

<sup>35</sup>Cl spin-spin relaxation time  $T_2$  in  $Rb_2ZnCl_4$  studied by nuclear quadrupole resonance

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The <sup>35</sup>Cl spin-spin relaxation time  $T_2$  of both the Goldstone and amplitude modes in  $Rb_2ZnCl_4$  was analytically calculated and verified experimentally. The theoretical approach shows that the spin-spin relaxation time  $T_2$  behaves in a similar way to the spin-lattice relaxation time  $T_1$  as a function of temperature. Experimental measurements were carried out at a <sup>35</sup>Cl nuclear site in  $Rb_2ZnCl_4$  in the paraelectric, incommensurate, and commensurate phases. The results agree with theoretical predictions.

I. INTRODUCTION

After almost a decade, incommensurate  $I$  systems, are still the focus of a great deal of attention. Although a considerable amount of work has been carried out in these systems using resonance techniques, dynamical studies are rather limited in the  $A_2BX_4$ -type ( $I$ ) systems.<sup>1,2</sup> Previous nuclear-quadrupole-resonance-spectroscopy (NQR) studies by us and other groups<sup>3-6</sup> of spin-lattice relaxation time  $T_1$  in  $Rb_2ZnCl_4$  at the anion position, gave new results and explained open problems for the pure and mixed systems and for both the amplitude and the Goldstone modes of fluctuations, such as the influence of impurities on  $T_1$  and the behavior of the chaotic region in the narrow soliton limit.

In contrast to the  $T_1$  measurements, not enough information is available for the spin-spin relaxation mechanism. Our aim in this work is to examine the way that an  $I$  system passes through the transition temperature  $T_I$

from the paraelectric  $P$  ordered phase to the inhomogeneous frequency distribution in the  $I$  phase, and then to the low-temperature commensurate  $C$  one through the transition temperature  $T_c$ . One of the best ways to get this information is by investigating the spin-spin relaxation time  $T_2$  as a function of temperature. As far as we know this is the first time that spin-spin relaxation has been studied in  $Rb_2ZnCl_4$  at a Cl nuclear site. For the sake of comparison, the  $T_1$  theoretical calculations and measurements were repeated on the same sample in order to have consistent results. Our measurements were done for both the Goldstone mode and the amplitude mode.

II. THEORY

Our system can be described by the total Hamiltonian,

$$\mathcal{H} = \mathcal{H}^Q + \mathcal{H}^D, \tag{1a}$$

which is the sum of a quadrupolar term  $\mathcal{H}^Q$ ,

$$\begin{aligned} \mathcal{H}^Q = E \{ & [3I_z^2 - I(I+1)]V_{zz} + (I_+I_z + I_zI_+)(V_{xz} - iV_{yz}) + (I_-I_z + I_zI_-)(V_{xz} + iV_{yz}) \\ & + I_+^2 [\frac{1}{2}(V_{xx} - V_{yy}) - iV_{xy}] + I_-^2 [\frac{1}{2}(V_{xx} - V_{yy}) + iV_{xy}] \}, \end{aligned} \tag{1b}$$

where  $E = e^2Q/4I(2I - 1)$ , and a dipolar term  $\mathcal{H}^D$  which is the sum of terms of the general form,

$$\begin{aligned} \mathcal{H}^D(i, j) = -\frac{3}{2}\gamma^2\hbar^2 \{ & [\frac{2}{3}I_z^{(i)}I_z^{(j)} + \frac{1}{6}(I_+^{(i)}I_-^{(j)} + I_-^{(i)}I_+^{(j)})]F_{zz} + (I_z^{(i)}I_+^{(j)} + I_+^{(i)}I_z^{(j)})(F_{zx} - iF_{zy}) \\ & + (I_z^{(i)}I_-^{(j)} + I_-^{(i)}I_z^{(j)})(F_{zx} + iF_{zy}) + I_+^{(i)}I_+^{(j)}[(F_{xx} - F_{yy}) - 2iF_{xy}] + I_-^{(i)}I_-^{(j)}[(F_{xx} - F_{yy}) + 2iF_{xy}] \}. \end{aligned} \tag{1c}$$

Here the tensor  $F$  is equal to

$$F(i, j) = \begin{cases} F_{zz}(i, j) = \frac{r^2 - 3z^2}{r^5} \\ F_{nm}(i, j) = \frac{nm}{r^5} \quad n, m = x, y, z \text{ (for the rest of the elements),} \end{cases} \tag{1d}$$

and  $r$  is the distance between two spins  $i, j$ .

