temperature of 273 ±2°K irrespective of Br isotopes or impurity concentration. We shall postpone until later the discussion of these results.

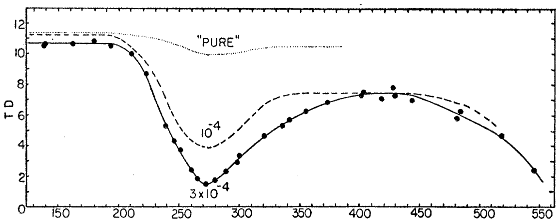

FIG. 3. Behavior of the Br^{81} resonance line intensity D as a function of temperature in samples of AgBr doped with $CdBr_2$. Dotted line: "pure" sample (less than 2×10^{-5} concentration of metallic impurities). Dashed line: molar concentration of Cd^{++} $=10^{-4}$. Solid line with experimental points: Cd^{++} concentration $=3\times10^{-4}$.

III. STATIC QUADRUPOLE INTERACTION

The interaction of a nucleus of spin I and electric quadrupole moment Q with an electrostatic potential V due to charges external to it is given by the Hamiltonian[11]:

$$\mathcal{H}=[eQ/4I(2I-1)]\{(3I_z^2-\mathbf{I}^2)V_0+(I_+I_z+I_zI_+)V_{-1}+(I_-I_z+I_zI_-)V_1+I_+^2V_{-2}+I_-^2V_2\}, \quad (1)$$

where $I_\pm=I_x\pm iI_y$, $V_0=V_{zz}$, $V_{\pm1}=V_{xz}\pm iV_{yz}$, $V_{\pm2}=\frac{1}{2}(V_{xx}-V_{yy})\pm iV_{xy}$, and where $V_{xy}=\partial^2V/\partial x\partial y$, etc. The z-axis can be taken along the direction of the external magnetic field H. We consider the specific case of interest, $I=\frac{3}{2}$. If V at the position of a nucleus has cubic symmetry (perfect ionic crystal), then the quadrupole interaction vanishes; the resonance line consists of three superposed lines at the nuclear Larmor frequency ω_0 and of a width determined solely by magnetic dipole-dipole interactions between all the nuclei. (See Fig. 4.) If V does not have cubic symmetry at the position of a nucleus, then to first-order perturbation theory the central line ($\frac{1}{2}\leftrightarrow-\frac{1}{2}$ transition) is not affected, while the $\frac{1}{2}\leftrightarrow\frac{3}{2}$ and $-\frac{1}{2}\leftrightarrow-\frac{3}{2}$ transitions give rise to two satellite lines at frequencies $\omega_0\pm\frac{1}{2}eQV_0\hbar^{-1}$, each of which has an intensity $\frac{3}{4}$ that of the central line.

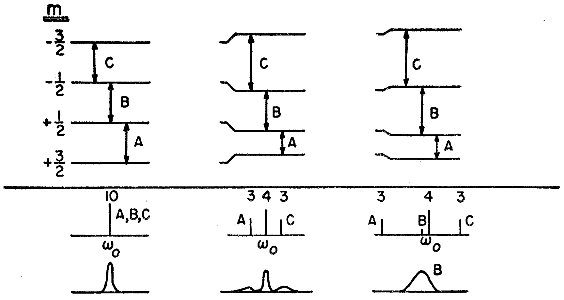

FIG. 4. Static electric quadrupole effects for a nucleus of spin 3/2. Top: energy levels. Middle: spectrum for a single nucleus. Bottom: resulting resonance in a crystal containing defects. Left: vanishing quadrupole interaction. Center: first-order effects of quadrupole interaction. Right: second-order effects of quadrupole interaction. ω_0= Larmor frequency.

In an imperfect crystal where field gradients vary from nucleus to nucleus this will lead to a resonance line which consists of a central component at frequency ω_0 and of width determined by magnetic interactions only, and of two smeared out satellite lines. The latter will in general tend to broaden the observed resonance line. If, however, the quadrupolar interaction is sufficiently large, the satellite lines become smeared out to the extent that they become unobservable and one then sees only the remnant central line. This last situation is one which seems to prevail in the case of nuclei with large quadrupole moments even in pure well-annealed crystals because of the inevitable presence of a sufficient number of dislocations in the lattice.[12] Finally, if the quadrupole interaction effects are large enough, one has to go to second-order perturbation theory. One then finds that the central line too becomes affected by quadrupole interaction so that in an imperfect crystal, where the field gradients vary, one can expect a broadening of the central line.

A divalent impurity like Cd^{++} or an interstitial Ag^+ ion may be looked upon as an extra positive charge, an Ag^+ vacancy as an extra negative charge in the lattice. The field gradient due to such a defect may then be computed from its electrostatic potential $V=\pm e/r$, provided one multiplies the result by a correction factor $\beta=\beta_\epsilon\beta_0$. Here β_ϵ is a factor taking into account the electric polarization of the ions in the solid; for defects sufficiently far away, a Lorentz type internal field argument based on a continuum model of the crystal of dielectric constant ϵ gives $\beta_\epsilon=(\epsilon+2)/3\epsilon$. Of much greater importance is the factor β_0 due to the distortion of the ion core surrounding the nucleus, since even a slight departure from spherical symmetry of the core can produce a large field gradient at this nucleus. In particular β_0 includes an "antishielding" factor β_a due to such a distortion of the core by the field gradient of the external charge; theoretical estimates[13] show that

---

[11] R. V. Pound, Phys. Rev. **79**, 685 (1950).

[12] G. D. Watkins and R. V. Pound, Phys. Rev. **89**, 658 (1953); R. V. Pound, J. Phys. Chem. **57**, 743 (1953).

[13] Foley, Sternheimer, and Tycko, Phys. Rev. **93**, 734 (1954).

