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^{35}Cl spin-lattice relaxation in incommensurate bis(4-chlorophenyl)sulfone

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The ^{35}Cl nuclear-quadrupole-resonance (NQR) spin-lattice relaxation rate in incommensurate bis(4-chlorophenyl)sulfone (BCPS) is determined by Raman processes below 60 K and by direct one-phonon processes above 60 K. The variation of the ^{35}Cl spin-lattice relaxation rate over the incommensurate NQR frequency distribution in BCPS has been also measured at various temperatures. The results are explained in terms of phason and amplitudon contributions to the effective spin-lattice relaxation rate. In contrast to Rb_2ZnCl_4-type crystals the changes in the Cl electric-field-gradient tensor produced by modulation wave fluctuations contain both first- and second-derivative terms.

The theory of incommensurate (I) systems predicts[1] that the soft mode of the high-temperature phase splits in the I phase into an acousticlike phason branch and an opticlike amplitudon branch. Experimental evidence for the existence of phasons and amplitudons in I systems has been obtained from NQR and NMR,[2,3] neutron scattering,[3,4] and Raman data.[3,5] Amplitudon and phason fluctuations contribute differently[2,3] to the spin-lattice relaxation rate at different parts of the inhomogeneous NMR or NQR line $f(\nu)$ thus allowing for a separate determination of the phason and amplitudon local spectral densities. Although the variation of the effective spin-lattice relaxation rate T_1^{-1} over the NMR line is one of the characteristic features of an I phase, relatively few quantitative studies[2,3] of this effect have been performed. Here we report on the variation of the effective ^{35}Cl NQR T_1^{-1} over the incommensurate frequency distribution $f(\nu)$ in bis(4-chlorophenyl)sulfone (BCPS), which is one of the few I systems which does not exhibit a low-temperature commensurate phase and where the I phase is known[6,7] to persist from $T_I = 150$ K down to the lowest temperatures investigated.

The rather broad NQR spectrum was measured point by point with the help of "soft" frequency selective pulses by observing the spin-echo amplitude in steps of 10 kHz while automatically retuning the probe at each frequency. The variation of the T_1 over the NQR line was measured by the same technique using the spin-echo inversion-recovery method: 180°-t-90°-τ-180°-τ-echo.

The variation of the effective ^{35}Cl T_1 over the NQR frequency distribution $f(\nu)$ at 90 K is shown in Fig. 1(a). It is of a form which has not been observed in other systems, and is rather different from that found in Rb_2ZnCl_4 and other A_2BX_4 compounds.[2,3] T_1 is long at the high-frequency singularity, decreases to a minimum near the center of the line, and then increases to a maximum between the second and third singularity. It decreases again on approaching the third low-frequency singularity.

At 140 K, on the other hand, the ^{35}Cl NQR line shape is bell shaped and T_1 hardly varies over the line. From the high-frequency side to the low-frequency side it decreases only by about 10% [Fig. 1(b)].

The line shape $f(\nu)$ at 90 K is characterized by the presence of three singularities $\nu_{(a)}$, $\nu_{(b)}$, and $\nu_{(c)}$ as expected for the case[2,3] where the expansion of the nuclear quadrupole resonance (NQR) frequency shift $\nu(x)-\nu_0$ in powers of the nuclear displacement induced by the I modulation wave $u(x)=A\cos\varphi(x)$ contains both linear and quadratic terms:

$$\nu(x)=\nu_0+a_1u(x)+a_2u^2(x). \tag{1a}$$

Equation (1a) can be rewritten as

$$\nu(x)=\nu_0+\nu_1\cos\varphi(x)+\nu_2\cos^2\varphi(x), \tag{1b}$$

where $\nu_1=a_1A \propto (T_I-T)^\beta$ and $\nu_2=a_2A^2 \propto (T_I-T)^{2\beta}$. The NQR frequency distribution $f(\nu)$ is here obtained[3] as

$$f(\nu)=\frac{c}{d\nu/dx}=\frac{\text{const}}{|\sin\varphi[\nu_1+2\nu_2\cos\varphi]|}, \tag{2a}$$

if $d\varphi/dx=$const. Two singularities appear when $\sin\varphi=0$, that is, when $\cos\varphi=\pm1$ and therefore