This Hamiltonian can be separated into a static part  $\overline{\mathcal{H}}$  and a perturbing time-dependent part  $\mathcal{H}_1(t)$ , so Eq. (1a) is now equal to

$$\mathcal{H} = \overline{\mathcal{H}} + \mathcal{H}_1(t) = \overline{\mathcal{H}}^Q + \overline{\mathcal{H}}^D + \mathcal{H}_1^Q(t) + \mathcal{H}_1^D(t). \tag{2}$$

Usually  $\overline{\mathcal{H}}^Q \gg \overline{\mathcal{H}}^D$  so that the static dipolar term  $\overline{\mathcal{H}}^D$  introduces, as we shall see later, negligible corrections to the energy spectrum of the unperturbed Hamiltonian  $\overline{\mathcal{H}}^Q$ . Things are completely different for the time-dependent dipolar term  $\mathcal{H}_1^D(t)$ . Looking to our experimental results we see that in the  $I$  region, the  $T_1$  values

are comparable to the values of  $T_2$ . This indicates that the contribution of the dipole-dipole interaction might be comparable to the contribution of the quadrupolar interaction in the relaxation processes. Having this in mind we proceed as follows.

The theoretical treatment will be presented for only one Cl nuclear site in  $\text{Rb}_2\text{ZnCl}_4$ , namely the Cl(1) (Ref. 7), which lies in the mirror plane  $m_y$ . The calculation can be readily extended for other Cl sites of this system. In this case the main dipolar interaction is produced from Cl(2), Cl(3), and Cl(4) of the  $\text{ZnCl}_4$  tetrahedra (the Zn nucleus being even-even has spin  $I=0$ ). In view of the fact that the perturbing dipolar term contains four equal spins  $I=\frac{3}{2}$ , the degenerate manifold of eigenstates of the unperturbed Hamiltonian  $\overline{\mathcal{H}}_0$  is taken to be  $|m(1), m(2), m(3), m(4)\rangle$ , where  $m(i)$  takes the values,  $m(i)=\frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$ . If we take into consideration that (i)  $e^2 QV_{zz} \gg \gamma^2 \hbar^2 F_{zz}$  and (ii)  $F_{zz} \gg F_{ij}$ , where  $F_{ij}$  stands for the rest of the tensor elements (a qualitative proof of this will be discussed later), we may conclude that the static dipolar part has little effect on the quadrupolar energy spectrum. Its main effect is the addition of small diagonal terms to the matrix representation of the unperturbed Hamiltonian in the extended 256-dimensional outer product space. These small dipolar contributions result only in the broadening of the two doubly degenerate quadrupolar energy levels  $E_{\pm 3/2}, E_{\pm 1/2}$  and therefore can be neglected in the  $T_2$  calculations. This argument also indicates that, since only one pair of energy levels exists, we have one single  $T_2$  relaxation mechanism. Since in our treatment we irradiate the Cl(1) nucleus selectively, we may suppose that Cl(2), Cl(3), and Cl(4) remain in the ground state, and as a result, we examine only the  $|\pm\frac{3}{2}, \pm\frac{1}{2}, \pm\frac{1}{2}, \pm\frac{1}{2}\rangle$ -to- $|\pm\frac{1}{2}, \pm\frac{1}{2}, \pm\frac{1}{2}, \pm\frac{1}{2}\rangle$  transitions.

Referring now to the spin-spin relaxation time  $T_2$  we know that<sup>8</sup>

$$\frac{1}{T_2} = \frac{1}{T_2'} + \frac{1}{2} \left( \frac{1}{\tau_a} + \frac{1}{\tau_b} \right), \quad (3)$$

where

$$\frac{1}{T_2'} = \frac{1}{\hbar^2} \int_0^\infty \overline{\omega(t)\omega(t-\tau)} d\tau, \quad (4)$$

$$\omega(t) = \langle a | \mathcal{H}_1(t) | a \rangle - \langle b | \mathcal{H}_1(t) | b \rangle, \quad (5)$$

$$\frac{1}{\tau_a} = \frac{1}{\hbar^2} \sum_{c \neq a} \int_{-\infty}^{+\infty} e^{i\omega_{ac}\tau} d\tau \overline{\langle a | \mathcal{H}_1(t) | c \rangle \langle c | \mathcal{H}_1(t-\tau) | a \rangle}, \quad (6)$$

and

$$\frac{1}{\tau_b} = \frac{1}{\hbar^2} \sum_{c \neq b} \int_{-\infty}^{+\infty} e^{i\omega_{bc}\tau} d\tau \overline{\langle b | \mathcal{H}_1(t-\tau) | c \rangle \langle c | \mathcal{H}_1(t) | b \rangle}, \quad (7)$$

where  $|a\rangle$ ,  $|b\rangle$ , and  $|c\rangle$  are the different eigenstates of the unperturbed Hamiltonian  $\overline{\mathcal{H}}_0$ , in our case  $a = \pm\frac{3}{2}$  and  $b = \pm\frac{1}{2}$ .

It is possible again to separate the spin-spin relaxation rate  $1/T_2$  into a quadrupolar and a dipolar contribution,

$$\frac{1}{T_2} = \frac{1}{T_2^Q} + \frac{1}{T_2^D}. \quad (8)$$

Let us examine each one separately.