$\beta_a \approx 50$ for ions like Cl^- or Rb^+. A second way in which a point imperfection can cause departures from cubic symmetry in the field gradient at a nucleus a distance r away is by virtue of the strain it introduces in the lattice. It can be shown that the net field gradient produced by the strain depends on the distance r in the same way as the field gradient produced by the charge of the defect, i.e., like r^{-3}.[14] Again the field gradient so calculated must be multiplied by a correction factor β which includes antishielding effects as well as the result of distortion of the ion core surrounding the nucleus by direct interaction with neighboring ion cores through polarization and covalent effects.[15,16]

For the discussion of the experimental results it is of interest to consider in slightly greater detail the second-order quadrupolar broadening of the central line. The frequency deviation ω' of the $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition from the Larmor frequency ω_0 is given by:

$$\omega' = -(2I+3)[8I^2(2I-1)]^{-1} \times (eQ/\hbar)^2 \omega_0^{-1} [|V_1|^2 - \tfrac{1}{2}|V_2|^2]. \quad (2)$$

Considering V_1 and V_2 as due to the electrostatic charges $\pm e$ of the defects labeled by n, one gets:

$$\begin{aligned} V_1 &= 3\beta \textstyle\sum_n e_n r_n^{-3} \cos\theta_n \sin\theta_n e^{i\varphi_n}, \\ V_2 &= \tfrac{3}{2}\beta \textstyle\sum_n e_n r_n^{-3} \sin^2\theta_n e^{2i\varphi_n}, \end{aligned} \quad (3)$$

where $\mathbf{r}_n$ denotes the position of the defect with respect to the nucleus under consideration, θ_n and φ_n being the polar and azimuthal angles of $\mathbf{r}_n$ with respect to the z-axis. Equation (2) then yields:

$$\omega' = -B \textstyle\sum_{m,n} \rho_m^{-3} \rho_n^{-3} \Psi_{mn}, \quad (4)$$

where

$$\Psi_{mn} = \{2 \sin 2\theta_m \sin 2\theta_n \cos(\varphi_m - \varphi_n) - \sin^2\theta_m \sin^2\theta_n \cos 2(\varphi_m - \varphi_n)\},$$

and where $\rho_n = r_n/R$, R being the nearest neighbor distance in the crystal lattice. B is a characteristic frequency given by

$$B = \frac{9}{64} \frac{2I+3}{I^2(2I-1)} \left(\beta \frac{e^2Q}{\hbar R^3}\right)^2 \omega_0^{-1}. \quad (5)$$

Equation (4) includes explicitly only charge effects; to the extent that strains caused by defects are important, their effect may be imagined as effectively increasing the value of β in (5).

The line shape will depend on the statistical properties of the sum in (4), but its calculation is rather difficult.[3,17] On the other hand assuming a completely random distrubution of N defects in the solid, a calculation of the moments of the resonance line[10] from Eq. (4) involves only simple algebra. In particular the second moment $\langle(\Delta\omega)^2\rangle_Q = \langle\omega'^2\rangle - \langle\omega'\rangle^2$ is found by suitable averaging over the angular factors in (4) to be:

$$\langle(\Delta\omega)^2\rangle_Q = \frac{64}{45} B^2 \left\{ \left(\sum_n \rho_n^{-6}\right)^2 + \frac{6}{7} \sum_n \rho_n^{-12} - \frac{6}{5N} \left(\sum \rho_n^{-6}\right)^2 \right\}. \quad (6)$$

Unfortunately, as we already pointed out, the moments of the line fail to give a satisfactory physical description of the line. The reason for this is that, if a defect is too close to a nucleus, the contribution to the resonance absorption from this nucleus will lie in the extreme wings of the line where it becomes unobservable, yet contributes markedly to the moments of the line. Thus defects which do affect the observable part of the resonance line will lie outside some critical distance ρ_c from the Br nuclei under consideration such that the approximate frequency shift $\Omega = B\rho_c^{-6}$ due to an impurity a distance ρ_c away is not too large. On a simple continuum model, denoting by vR^3 the volume occupied per defect, the sums in (6) can be replaced by integrals to give the second moment due to defects at distances $\rho > \rho_c$ as

$$\begin{aligned} \langle(\Delta\omega)^2\rangle_Q &= 1.70 B^2 x v^{-1} \rho_c^{-9} [1 + 14.7 x v^{-1} \rho_c^3], \\ \rho_c^{-3} &= (\Omega/B)^{\frac{1}{2}}, \end{aligned} \quad (7)$$

where x is the atomic fraction of defects in the solid. It must be emphasized that, in the absence of a knowledge of the line shape, (7) can only give a very crude estimate of the line width and its concentration dependence.

IV. QUADRUPOLAR RELAXATION EFFECTS

In a salt like AgBr the motion of point imperfections in the lattice creates fluctuating electric fields at the position of a Br nucleus and thus may constitute an important relaxation mechanism for this nucleus through interaction with its electric quadrupole moment. We should like to obtain a simple expression for the relaxation time T_1 due to this process for a nucleus of spin $I = \frac{3}{2}$ for the particular case that only the central line is observed.

This situation is slightly unusual since one only observes the absorption of rf power in the $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition, while the quadrupolar Hamiltonian $\mathcal{H}_Q$ responsible for the relaxation induces transitions between all energy levels and, to first order, $\langle\frac{1}{2}|\mathcal{H}_Q|-\frac{1}{2}\rangle = 0$. To examine the precise meaning of T_1 under these conditions, we first establish the behavior of the absorption line when saturation effects are included. Let w denote the transition probability per unit time for $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transitions induced by the applied rf field. Since

---

[14] See, for example, reference 3. It is there also shown that the magnitude of the strain effect is about 10% that of the charge effect if one assumes the same ion core distortion in both cases.

[15] N. Bloembergen, Proceedings of the Conference on Defects in Crystalline Solids, Bristol, 1954 (Physical Society, London, 1955), p. 1.

[16] J. van Kranendonk, Physica 20, 781 (1954).