$$\nu_{(a,b)}=\nu_0\pm\nu_1+\nu_2. \tag{2b}$$

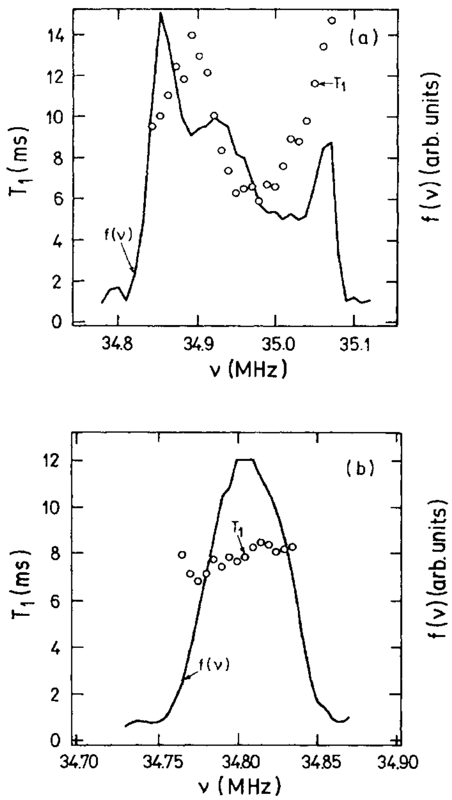

FIG. 1. (a) Variation of ^{35}Cl NQR T_1 over the inhomogeneous ^{35}Cl NQR line $f(\nu)$ in incommensurate BCPS at 90 K. The experimental NQR line shape can be described by expressions (2a)–(2d) with $\nu_2 \approx 2\nu_1$. (b) Variation of the ^{35}Cl NQR T_1 over the NQR line shape in incommensurate BCPS at 140 K.

The third singularity appears when $\nu_1 + 2\nu_2 \cos\varphi = 0$, that is, when

$$\nu_{(c)} = \nu_0 - \nu_1^2/(4\nu_2). \tag{2c}$$

If $\nu_a \leq \nu \leq \nu_b$, only the positive root of

$$X_\pm = \cos\varphi_\pm = \left[-\nu_1 \pm \sqrt{\nu_1^2 + 4(\nu - \nu_0)\nu_2} \right] / (2\nu_2) \tag{2d}$$

has to be taken into account, whereas for $\nu_b \leq \nu \leq \nu_c$ both X_+ and X_- contribute to $f(\nu)$.

The variation of T_1 over $f(\nu)$ is produced[2,3] by electric-field-gradient (EFG) tensor fluctuations induced by thermal fluctuations of the modulation wave:

$$u(x,t) = u_0(x) + \delta u(x,t), \tag{3a}$$

where

$$\delta u(x,t) = \delta A(x,t)\cos\varphi - A\,\sin\varphi\,\delta\varphi(x,t). \tag{3b}$$

For direct one-phonon processes the linear term[2,3] in the expansion of the EFG tensor T in powers of $\delta u(x,t)$ is important and after a Fourier series expansion we get[2,3,8]

$$\Delta T_1^{(n)}(t) = \frac{1}{\sqrt{2Nm_i}} \Bigg\{ [T_{01}^{(n)}\cos\varphi + T_{02}^{(n)}\cos^2\varphi] \sum_k [P(t)_{A,k} + P(t)_{A,-k}] - [T_{01}^{(n)}\sin\varphi + T_{02}^{(n)}\sin\varphi\,\cos\varphi] \sum_k [P(t)_{P,k} + P(t)_{P,-k}] \Bigg\}. \tag{4a}$$

Here $P(t)_{A,\pm k}$ and $P(t)_{P,\pm k}$ are phason and amplitudon operators, m_i is the mass of the ith nucleus, and N is the number of unit cells. $T_{01}^{(n)}$ and $T_{02}^{(n)}$ characterize the dependence of the EFG tensor on the modulation wave

$$T_{01}^{(n)} = \sum_i \left(\frac{\partial T}{\partial \bar{u}_i} \right)_0, \quad T_{02}^{(n)} = \sum_{i,j} \left(\frac{\partial^2 T}{\partial \bar{u}_i \partial \bar{u}_j} \right)_0. \tag{4b}$$

The effective spin-lattice relaxation rate T_1^{-1} is now obtained from the transition probabilities

$$W^{(n)} = \sum_m \frac{F^2}{\hbar^2} J^{(n)}(\omega) |\langle m|D|m+n\rangle|^2 \tag{4c}$$

since $T_1^{-1} = W^{(1)} + W^{(2)}$. Here $F = e^2Q/4I(2I-1)$, $D^{(\pm 1)} = I_z I_\pm + I_\pm I_z$, and $D^{(\pm 2)} = I_\pm^2$ whereas $J^{(n)}(\omega)$ describes the local spectral densities of the EFG tensor fluctuations

$$J^n(\omega) = \int_{-\infty}^{+\infty} \overline{\Delta T_1^{(n)}(0) \Delta T_1^{(n)}(t)} e^{i\omega t} dt. \tag{4d}$$