#### A. The quadrupolar contribution

Taking into consideration the local symmetry at the nuclear site of Cl(1) (Ref. 9), the time-averaged quadrupole electric-field-gradient EFG tensor (Ref. 10) in the  $P$  phase has the elements  $V_{xy} = V_{yx} = V_{zy} = V_{yz} = 0$  in view of the  $m_y$  mirror symmetry. Therefore, for  $T > T_I$  the  $^{35}\text{Cl}$  EFG tensor in the crystal fixed frame  $\mathbf{x}||\mathbf{a}, \mathbf{y}||\mathbf{b}, \mathbf{z}||\mathbf{c}$  has the form<sup>11</sup>

$$\overline{V}^{(P)} = \begin{vmatrix} V_{xx}^{(0)} & 0 & V_{xz}^{(0)} \\ 0 & V_{yy}^{(0)} & 0 \\ V_{xz}^{(0)} & 0 & V_{zz}^{(0)} \end{vmatrix}. \quad (9)$$

Below  $T_I$ , because of the frozen-in soft-mode displacements, the tensor elements  $V_{xy}$  and  $V_{yz}$  are different from zero.<sup>12</sup> If we expand the time-averaged EFG tensor in a Taylor series in powers of the static nuclear displacements  $u[\varphi(z)]$  around the value  $V^{(0)}$  which corresponds to the average structure of the  $P$  phase,<sup>2</sup> we can express the tensor in the  $I$  phase in the form

$$\overline{V}^{(I)} = \begin{vmatrix} V_{xx}^{(0)} & 0 & V_{xz}^{(0)} \\ 0 & V_{yy}^{(0)} & 0 \\ V_{xz}^{(0)} & 0 & V_{zz}^{(0)} \end{vmatrix} + \begin{vmatrix} 0 & V_{xy}^{(1)} & 0 \\ V_{xy}^{(1)} & 0 & V_{yz}^{(1)} \\ 0 & V_{yz}^{(1)} & 0 \end{vmatrix} A \cos\varphi + \begin{vmatrix} V_{xx}^{(2)} & 0 & V_{xz}^{(2)} \\ 0 & V_{yy}^{(2)} & 0 \\ V_{xz}^{(2)} & 0 & V_{zz}^{(2)} \end{vmatrix} A^2 \cos^2\varphi. \quad (10)$$

In expression (10) we assume that  $u[\varphi(z)] = A \cos\varphi(z)$  represents the frozen-in  $I$  distortion wave in the plane-wave-model (PWM) limit.<sup>2</sup> The quadrupolar part of the perturbing Hamiltonian  $\mathcal{H}_1^Q$  has a form similar to Eq. (1b), i.e.,

$$\begin{aligned} \mathcal{H}_1^Q = & E([3I_z^2 - I(I+1)]\Delta V_{zz}(t) + (I_+ I_z + I_z I_+)[\Delta V_{xz}(t) - i\Delta V_{yz}(t)] + (I_- I_z + I_z I_-)[\Delta V_{xz}(t) + i\Delta V_{yz}(t)] \\ & + I_+^2 \{ \frac{1}{2}[\Delta V_{xx}(t) - \Delta V_{yy}(t)] - i\Delta V_{xy}(t) \} + I_-^2 \{ \frac{1}{2}[\Delta V_{xx}(t) - \Delta V_{yy}(t)] + i\Delta V_{xy}(t) \}), \end{aligned} \quad (11)$$

where  $\Delta V(t) = V(t) - \bar{V}$ . In this case according to Eq. (4)  $1/T_2^Q$  is equal to

$$\frac{1}{T_2^Q} = 3E^2 \int_{-\infty}^{\infty} \overline{\Delta V_{zz}(t) \Delta V_{zz}(0)} dt \quad (12)$$

or

$$\frac{1}{T_2^Q} = 3E^2 J_{(0)}^Q \quad (I = \frac{3}{2}) . \quad (13)$$

For the state  $a = \pm \frac{3}{2}$

$$\frac{1}{\tau_{3/2}^Q} = 12E^2 (J_{(1)}^Q + J_{(2)}^Q) , \quad (14a)$$

and for the state  $b = \pm \frac{1}{2}$

$$\frac{1}{\tau_{1/2}^Q} = 12E^2 (J_{(-1)}^Q + J_{(-2)}^Q) , \quad (14b)$$

where

$$J_{(\pm\mu)}^Q = \int_{-\infty}^{\infty} \overline{\Delta V_{(\mu)}(0) \Delta V_{(\mu)}^*(t)} e^{\pm i\omega t} dt \quad (\mu = 1, 2) \quad (15)$$

are the spectral densities.