[17] A diagram showing the shape to be expected for the simplest case of a single defect at a fixed distance r from the nucleus can be found in reference 15.

the spectral densities of the fluctuating fields are slowly varying functions of frequency, we shall as a first approximation in computing transition probabilities due to $\mathcal{H}_Q$ consider the four energy levels of a Br nucleus as essentially equally spaced by amounts $\hbar\omega_0$. Then, by (1), the matrix elements of $\mathcal{H}_Q$ are such that we can write for the upward transition probabilities per unit time due to $\mathcal{H}_Q$: $W_{\frac{1}{2},-\frac{1}{2}}=0$, $W_{\frac{3}{2},\frac{1}{2}}=W_{-\frac{1}{2},-\frac{3}{2}}\equiv W_1$, $W_{\frac{3}{2},-\frac{1}{2}}=W_{\frac{1}{2},-\frac{3}{2}}\equiv W_2$, where the quantities W_1 and W_2 thus defined represent transition probabilities between levels separated by amounts $\hbar\omega_0$ and $2\hbar\omega_0$ respectively. One can then write the downward transition probabilities in the form: $W_{-\frac{1}{2},\frac{1}{2}}=0$, $W_{\frac{1}{2},\frac{3}{2}}=W_{-\frac{3}{2},-\frac{1}{2}}=W_1(1+\Delta)$, $W_{-\frac{1}{2},\frac{3}{2}}=W_{-\frac{3}{2},\frac{1}{2}}=W_2(1+2\Delta)$, where $\Delta=\hbar\omega_0/kT\ll 1$. The four equations determining the number of nuclei in each of the four energy levels, denoted by index m (or n), are then:

$$\dot{N}_m=\sum_{n\neq m}{}_n\{-N_m(W_{mn}+w_{mn})+N_n(W_{nm}+w_{nm})\},\quad (8)$$

where $w_{mn}=0$, except $w_{\frac{1}{2},-\frac{1}{2}}=w_{-\frac{1}{2},\frac{1}{2}}=w$. For a steady state the left sides of these equations are put equal to zero and the resulting algebraic equations are readily solved. One thus obtains for the power absorbed from the rf field $H_x=H'\cos\omega t$:

$$\begin{aligned}\mathcal{P}=\hbar\omega w(N_{\frac{1}{2}}-N_{-\frac{1}{2}})&=\tfrac{1}{4}N\Delta\hbar\omega w\\ &\times[1+\tfrac{1}{2}w(W_1+W_2)/W_1W_2]^{-1}.\end{aligned}\quad (9)$$

Here $w=\frac{1}{2}\pi\gamma^2H'^2g(\omega)$, where $g(\omega)$ is the normalized line shape function. Hence the saturation term in (9) assumes the customary form[18] $(1+\frac{1}{4}\gamma^2H'^2T_1T_2)$ if one makes the usual definition $T_2=\pi g(\omega)_{\max}$ and the identification:

$$T_1=(W_1+W_2)/W_1W_2.\quad (10)$$

This somewhat unusual form of composition of W_1 and W_2 to yield T_1 implies that it is the smaller of the two quantities W_1 and W_2 which mainly determines T_1. This is physically plausible since, in order to restore the thermal equilibrium between the levels $\frac{1}{2}$ and $-\frac{1}{2}$, $\mathcal{H}_Q$ must give rise to transitions involving both W_1 and W_2 in succession.

It remains to determine W_1 and W_2 due to the motion of point imperfections. V_1 and V_2 in the expression (1) for $\mathcal{H}_Q$ are now random functions of time and we can evaluate the pertinent matrix elements for spin $I=\frac{3}{2}$ to write the general result[19]:

$$\begin{aligned}W_1&=W_{\frac{3}{2},\frac{1}{2}}=(\pi/6\hbar^2)e^2Q^2J_1(\omega_0),\\ W_2&=W_{\frac{3}{2},-\frac{1}{2}}=(\pi/6\hbar^2)e^2Q^2J_2(2\omega_0),\end{aligned}\quad (11)$$

where J_1 and J_2 are the spectral densities of the functions V_1 and V_2 respectively. In particular, if we consider V_1 and V_2 as due to the electrostatic effects of charged point defects, then Eqs. (3) apply where now r_n, θ_n, φ_n are random functions of time. The form of Eqs. (3) makes it clear, however, that mathematically the calculation of the correlation functions and spectral densities of V_1 and V_2 is very similar to the corresponding computations occurring in the theory of nuclear relaxation via magnetic dipole-dipole interaction between diffusing nuclei.[20] Torrey's results can therefore be carried over to the present problem with practically no modification. Specifically we wish to consider the situation in which the Br nuclei are fixed in position while singly charged point defects (vacancies or interstitials) diffuse independently through the lattice with a mean jump frequency ν per second. We further assume a quasi-continuum model in which the defect moves a distance b in arbitrary direction in each jump, its distance of closest approach to a Br nucleus being denoted by a. If c is the atomic concentration of defects in the solid, $4c/(2R)^3$ will give the number of defects per cm^3 in the AgBr lattice. W_1 and W_2 can then be written in the form:

$$\begin{aligned}W_1&=(32\pi/15)(R/a)^3Bc(\omega_0/\nu)G(k,\omega_0/\nu),\\ W_2&=(32\pi/15)(R/a)^3Bc(\omega_0/\nu)G(k,2\omega_0/\nu),\end{aligned}\quad (12)$$

where B is the characteristic frequency already defined in (5) and where G is an integral involving a spherical Bessel function and defined by Torrey as:

$$G(k,y)=\frac{2k}{\pi}\int_0^\infty\frac{1-x^{-1}\sin x}{(1-x^{-1}\sin x)^2+y^2}j_1{}^2(kx)dx,\ k\equiv a/b.\quad (13)$$

An approximate evaluation of G can be obtained by considering $x^{-1}\sin x\ll 1$ everywhere in the integrand and expanding the latter accordingly. After integration one then obtains for $k>\frac{1}{2}$:

$$\begin{aligned}G(k,y)&=\tfrac{1}{3}(1+y^2)^{-1}[1+k'(1-y^2)(1+y^2)^{-1}],\\ k'&=\tfrac{1}{16}k^{-3}-\tfrac{3}{4}k^{-1}+1.\end{aligned}\quad (14)$$