$J^{(n)}(\omega)$ contains quantities

$$J_A(\omega) = \int_{-\infty}^{+\infty} \sum_k \overline{P_{Ak}(0) P_{Ak}^*(t)} e^{i\omega t} dt \tag{5a}$$

and

$$J_\phi(\omega) = \int_{-\infty}^{+\infty} \sum_k \overline{P_{\phi k}(0) P_{\phi k}^*(t)} e^{i\omega t} dt, \tag{5b}$$

which are, respectively, proportional to T_{1A}^{-1} and $T_{1\phi}^{-1}$ (i.e., the amplitudon and phason contributions to the effective spin-lattice relaxation rate T_1^{-1}). The values of $\cos\varphi$ and $\sin\varphi$ occurring in expression (4a) have to be determined from expressions (1b) and (2d).

When the "first derivative" term is dominant, $T_{01}^{(n)} \neq 0$, $T_{02}^{(n)} = 0$, the variation of T_1^{-1} over the NQR spectrum is given by

$$T_1^{-1} = K[X^2 J_A + (1 - X^2) J_\phi], \tag{6}$$

where $X = \cos\varphi$ and K is proportional to (kT). This is the expression used to describe the variation of the ^{87}Rb T_1^{-1} in Rb_2ZnCl_4.[2,3] The application of Eq. (6) to the present case is shown in Fig. 2(a).

The situation is quite different for $T_{01}^{(n)} = 0$, $T_{02}^{(n)} \neq 0$ (i.e., for the case that the "second derivative" term is dominant). Here

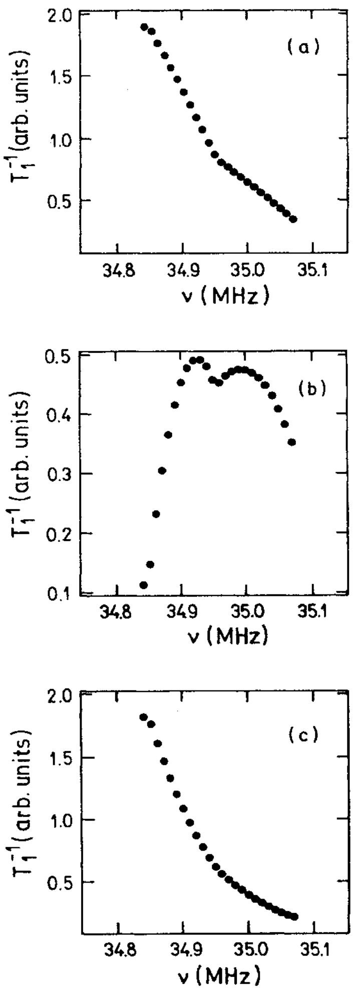

FIG. 2. (a) Calculated T_1^{-1} variation over $f(\nu)$ for direct processes and $T_{01}^{(n)} \neq 0$, $T_{02}^{(n)}=0$. (b) Calculated T_1^{-1} variation over $f(\nu)$ for direct processes and $T_{01}^{(n)}=0$, $T_{02}^{(n)} \neq 0$. (c) Calculated T_1^{-1} variation over $f(\nu)$ for Raman processes.

$$T_1^{-1}=\tilde{K}[X^4 J_A+(1-X^2)X^2 J_\phi], \tag{7}$$

and $\tilde{K}$ is again proportional to (kT). Here T_1^{-1} exhibits a maximum between ν_a and ν_b and then decreases down to ν_c [Fig. 2(b)].

The $T_{01}^{(n)}$ and $T_{02}^{(n)}$ contributions have thus opposite X (and thus frequency) dependencies. In contrast to the A_2BX_4 compounds,[2,3,8] the $T_{02}^{(n)}$ contribution here cannot be neglected. Thus competing effects of the $T_{01}^{(n)}$ and $T_{02}^{(n)}$ terms account for the fact that T_1 reaches a maximum between ν_b and ν_c and not at the edge singularities. The results show that, at 90 K, $T_{01}^{(n)}/T_{02}^{(n)} \simeq 0.5$ (provided that $T_{01}^{(1)} \simeq T_{01}^{(2)}$ and $T_{02}^{(1)} \simeq T_{02}^{(2)}$ as inferred from the line-shape fits where we find $\nu_2 \approx 2\nu_1$) and that $J_\phi/J_A=T_{1\phi}^{-1}/T_{1A}^{-1} \simeq 2.23$. The resulting fit is shown in Fig. 3(a).