Finally, Eq. (3) can be rewritten with the the help of Eqs. (13) and (14) as follows:

$$\frac{1}{T_2^Q} = 6E^2 (\frac{1}{2} J_{(0)}^Q + J_{(1)}^Q + J_{(-1)}^Q + J_{(2)}^Q + J_{(-2)}^Q) . \quad (16)$$

Expanding now the time-dependent part of the EFG tensor  $\Delta V(t)$  in a Taylor series of the fluctuating part of the nuclear displacements of all the sites  $\delta \mathbf{u}(t)$ , we arrive at the following expression:<sup>2</sup>

$$\Delta V = (V^{(1)} + V^{(2)} A \cos\varphi) |\delta \mathbf{u}| + \frac{1}{2} V^{(2)} |\delta \mathbf{u}|^2 + \dots , \quad (17)$$

If we consider the one-phonon process for the relaxation mechanism,<sup>2</sup> Eq. (17) transforms to<sup>2</sup>

$$\Delta V = \left[ \frac{2}{Nm} \right]^{1/2} (V^{(1)} + V^{(2)} A \cos\varphi) \sum_k [P_{Ak}(t) \cos\varphi + P_{\phi k}(t) \sin\varphi] , \quad (18)$$

where  $N$  is the number of unit cells,  $m$  is the mass of the Cl atom, and  $P_{Ak}, P_{\phi k}$  are the amplitude and Goldstone mode operators. In this case for the spectral density we get<sup>2</sup>

$$J^Q = \text{const} |V^{(1)} + V^{(2)} A \cos\varphi|^2 (\cos^2\varphi J_A + \sin^2\varphi J_\phi) . \quad (19)$$

Here  $J_A$  and  $J_\phi$  are the spectral densities for the amplitude and phase fluctuations which in the PWM can be set equal to

$$J_\beta = \frac{K \Gamma_\beta}{\Delta_\beta} , \quad \beta = A, \phi \quad (20)$$

where  $K$  is a constant,  $\Delta_\beta$  the Goldstone mode–amplitude mode energy gap, and  $\Gamma_\beta$  is the damping constant.

With the help of Eqs. (16) and (21) for  $(J_{\pm\mu}^Q)$

$$\begin{aligned} J_{(\pm 1)}^Q &= \int_{-\infty}^{\infty} \overline{[\Delta V_{xz}(0) + i\Delta V_{yz}(0)][\Delta V_{xz}(t) - i\Delta V_{yz}(t)]} e^{\pm i\omega t} dt \\ &= \int_{-\infty}^{\infty} \overline{\Delta V_{xz}(0) \Delta V_{xz}(t)} e^{\pm i\omega t} dt + \int_{-\infty}^{\infty} \overline{\Delta V_{yz}(0) \Delta V_{yz}(t)} e^{\pm i\omega t} dt , \end{aligned} \quad (21a)$$

$$\begin{aligned} J_{(\pm 2)}^Q &= \int_{-\infty}^{\infty} \overline{\frac{1}{4} [\Delta V_{xx}(0) - \Delta V_{yy}(0) + i\Delta V_{xy}(0)][\Delta V_{xx}(t) - \Delta V_{yy}(t) - i\Delta V_{xy}(t)]} e^{\pm i\omega t} dt \\ &= \frac{1}{4} \int_{-\infty}^{\infty} \overline{\Delta V_{xx}(0) \Delta V_{xx}(t)} e^{\pm i\omega t} dt + \frac{1}{4} \int_{-\infty}^{\infty} \overline{\Delta V_{yy}(0) \Delta V_{yy}(t)} e^{\pm i\omega t} dt + \frac{1}{4} \int_{-\infty}^{\infty} \overline{\Delta V_{xy}(0) \Delta V_{xy}(t)} e^{\pm i\omega t} dt , \end{aligned} \quad (21b)$$

we get, finally, for the quadrupolar contributions to the spin-spin relaxation time  $T_2$ ,

$$\begin{aligned} \frac{1}{T_2^Q} &= 12E^2 \left\{ \frac{1}{4} (V_{zz}^{(2)} A \cos\varphi)^2 + \frac{1}{4} [(V_{xx}^{(2)} A \cos\varphi)^2 + (V_{yy}^{(2)} A \cos\varphi)^2] \right. \\ &\quad \left. + (V_{xz}^{(2)} A \cos\varphi)^2 + (V_{xy}^{(1)})^2 + (V_{yz}^{(1)})^2 \right\} (\cos^2\varphi J_A + \sin^2\varphi J_\phi) . \end{aligned} \quad (22)$$