This approximation is very good for $y>1$, it determines quite well the value of y for which $yG(y)$ is a maximum, and it gives results about 35% too low for $y\ll 1$. By (10) one then gets an approximate expression for the relaxation time T_1 due to a particular kind of defect:

$$\begin{aligned}1/T_1=(16\pi/45)&(1+k')(a/R)^{-3}Bc\nu\omega_0{}^{-1}\\ &\times[(\nu\omega_0{}^{-1})^2+(5/2)(1+k')^2]^{-1}.\end{aligned}\quad (15)$$

For vacancies $a=R$, $b=\sqrt{2}R$, so that $1+k'=1.116$. The temperature dependence of ν is given by $\nu=\nu^0\exp(-U/kT)$, while at the lower temperatures c is a constant determined by the concentration of divalent impurity atoms added to the lattice. Hence, with increasing temperature $T_1{}^{-1}$ will increase to a characteristic maximum reached when $\nu\approx(5/2)^{\frac{1}{2}}(1+k')\omega_0$, after which $T_1{}^{-1}$ will decrease again. At sufficiently high temperatures, however, c will increase exponentially because of the generation of intrinsic defects in themal equilibrium, and as a result $T_1{}^{-1}$ will tend to increase again. The

---

[18] Bloembergen, Purcell, and Pound, Phys. Rev. **73**, 679 (1948).

[19] A. Abragam and R. V. Pound, Phys. Rev. **92**, 954 (1953).

[20] H. C. Torrey, Phys. Rev. **92**, 962 (1953).

general behavior is shown in Fig. 6. Note also that the magnitude of T_1^{-1} at its maximum is determined by the parameter Bc. Hence, when quadrupolar interactions are large enough so that a static configuration of defects gives rise to second-order quadrupolar broadening of the resonance line, one can expect that these defects in motion will also give rise to appreciable relaxation effects.

V. DISCUSSION OF AgBr RESULTS

The experimental data on AgBr seem to indicate that, in agreement with the findings of Pound and Watkins,[12] the number of imperfections, such as dislocations, in any crystal is large enough so that, even in our purest sample of AgBr, we observe essentially only the $\frac{1}{2}\leftrightarrow-\frac{1}{2}$ transition of the Br resonance line. There are two kinds of evidence in support of this conclusion. First, an absolute intensity measurement shows that the integrated intensity of the line, neglecting contributions far out in the wings, is closer to 40% than to 100% of the combined intensity to be expected from all three transitions.[1] Second, the width of the line in the pure sample is *smaller* than one would compute even from magnetic interactions only by naively using Van Vleck's formula.[10] Specifically the line shape, except far out in the wings, is approximately Gaussian with a width $\Delta\nu'$, measured between points of maximum slope, $\Delta\nu_{79}'=0.925$ kc/sec and $\Delta\nu_{81}'=1.030$ kc/sec for the two isotopes respectively.[21] Now, the width of the central line caused by magnetic interactions should indeed be somewhat smaller than the width for all three transitions superimposed, the case to which Van Vleck's formula[10] is applicable. The physical reason for this is that, as the quadrupolar interaction causes the energy levels of a Br nucleus to be unequally spaced, some of the flip-flop processes between pairs of Br nuclei are no longer possible with conservation of energy, and thus such processes no longer contribute to the magnetic line width. If the field gradient varies from nucleus to nucleus in the crystal, then the second moment of the central line due to magnetic interactions can be computed to yield a result identical with Van Vleck's formula,[10] except that the factor $\frac{3}{4}I(I+1)$ in the term for "like" nuclei must be replaced by: $[\frac{1}{3}I(I+1)+\frac{1}{32}(2I+1)+\frac{1}{4}]$.[22] The resulting formula yields the calculated line widths $\Delta\nu_{79}'=0.945$ kc and $\Delta\nu_{81}'=1.025$ kc/sec,[23] values about 0.84 as large as those given by Van Vleck's unmodified expression. These values are in good agreement with the experimental ones, and indicate incidentally that the central line in the pure sample is not appreciably broadened by second-order quadrupole interactions.

In order to discuss the specifically quadrupolar effects caused by the point defects, we need to estimate the characteristic (angular) frequency B. In our magnetic field the Br^{81} resonance frequency lies at 6630 kc, so that $\omega_0=4.16\times10^7$ radians/sec. Taking the lattice constant R as 2.88×10^{-8} cm Eq. (5) gives for Br^{81}:

$$B=2.95\times10^4\beta^2 \text{ rad/sec.} \qquad (16)$$

As for the correction factor β, the discussion in Sec. III shows that only exceedingly crude estimates are possible. β includes an antishielding factor which is expected to be larger for the negative Br^- ion than that calculated for Rb^+,[13] i.e., larger than 50. The dielectric constant correction, only meaningful for defects sufficiently far from the nuclei they effect, amounts to about 0.4. Strain and covalent effects will tend to increase β, but as a conservative order of magnitude estimate let us assume $\beta\approx20$. Then $B=1.2\times10^7$ sec^{-1}. It is therefore clear that quadrupolar effects can be very important both for line-broadening and relaxation effects.

In interpreting the experimental results it is essential to keep in mind the fact that point imperfections in the lattice can be highly mobile. Careful conductivity measurements[7,8] on single crystals of AgBr allow (subject to certain assumptions about the association of the defects[7]) the determination of the mobilities μ_v and μ_i of Ag vacancy and interstitial ions respectively, in addition to the determination of c_{i0}, the atomic concentration of thermally produced Frenkel defects existing in the pure crystal. Using the Einstein relation $D=(kT/e)\mu$, one can compute the diffusion coefficients of the defects and thence the jump frequencies $\nu_v=3R^{-2}D_v$ for vacancies and $\nu_i=6R^{-2}D$ for interstitial ions. The results, using Kurnick's data,[8] are shown in

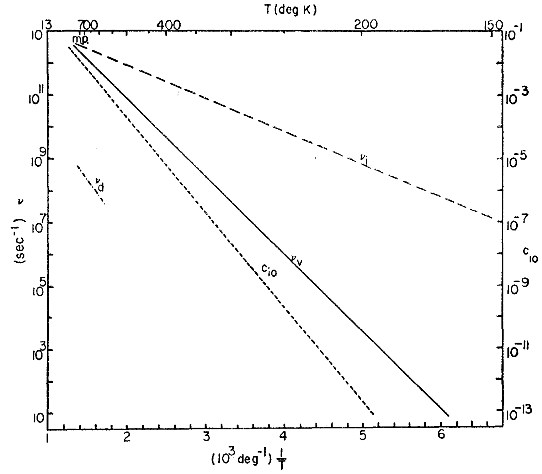

FIG. 5. Jump frequencies and concentration of interstitial defects calculated from Kurnick's[8] data. Solid line: jump frequency of Ag vacancies, $\nu_v=5.9\times10^{15}\exp(-5620/T)$. Dashed line: jump frequency of Ag interstitial ions, $\nu_i=9.4\times10^{13}\exp(-2360/T)$. Dotted line: fractional concentration of Ag interstitial ions in a pure sample of AgBr, $c_{i0}=1.9\times10^{-2}\exp(-6900/T)$. Dash-dotted line: Cd^{++} jump frequency ν_d estimated from data in reference 24.

---

[21] These measurements were checked at 150°K to eliminate any possible misleading effects due to residual impurities in the pure sample.

[22] We wish to thank Professor N. Bloembergen for communicating this result to us.

[23] Since the magnetic moments of the Ag isotopes are very small, they contribute only slightly to the calculated widths.

Fig. 5. It should be pointed out that, since the conductivity measurements were all made at temperatures above 200°C, the jump frequencies computed for low temperatures represent somewhat of an extrapolation. Conductivity measurements also indicate that the Br^- ions remain relatively immobile up to very high temperatures[8] and that Cd^{++} impurity ions diffuse only very slowly.[24]

One can expect that, when the motion of a defect is sufficiently rapid, its contribution to the static quadrupolar line width of a nucleus will average to zero. The problem of the "line narrowing" of the second-order quadrupolar interaction is a rather complex one.[25] But, crudely speaking, one would expect the customary criterion,[18] i.e., that the contribution to the static quadrupolar line width due to a defect disappears when the jump frequency of the defect is large compared to the magnitude of the quadrupolar width produced by this defect. Hence purely static quadrupolar effects of the kind discussed in Sec. III should only come into play at sufficiently low temperatures where the point defects are not too mobile, i.e., below about 200°K for Ag vacancies and below about 350°K for Cd^{++} ions.

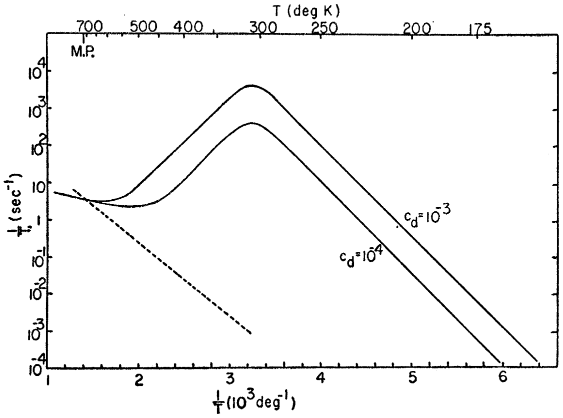

FIG. 6. Behavior of the Br^{81} relaxation time T_1 as a function of temperature calculated from Eq. (15), using the conservative estimate $\beta = 20$ and the results of Fig. 5 as obtained from Kurnick's data for AgBr. Solid line: $1/T_1$ due to quadrupolar interaction with vacancies in AgBr samples containing Cd^{++} ion concentrations of 10^{-3} and 10^{-4} respectively. Dotted line: $1/T_1$ due to interstitial ions in a pure sample.

On the other hand, the rapid motion of defects should have marked effects on the relaxation time T_1 of the Br nuclei. At temperatures below about 450°K Fig. 5 shows that the mobile defects in the lattice[26] are predominantly the Ag^+ vacancies whose concentration is equal to c_d, the concentration of divalent Cd^{++} ions in the lattice. By Eq. (15), $1/T_1$ will be a maximum when the vacancy jump frequency ν_v reaches a critical value ν_v^* given by $\nu_v^* = 1.83\omega_0 = 7.6 \times 10^7$ sec^{-1} for Br^{81} in our magnetic field. Also, since B is so large, it is possible that $(1/T_1)_{\max}$ becomes comparable to or larger than 6×10^3 sec^{-1}, the magnetic line width in angular frequency units. In that event, the short relaxation time should lead to a lifetime broadening of the nuclear resonance line in the solid. We believe that the maximum in width (or minimum in intensity) observed at about 273°K (see Fig. 3) is due to this effect. Note that Eq. (15) predicts that the temperature at which the maximum of $1/T_1$ occurs depends only on the magnitude of the jump frequency ν_v and is thus independent of c_d, while the magnitude of $(1/T_1)_{\max}$ is a function of c_d. The experimental results discussed in Sec. II and shown in Fig. 3 appear in agreement with this conclusion. The conductivity data allow one to estimate the temperature T^* for which ν_v reaches its critical value ν_v^*. Kurnick's data[7] give $T^* = 308$°K, Teltow's[8] give $T^* = 287$°K; these are in fair agreement with the observed minimum in intensity at 273°K. Figure 6 shows a plot of $1/T_1$ due to vacancies obtained if Kurnick's data are used in Eq. (15) with our conservative estimate $\beta \approx 20$. It is seen that $1/T_1$ at its maximum is indeed of the right order of magnitude to cause lifetime broadening of the resonance line. E.g., in Fig. 3, the quantity TD at the temperature T^* of its minimum is, in the sample with $c_d = 10^{-4}$, about 3.4 times less than at low temperatures; i.e., the width of the line at temperature T^* is, crudely speaking, about $\sqrt{3.4}$ times the magnetic width of 6.5×10^3 radians/sec. The extra width, when attributed to relaxation time broadening, should be of order $2/T_1$; hence one arrives at the order of magnitude estimate $1/T_1 \approx 2.3 \times 10^3$ sec^{-1}. Comparison with Fig. 6 shows then that a value of β about 2.5 times larger than was assumed, i.e., $\beta \approx 50$, would lead to better agreement with the observed broadening. Finally, an attempt was made to check the relaxation time more directly by investigating the saturation behavior of the resonance line as the rf magnetic field is increased. It was found that, while a pure sample of AgBr at room temperature (which is fairly close to T^*, the temperature of the maximum in $1/T_1$) or a doped sample ($c_d = 10^{-4}$) at 185°K could be made to show some saturation effects, this doped sample at room temperature showed no trace of saturation of its resonance line at the highest rf power level available in our equipment. From this one can make the rough estimate that T_1 in this sample at room temperature is shorter than 5 millisec, a result which is consistent with the possibility of lifetime broadening effects. There is one more experiment which suggests itself as a check of the interpretation of the data, namely to increase the Larmor frequency ω_0 by, say, doubling the value of the external magnetic field. Equation (15) would predict that the