## B. The dipolar contribution

We have three different dipolar contributions to the spin-spin relaxation at the Cl(1) site, from the Cl(2), Cl(3), and Cl(4) neighbors of the  $\text{ZnCl}_4$  tetrahedra (Zn has a zero dipole moment). The dipolar part of the perturbing Hamiltonian  $\mathcal{H}_1$  thus takes the form

$$\mathcal{H}_1^D(t) = \mathcal{H}_1^D(1,2)(t) + \mathcal{H}_1^D(1,3)(t) + \mathcal{H}_1^D(1,4)(t) , \quad (23)$$

where, according to Eq. (1c),

$$\begin{aligned}
\mathcal{H}_1^D(1,i)(t) = & -\frac{3}{2}\gamma^2\hbar^2\left(\left[\frac{2}{3}I_z^{(1)}I_z^{(i)} + \frac{1}{6}(I_+^{(1)}I_-^{(i)} + I_-^{(1)}I_+^{(i)})\right]\Delta F_{zz}(1,i)(t) + (I_z^{(1)}I_+^{(i)} + I_+^{(1)}I_z^{(i)})[\Delta F_{zx}^{(1,i)}(t) - i\Delta F_{zy}(1,i)(t)] \right. \\
& + (I_z^{(1)}I_-^{(i)} + I_-^{(1)}I_z^{(i)})[\Delta F_{zx}(1,i)(t) + i\Delta F_{zy}(1,i)(t)] \\
& + I_+^{(1)}I_+^{(i)}\{\Delta F_{xx}(1,i)(t) - \Delta F_{yy}(1,i)(t)\} - 2i\Delta F_{xy}(1,i)(t)\} \\
& \left. + I_-^{(1)}I_-^{(i)}\{\Delta F_{xx}(1,i)(t) - \Delta F_{yy}(1,i)(t)\} + 2i\Delta F_{xy}(1,i)(t)\}, \quad i=2,3,4 \quad (24)
\end{aligned}$$

and  $\Delta F(t) = F(t) - \bar{F}$ .

In the  $P$  phase, taking into account that the Cl(1) and Cl(2) nuclei lie approximately on the  $xz$  plane, which passes through the axis origin (0,0,0) at Cl(1),<sup>9</sup> from relation (1d), we see that  $F_{xy}(1,2) = F_{yx}(1,2) = F_{zy}(1,2) = F_{yz}(1,2) = F_{yy}(1,2) = 0$  so that

$$F_{(1,2)}^{(P)} \begin{vmatrix} F_{xx}^{(0)}(1,2) & 0 & F_{xz}^{(0)}(1,2) \\ 0 & 0 & 0 \\ F_{xz}^{(0)}(1,2) & 0 & F_{zz}^{(0)}(1,2) \end{vmatrix}. \quad (25)$$

Below  $T_I$  in the  $I$  phase, due to the fact that the frozen-in nuclear displacements takes place in the  $y$  direction, we see that  $F(1,2)(\varphi) = -F(1,2)(\varphi + \pi)$  for the  $xy, yz$  elements, and  $F(1,2)(\varphi) = F(1,2)(\varphi + \pi)$  for the rest of the elements. If we develop the tensor  $F(1,2)$  in powers of the nuclear displacements  $u[\varphi(z)]$  around the value  $F^{(0)}$  we get an expression similar to relation (10):

$$\begin{aligned}
F^{(I)}(1,2) = & \begin{vmatrix} F_{xx}^{(0)}(1,2) & 0 & F_{xz}^{(0)}(1,2) \\ 0 & 0 & 0 \\ F_{xz}^{(0)}(1,2) & 0 & F_{zz}^{(0)}(1,2) \end{vmatrix} + \begin{vmatrix} 0 & F_{xy}^{(1)}(1,2) & 0 \\ F_{xy}^{(1)}(1,2) & 0 & F_{yz}^{(1)}(1,2) \\ 0 & F_{yz}^{(1)}(1,2) & 0 \end{vmatrix} A \cos\varphi \\
& + \begin{vmatrix} F_{xx}^{(2)}(1,2) & 0 & F_{xz}^{(2)}(1,2) \\ 0 & F_{yy}^{(2)}(1,2) & 0 \\ F_{xz}^{(2)}(1,2) & 0 & F_{zz}^{(2)}(1,2) \end{vmatrix} A^2 \cos^2\varphi. \quad (26)
\end{aligned}$$

For the Cl(1)-Cl(3) and Cl(1)-Cl(4) dipolar interactions, which do not lie on the  $xz$  plane, all the tensor elements in the expansion are different from zero:

$$F_{ij}^{(I)}(1,n) = F_{ij}^{(0)}(1,n) + F_{ij}^{(1)}(1,n) A \cos\varphi + F_{ij}^{(2)}(1,n) A^2 \cos^2\varphi, \quad (27)$$

where  $i, j = x, y, z$  and  $n = 3, 4$ .