---

[24] Schöne, Stasiw, and Teltow, Z. physik. Chem. **197**, 145 (1951).

[25] For further discussion see reference 3. For example, the first moment $\langle \Delta\omega' \rangle$ of a line does not average to zero in second order.

[26] It should be remembered that the jump frequencies shown in Fig. 5 are based on the assumption of negligible association of the defects. Note also that the concentration of interstitial ions is negligible (i.e., less than $2 \cdot 10^{-5}$, the concentration of defects in a "pure" sample) below 450°K, especially since, by virtue of the law of mass action, the presence of the deliberately introduced vacancies in a doped sample tends to decrease the number of Frenkel defects at a given temperature compared to that existing in a pure sample.

minimum in intensity in Fig. 3 would then be shifted to a somewhat higher temperature. Unfortunately, since our equipment consisted of a permanent magnet, this particular check could not be made.[27]

It is clear that the quadrupolar interaction with point defects becomes the dominant relaxation mechanism only in certain temperature ranges. There always must be added to it the quadrupolar interaction with lattice vibrations.[16] This leads to a relaxation time which may be relatively short even at liquid nitrogen temperature, but which is a monotonically rather slowly decreasing function of the temperature, especially above the Debye temperature[16] (144°K for AgBr). We wish to attribute the very rapid decrease in intensity of the resonance line in all samples, whether pure or doped, at high temperatures to lifetime broadening of the line by virtue of interaction of the Br nuclei with the moving point defects created in thermal equilibrium with the lattice. Incidentally an experimental check showed that the resonance line is not observable in liquid AgBr, presumably because of too short a relaxation time[28]; i.e., at high temperatures the line becomes too weak to observe in the solid and does not reappear at the melting point. Equation (15), with $a=(\sqrt{3}/2)R$, should allow one to estimate T_1 due to Ag^+ interstitial ions. It must be pointed out, however, that the effective correction factor β for interstitials may well be different from that for vacancies. The reason for this is that point defects closest to a nucleus make the largest contribution to the transition probability of the nucleus and hence to $1/T_1$,[29] and that an interstitial ion next to a Br^- ion can be expected to give rise to large strains and to distortion of the Br^- ion core by covalent effects tending to make the net field gradient at the Br nucleus exceptionally large, i.e., effectively enhancing the value of β contained in Eq. (15). Returning to Eq. (15) we note further that the contribution of defects to the relaxation time T_1 and to the electrical conductivity σ is quite different. Putting $c_i=c_i^0 \exp(-W/kT)$ and $\nu_i=\nu_i^0 \exp(-U/kT)$, we have in the temperature range where $\nu_i \gg \omega_0$:

$$\begin{aligned} 1/T_1 &\sim c_i/\nu_i \sim \exp[(W-U)/kT], \\ \sigma &\sim c_i\nu_i \sim \exp[(W+U)/kT]. \end{aligned} \tag{17}$$

The large jump frequencies ν_i make $1/T_1$ due to interstitial Ag ions rather small unless B is large; computed values for $1/T_1$ are shown in Fig. 6. It is seen that, in order to account for the line broadening at high temperatures by a sufficiently short T_1 due to Ag interstitials, one would need an effective value of β about 20 times as large as that assumed for vacancies, i.e., $\beta \approx 1000$. Such a value seems rather large, though it cannot be considered entirely impossible; e.g., values of the correction factor β between 100 and 1000 have been invoked to account for nuclear relaxation times due to quadrupolar interaction with lattice vibrations.[16] Figure 6 also shows that Ag^+ vacancies at high temperatures are not responsible for a very short T_1. There is, however, another mechanism which may determine T_1 at high temperatures. Kurnick[8] has some evidence for the formation of Br^- vacancies (Schottky defects) in the lattice above 570°K, their concentration being about equal to that of the Ag vacancies at 680°K. These Br^- vacancies contribute negligibly to the conductivity at this temperature. Some diffusion measurements[30] show, however, that such Br^- vacancies are by no means completely immobile, though their jump frequency at 680°K may be somewhat more than 1000 times less than that of the Ag^+ interstitials in the lattice. By Eq. (17), the small jump frequency of the Br^- vacancies will make their contribution to the electrical conductivity correspondingly small, but their contribution to $1/T_1$ correspondingly large. Very careful measurements of T_1 might decide whether such Br^- vacancies constitute indeed the main relaxation mechanism in the high-temperature range and could help to clarify some of the still unsettled questions of the behavior of Schottky defects in AgBr.

Finally we turn our attention to the low temperatures where the line shape is determined by static effects only. We note at the very outset that the defects in the solid at these low temperatures would not be expected to be randomly distributed. The reason for this is that the electrostatic attraction existing between Ag^+ vacancies and Cd^{++} impurities leads to correlation between their positions; in particular, it makes the state of lowest energy of the crystal one in which Ag^+ vacancies and Cd^{++} impurities lie on adjacent positions of the Ag sublattice, thus forming associated pairs ("complexes").[31] When the association process is complete, the field gradients due to $2N$ charges are replaced by field gradients approximately like those of N point dipoles. Hence association of defects at low temperatures should lead to smaller field gradients at the Br nuclei and hence to smaller quadrupolar broadening.