According to relations (4) and (5), for each one of the three different dipolar contributions Cl(1)-Cl(2), Cl(1)-Cl(3), and Cl(1)-Cl(4), we get

$$\frac{1}{T_2^D(1,i)} = \frac{1}{4}\gamma^4\hbar^2 \int_{-\infty}^{+\infty} \overline{\Delta F_{zz}(1,i)(t)\Delta F_{zz}(1,i)(0)} dt = \frac{1}{4}\gamma^4\hbar^2 J_{(0)}^D(1,i), \quad (28)$$

$$\frac{1}{\tau_{3/2}^D(1,i)} = \frac{3}{2}\gamma^4\hbar^2 \int_{-\infty}^{+\infty} e^{i\omega t} \overline{[\Delta F_{zx}(1,i)(t) + i\Delta F_{zy}(1,i)(t)][\Delta F_{zx}(1,i)(0) - i\Delta F_{zy}(1,i)(0)]} dt = \frac{3}{2}\gamma^4\hbar^2 J_{(1)}^D(1,i), \quad (29a)$$

$$\frac{1}{\tau_{1/2}^D(1,i)} = \frac{3}{2}\gamma^4\hbar^2 \int_{-\infty}^{+\infty} e^{-i\omega t} \overline{[\Delta F_{zx}(1,i)(t) + i\Delta F_{zy}(1,i)(t)][\Delta F_{zx}(1,i)(0) - i\Delta F_{zy}(1,i)(0)]} dt = \frac{3}{2}\gamma^4\hbar^2 J_{(-1)}^D(1,i), \quad (29b)$$

where  $i = 2, 3, 4$ .

Using similar reasoning to that which leads to relation (19), we see that

$$J^D(1,i) = \text{const} |F^{(1)}(1,i) + F^{(2)}(1,i) A \cos\varphi|^2 (\cos^2\varphi J_A + \sin^2\varphi J_\phi). \quad (30)$$

Finally, if we take into consideration the dipolar contribution to the spin-spin relaxation mechanism from all the Cl neighbors, the dipolar spin-spin relaxation rate can be expressed as

$$\begin{aligned}
\frac{1}{T_2^D} = & \frac{1}{4}\gamma^4\hbar^2 \{ [F_{zz}^{(2)}(1,2) A \cos\varphi]^2 + [F_{zz}^{(1)}(1,3) + F_{zz}^{(2)}(1,3) A \cos\varphi]^2 \\
& + [F_{zz}^{(1)}(1,4) + F_{zz}^{(2)}(1,4) A \cos\varphi]^2 + 6\{ [F_{xz}^{(2)}(1,2) A \cos\varphi]^2 + [F_{yz}^{(1)}(1,2)]^2 \} \\
& + 6\{ [F_{xz}^{(1)}(1,3) + F_{xz}^{(2)}(1,3) A \cos\varphi]^2 + [F_{yz}^{(1)}(1,3) + F_{yz}^{(2)}(1,3) A \cos\varphi]^2 \} \\
& + 6\{ [F_{xz}^{(1)}(1,4) + F_{xz}^{(2)}(1,4) A \cos\varphi]^2 + [F_{yz}^{(1)}(1,4) + F_{yz}^{(2)}(1,4) A \cos\varphi]^2 \} \} (\cos^2\varphi J_A + \sin^2\varphi J_\phi). \quad (31)
\end{aligned}$$

Going back to the expression for the total spin-spin relaxation rate and using relations (8), (22), and (31) we finally have

$$\frac{1}{T_2} = (C_0 + C_1 A \cos\varphi + C_2 A^2 \cos^2\varphi)(\cos^2\varphi J_A + \sin^2\varphi J_\phi), \quad (32)$$

where  $C_0$ ,  $C_1$ , and  $C_2$  are constants depending on the components of the two tensors  $V$  and  $F$  [Eqs. (9), (10), (25), and (26)]. Keeping in mind the results obtained for the spin-lattice relaxation time  $T_1$  (Refs. 1 and 2), we may conclude that the spin-spin relaxation time  $T_2$  in the  $I$  region  $T_c < T < T_I$  behaves in a similar way to the spin-lattice relaxation time  $T_1$ . We know that the edge singularity  $\nu_\phi$  of the inhomogeneous spectrum that corresponds to  $\cos\phi=0$  is relaxing by phase fluctuations of the modulation wave and the edge singularities  $\nu_A$ , where  $|\cos\varphi|=1$  are relaxing mainly by amplitude fluctuations of the modulation wave.<sup>1,3</sup> According to relations (20) and (32) we get the following expression for the spin-spin relaxation rate  $1/T_2$  at the  $\nu_\phi(1/T_{2\phi})$  and  $\nu_A(1/T_{2A})$  edge singularities separately:

$$\frac{1}{T_{2\phi}} = C_0 \frac{K\Gamma_\phi}{\Delta_\phi}, \quad (33a)$$

$$\frac{1}{T_{2A}} = (C_0 + C_1 A + C_2 A^2) \frac{K\Gamma_A}{\Delta_A}. \quad (33b)$$

The phason gap  $\Delta_\phi$  for a pure system without impurities is in the PWM temperature independent,<sup>13</sup> therefore, according to relation (34a), we expect that the  $T_{2\phi}$  will also be temperature independent. Near the critical temperature  $T_c$ , this model starts to break down, and the phason-induced spin-spin relaxation time  $T_{2\phi}$  becomes temperature dependent.<sup>1,5</sup> In a similar way, since  $\Delta_A = [2a(T_I - T)]^{1/2}$ , where  $a$  is a constant, we may say that the amplitude mode-induced spin-spin relaxation time  $T_{2A}$  will be temperature dependent.