Following the discussion of Sec. III, one can try to estimate the order of magnitude of the static quadrupolar line width, assuming all defects to be randomly distributed. The concentration of defects $x=2c_d$, since the number of vacancies is equal to that of the impurity ions; also the volume vR^3 available to a defect is $2R^3$, since there are four Ag lattice sites in a cube of volume $(2R)^3$. We can say that, roughly speaking, contributions to the line more than 10 kc/sec from its center can be considered unobservable, i.e., we chose the cut-off

---

[27] Variation of the external magnetic field would also constitute a useful check in the study of lines broadened by *static* second-order quadrupole interaction since the line width should then be field-dependent.

[28] There are several cases known where the Br nuclear resonance is not observable in a liquid because of too short a relaxation time caused by quadrupole interaction. See R. V. Pound, Phys. Rev. **72**, 1273 (1947).

[29] This is in contrast to the static line width where defects which are close to a nucleus contribute only to the unobservable wings of the resonance line.

[30] A. Murin, Doklady Akad. Nauk. S.S.S.R. **99**, 529 (1954).

[31] For a recent discussion of association, see A. B. Lidiard, Phys. Rev. **94**, 29 (1954).

frequency in Eq. (7) as $\Omega = 2\pi \times 10^4$ sec^{-1}. We shall take the correction factor $\beta \approx 50$, as suggested by the discussion of relaxation effects connected with vacancies. For $c_d = 10^{-3}$, Eq. (7) then yields $\langle(\Delta\omega)^2\rangle_Q = 3.5 \times 10^8$ sec^{-2} as compared to the second moment due to magnetic interactions only, $\langle(\Delta\omega)^2\rangle_m = 10^7$ sec^{-2}. Since $\langle(\Delta\omega)^2\rangle_Q \sim B^{\frac{1}{2}}\Omega^{\frac{3}{2}}$, the result would not be greatly changed if a somewhat different cut-off frequency had been chosen. One thus sees that the assumption of a completely random distribution of defects at temperatures below 200°K would seem to lead to more pronounced effects on the line width in going from a pure sample to our most highly doped one than were actually observed. This conclusion is in agreement with the expectation that the defects are associated at these low temperatures. Finally, it seems possible that the *initial* broadening of the lines at about 200°K is connected with the onset of dissociation of the defects. Comparison with Lidiard's curves[31] and the fact that, unlike what one would expect from simple lifetime broadening due to vacancies, this initial broadening occurs at essentially the same temperature irrespective of impurity concentration, would suggest such an interpretation.[1] But both Fig. 6, which is based on a somewhat uncertain extrapolation of the conductivity data to these low temperatures, and some very crude experimental estimates of T_1 show that one cannot completely exclude the possibility of lifetime broadening effects already making some contribution to the line width around this temperature. Only careful relaxation time measurements might help to separate unambiguously the various effects. Such measurements in the low-temperature region would also be of interest since they might show an influence on T_1 due to the possibility of reorientation of complexes.

VI. FURTHER EXPERIMENTS

We want to mention briefly some experiments which illustrate the narrowing of resonance lines produced by the motion of defects. As a first example we consider NaCl doped with $CdCl_2$. Na has a small nuclear electric quadrupole moment (approximately 0.1×10^{-24} cm^2)[32] and, since the Na^+ ion is small, the effects of ion core distortion are correspondingly less important. As a result the parameter B for Na^+ is probably about 200 times smaller than that for Br^-. One thus expects Na quadrupolar interaction effects in NaCl to be much less significant than they are for Br in AgBr. Figure 7 shows the effect on the Na resonance line width $\Delta\nu'$ (measured between points of maximum slope) of increasing the temperature of a doped sample of NaCl.[33] The resulting curve is of the form characteristic of the motional narrowing of resonance lines.[34,35] One would expect that the width of the Na line would begin to decrease appreciably when the jump frequency ν_{Na} of the Na^+ ions, which determines the rate of fluctuation of the internal magnetic fields at the position of a Na nucleus, becomes comparable to the static Na line width $\Delta\omega$ at low temperatures.[36] But $\nu_{Na} \approx c_v \nu_v$, where c_v is the atomic concentration of Na^+ vacancies ($\ll 1$), or probability of a vacancy being next to a Na^+ ion, and ν_v is the vacancy jump frequency. Below 500°C the thermal production of defects is negligible[37] and $c_v = c_d$, the concentration of divalent impurity ions. Thus one expects the line width to show appreciable narrowing when the temperature becomes high enough so that:

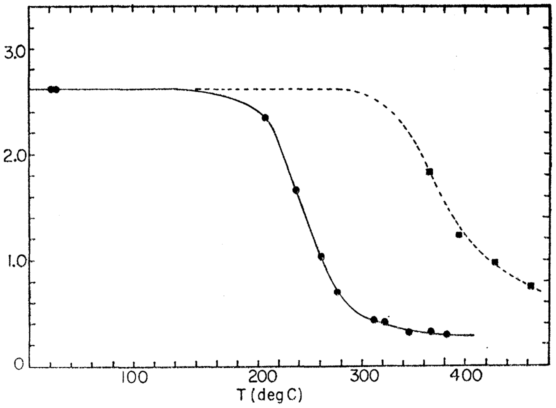

FIG. 7. Behavior of Na line width $\Delta\nu'$ (measured between points of maximum slope) as a function of temperature in NaCl. Solid curve: NaCl sample doped with a molar concentration 6×10^{-4} of $CdCl_2$. Dotted curve: "pure" NaCl sample.

$$\nu_{Na} = c_v \nu_v \approx \Delta\omega. \qquad (18)$$

In agreement with Fig. 7, the Na line in samples of higher impurity concentration should therefore begin to narrow at a lower temperature. The conductivity data[37] give information as to the mobility of the Na^+ vacancies and hence allow the calculation of ν_v. Using these data one predicts that in a sample containing 6×10^{-4} atomic fraction of $CdCl_2$, the narrowing criterion (18) should be satisfied at 230°C, in fair agreement with Fig. 7. The simplified theory of motional narrowing[18,34] permits one to construct from Fig. 7 a curve of ν_v *vs* $1/T$. From the slope of the resulting straight line one can estimate the activation energy for the diffusion of Na^+ ions to be 0.66 ev. This compares with a value of 0.77 ev obtained from diffusion[38] and 0.83 ev from conductivity measurements.

---

[32] Perl, Rabi, and Senitzky, Phys. Rev. **98**, 611 (1955).

[33] $\Delta\nu'$ at room temperature is about 1 kc/sec larger than one would compute from magnetic interactions alone, but independent of impurity concentration. Though we did not investigate in detail the source of the extra width, it is likely to be due to first-order quadrupole interaction with dislocations in the crystal.

[34] H. S. Gutowsky and G. E. Pake, J. Chem. Phys. **18**, 162 (1950).

[35] H. S. Gutowsky, Phys. Rev. **83**, 1073 (1951).

[36] Note that motional narrowing will be caused by *any* type of jumping of Na ions in the lattice, e.g., even by a localized jumping which only causes reorientation of an impurity complex without contributing to diffusion or electrical conductivity in the crystal.

[37] H. W. Etzel and R. J. Maurer, J. Chem. Phys. **18**, 1003 (1950).

[38] Mapother, Crooks, and Maurer, J. Chem. Phys. **18**, 1231 (1950).

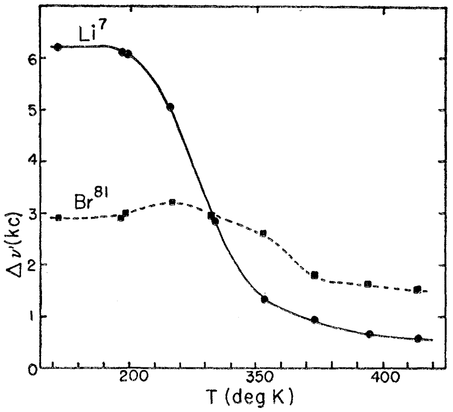

FIG. 8. Behavior of the resonance line widths $\Delta\nu'$ (measured between points of maximum slope) in a LiBr sample containing a molar concentration 2×10^{-3} of $MgBr_2$. Solid curve: Li^7 line width. Dotted curve: Br^{81} line width.

As a final illustration we want to mention the case of LiBr, which is also of some interest in connection with our interpretation of the AgBr results. Both Li and Br have magnetic moments large enough to make their resonance lines readily observable; on the other hand, Li has a very small quadrupole moment, unlike the Br nuclei already discussed in connection with AgBr. The electrical conductivity of LiBr has been studied by Haven[39]; Li vacancies are readily introduced into the salt by doping with $MgBr_2$. We want to consider what one would expect about the behavior of the line widths in a sample of LiBr containing, say, a concentration $c_d=2\times10^{-3}$ of $MgBr_2$. Turning our attention first to the Li line, it should begin to narrow when the jump frequency of Li ions is equal to the static Li line width $(\Delta\omega)_{Li}$, i.e., at about 310°K estimated from the conductivity measurements. At higher temperatures the line width should approach essentially zero since the internal fields at a Li^+ ion, whether due to Li^+ or Br^- ions, will average to zero when the Li^+ ion jumps fast enough. The situation here is analogous to that of Na^+ ions in NaCl. Now consider the Br line, neglecting at first the Br quadrupole moment. This line will begin to narrow when $\nu_{Li}\approx(\Delta\omega)_{Br}$, i.e., at about the same temperature where the Li line narrows, since then the magnetic width due to the Li nuclei begins to disappear. But, since the Br^- ions remain stationary, the line width at higher temperatures should not go to zero, but should approach a width due to magnetic interactions among the Br nuclei only. (From magnetic interactions one would calculate, for Br^{81}, $\Delta\nu'=3.2$ kc/sec in the limit of low, and $\Delta\nu'=1.2$ kc/sec in the limit of high temperatures.) Now, remembering the large Br electric quadrupole moment, one would expect, in analogy to our interpretation of the AgBr results, a line *broadening* due to the short relaxation time produced by quadrupole interaction with moving vacancies to occur when $\nu_v\approx1.8\omega_0$ (ω_0=Larmor frequency of Br ion), i.e., at about 335°K for Br^{81}. Thus the Br line width should be a rather complicated function of temperature, a maximum in width due to lifetime broadening being superposed in the same temperature range where the line would otherwise tend to narrow. Figure 8 shows the experimental results obtained for one such doped sample of LiBr prepared to check these general predictions.[40] The maximum in the Br line width is confirmed by a corresponding decrease in its intensity, and the temperature dependence of the curves is seen to be essentially as expected.

VII. CONCLUDING REMARKS

We have seen that nuclear magnetic resonance techniques provide a means of studying point defects in ionic crystals from a rather microscopic point of view. Measurements can be made on polycrystalline samples to yield values of the defect jump frequencies and their approximate activation energies by line narrowing or relaxation time observations; in some cases information may be obtained as to the association of defects in the solid. Our general discussion shows that variation of the external magnetic field and, most particularly, careful measurements of nuclear relaxation times as affected by the presence of point defects would certainly be of physical interest, as well as being desirable as a check on the interpretation of some of our results.

ACKNOWLEDGMENTS

We wish to thank Professor M. H. Cohen for his continuing interest in this work and for many discussions. Professor A. W. Lawson kindly lent us some specimens of AgBr for use in preliminary measurements. Finally, we are very grateful to Professor N. H. Nachtrieb for his generous help with the chemical preparation of the samples.

---

[39] Y. Haven, Rec. trav. chim. 69, 1471 (1950).

[40] Note that experimental line width curves of the type shown in Fig. 8 allow an immediate determination as to which ion in the crystal is the mobile one.