### III. EXPERIMENTAL RESULTS AND DISCUSSION

All experimental work was performed on a pulsed NQR spectrometer with a coherent pulse technique based on the storage of the free-induction decay (FID) signals and Fourier transformation. The spin-spin relaxation time was measured using the  $\pi/2 - \tau - \pi$  Hahn pulse sequence. Single crystals were grown by slow evaporation of an aqueous solution of  $\text{RbCl}$  and  $\text{ZnCl}_2$  in a 2:1 molar mixture. The samples were cooled or heated in a specially constructed oven and the temperature stabilization was  $\approx 0.1$  K. Figure 1 shows the data at the edge singularities  $\nu_A$  and  $\nu_\phi$ . According to this theoretical treatment the relaxation process is governed mainly by amplitude modes for an edge singularity  $\nu_A$  and by Goldstone modes for the singularity  $\nu_\phi$ .<sup>1,3</sup> The measurements were made for only one Cl site, namely, the one with the highest NQR frequency, on a nominally pure single crystal of  $\text{Rb}_2\text{ZnCl}_4$ . This choice was made because the quasicontinuous  $I$  spectrum covers only a range of 100

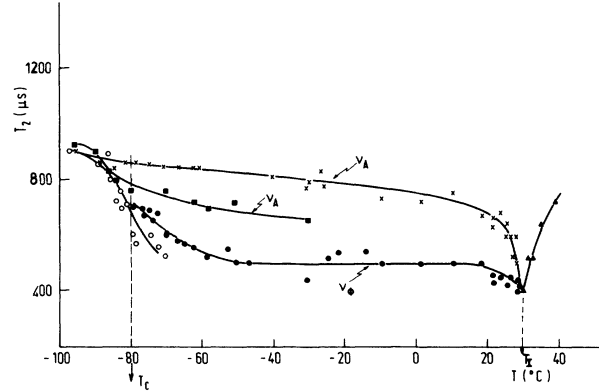


FIG. 1. Temperature dependence of the  $^{35}\text{Cl}$  spin-spin relaxation time  $T_2$  in the  $P$ ,  $I$  and  $C$  phase of  $\text{Rb}_2\text{ZnCl}_4$  at the singularities  $\nu_\phi$  (●) and  $\nu_A$  [(×) and (■)]. Measurements were also made on the commensurate (soliton)  $\nu_c$  line (○).

kHz and not 500 kHz as for the other lines and gives a higher signal-to-noise ratio.<sup>3</sup> For the sake of comparison and in order to have consistent results, the  $T_1$  measurements were repeated for this crystal.

As we can see from Fig. 1,  $T_2$  shows exactly the same behavior as  $T_1$  (Fig. 2) for the same nuclear site and when measured on the same edge singularities.<sup>3</sup> This is also in agreement with the  $T_2$  measurements, which have been made in  $\text{Rb}_2\text{ZnBr}_4$  and  $\text{Cs}_2\text{HgBr}_4$ .<sup>4</sup> As expected,  $T_2$  rapidly decreases and produces a sharp  $T_2$  minimum at  $T_I$ . In the  $I$  phase the relaxation times could be easily separated and observed at the different edge singularities. (i) At the  $\nu_\phi$  edge singularity,  $T_2$  stays short and temperature independent, in agreement with the  $T_1$  measurements. Close to the transition temperature  $T_c$ ,  $T_2$  becomes temperature dependent and increases in the region where the formation of the soliton lattice starts to become observable and the phason excitation spectrum splits into an acousticlike and opticlike branch.<sup>1,3</sup> This

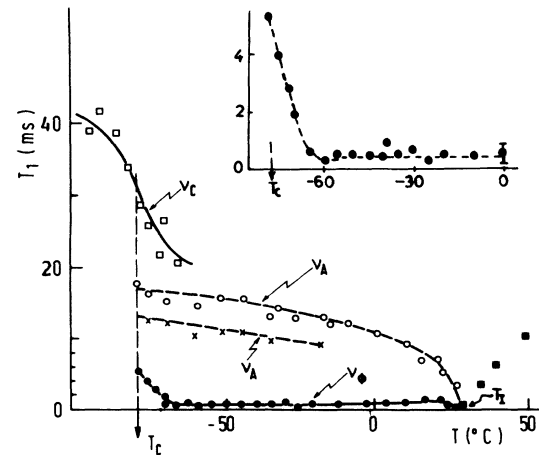


FIG. 2. Temperature dependence of the  $^{35}\text{Cl}$  spin lattice relaxation time  $T_1$  in the  $P$ ,  $I$ , and  $C$  phase of  $\text{Rb}_2\text{ZnCl}_4$  at different edge singularities (from Ref. 3).

singularity stops as predicted at  $T_c$ . (ii) For the amplitude mode relaxing edge singularities  $\nu_A$ ,  $T_2$  increases with decreasing temperature over the whole  $I$  region, as expected, and goes through  $T_c$  without any discontinuity. This, we believe, means that commensurate lines that appear in the multisoliton lattice region coincide with the edge singularities.<sup>3</sup> (iii)  $T_2$  of the commensurate ferroelectric line, which starts around the same temperature at which the Goldstone mode  $T_2$  starts to increase, shows the onset of the soliton region. This commensurate line passes through  $T_c$  in exactly the same way as  $T_1$ , measured on the same line, without any discontinuity. This line belongs to the opticlike branch of the Goldstone mode.<sup>1,3</sup>

We see that the theoretical model agrees very well with the experimental results and describes accurately the spin-spin relaxation process. Here we want to make the following remark. The spin-lattice relaxation time  $T_1$  is known to be given by the relation<sup>8</sup>

$$1/T_1 = 2(W_1 + W_2), \quad (34)$$

$$\frac{1}{T_2^{D'}} = \frac{1}{4}\gamma^4\hbar^2\{[F_{zz}^{(2)}(1,2)A \cos\varphi]^2 + [F_{zz}^{(1)}(1,3) + F_{zz}^{(2)}(1,3)A \cos\varphi]^2 + [F_{zz}^{(1)}(1,4) + F_{zz}^{(2)}(1,4)A \cos\varphi]^2\}(\cos^2\varphi J_A + \sin^2\varphi J_\phi). \quad (38b)$$

For the edge singularity  $\nu_\phi$ , we know that  $\cos\varphi=0$ , and since  $1/T_2^{Q'}=0$  in this case, relation (37) becomes

$$\frac{1}{T_{2\phi}} = \frac{1}{T_{2\phi}^{D'}} + \frac{1}{2T_{1\phi}}. \quad (39)$$

If we compare our experimental results for  $T_{1\phi}$  and  $T_{2\phi}$  we see that in the  $I$  region, close to the transition temperature  $T_I$ ,

$$\frac{T_{1\phi}}{T_{2\phi}} \cong 1 \quad (40)$$

so that

$$\frac{1}{T_{2\phi}^{D'}} = \frac{1}{2T_{2\phi}}, \quad (41)$$

which shows that the dipolar contribution at this edge singularity is at least of equal importance as the quadrupolar contribution. This looks reasonable if we take into consideration the following. (i) The main contribution to the EFG tensor  $V$  probably comes from the neighboring Zn ion and, since the Zn-Cl(1) bond lies on the  $z$  axis,<sup>9</sup> the dominant EFG tensor element is  $V_{zz}$  and  $V_{xy}$ ,  $V_{yz}$  are correspondingly small. Therefore, the quadrupolar contribution to the spin-spin relaxation rate of the  $\nu_\phi$  edge singularity is small according to relation (22). (ii) The

where  $W_1$ , and  $W_2$  are the transition probabilities for the different eigenstates; for a <sup>35</sup>Cl nucleus we have

$$2(W_1 + W_2) = \left[ \frac{1}{\tau_a} + \frac{1}{\tau_b} \right] \quad (35)$$

so that

$$\frac{1}{T_1} = \left[ \frac{1}{\tau_a} + \frac{1}{\tau_b} \right]. \quad (36)$$

According to relations (3), (8), and (36) we have

$$\frac{1}{T_2} = \frac{1}{T_2^{Q'}} + \frac{1}{T_2^{D'}} + \frac{1}{2T_1}, \quad (37)$$

where, with the help of relations (12), (18), and (22),

$$\frac{1}{T_2^{Q'}} = 3E^2(V_{zz}^{(2)}A \cos\varphi)^2(\cos^2\varphi J_A + \sin^2\varphi J_\phi), \quad (38a)$$

and relations (28) and (31)

distance  $r$  between the Cl(1) and Cl(2), Cl(3), Cl(4) neighbors has a larger  $z$  component so that the  $F_{zz}$  tensor element is much larger than the rest of the elements. From this discussion and relations (22) and (31), we see that for the edge singularity  $\nu_\phi$ , the relaxation mechanism is governed mainly by the dipolar interaction. For the amplitude mode at the  $\nu_A$  singularities, where the EFG tensor elements  $V_{zz}$  take part in the calculation, the relaxation mechanism is governed mainly by the quadrupolar interaction. A comparison between a rough estimate of both tensor elements,  $V'_{zz} = e^2QV_{zz} \cong 8e^2Q/\hbar r^3$  and  $F'_{zz} = \gamma^2\hbar F_{zz} \cong \gamma^2\hbar/r^3$ , shows that

$$\frac{V'_{zz}}{F'_{zz}} \cong \frac{24 \times 10^4}{10^3} = 240. \quad (42)$$

Since the tensor elements appear in the spin-spin relaxation rate formula to the second power, we see that the  $\nu_A$  edge singularity is relaxing almost solely through the quadrupolar interaction.

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