The line shape at 140 K is dominated by the quadratic term, $\nu=\nu_0+\nu_2\cos^2\varphi(x)$, where $\nu_2=0.045$ MHz and $\nu_0=34.784$ MHz. The slight variation of T_1 over $f(\nu)$ can be

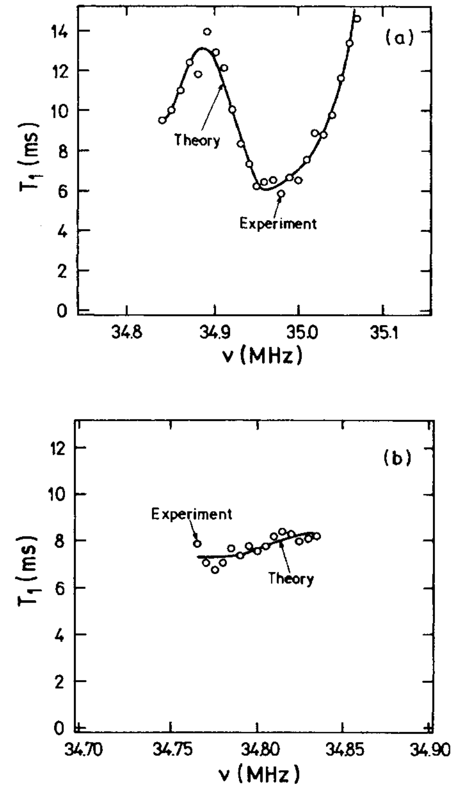

FIG. 3. (a) Comparison between the theoretical and the experimentally observed variation of the ^{35}Cl T_1 over the NQR line in BCPS at 90 K. (b) Comparison between the theoretical and experimentally observed variation of the ^{35}Cl T_1 over the NQR line in BCPS at 140 K.

here explained by direct one-phonon processes with $T_{01}^{(n)} \neq 0$, $T_{02}^{(n)}=0$. The fit [Fig. 3(b)] yields $J_\phi/J_A=T_{1\phi}^{-1}/T_{1A}^{-1}=1.14$, showing that the amplitudon gap is here only slightly larger than the phason gap. If we compare the above result with the one at 90 K, where $T_{1\phi}^{-1}/T_{1A}^{-1} \simeq 2.23$ we see

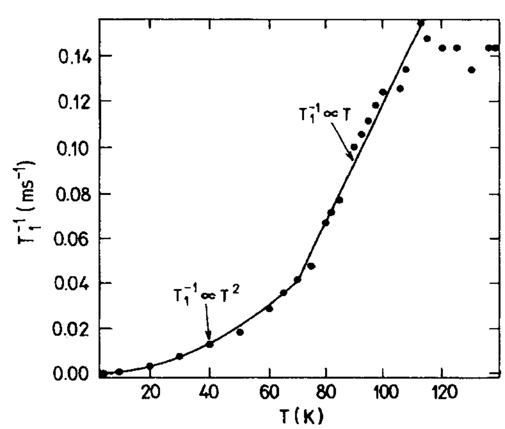

FIG. 4. ^{35}Cl NQR T_1^{-1} at the low-frequency edge singularity versus temperature in BCPS.

that the amplitudon gap indeed increases with decreasing T as expected.

In addition to direct one-phonon processes one should consider also Raman processes,[2,3,9] where the frequency differences of phason-phason, phason-amplitudon, and amplitudon-amplitudon modes with different wave vectors equal the quadrupolar level splitting. These processes are induced by the term

$$\Delta T_2^{(n)}(t)=\frac{1}{2}\sum_{i,j}\left(\frac{\partial^2 T}{\partial \bar{u}_i \partial \bar{u}_j}\right)_0 \delta\mathbf{u}_i \otimes \delta\mathbf{u}_j, \tag{8}$$

which is proportional to $T_{02}^{(n)}$ but is quadratic in the modulation wave displacements $\delta u(x,t)$.

The spin-transition probability $W^{(n)}$ is here proportional to $(kT)^2$ and to $|T_{02}^{(n)}|^2$. One finds[2,3,9]

$$T_1^{-1} \propto (kT)^2[X^4 J_{AA}+(1-X^2)^2 J_{\phi\phi} + X^2(1-X^2)(J_{A\phi}+J_{\phi A})], \tag{9}$$

where $X=\cos\varphi$ has to be determined from Eqs. (1b) and (2d).

The absence of a low-temperature commensurate phase and the wide temperature range over which the incommensurate phase in BCPS exists allow for a determination of the relative importance of the direct and Raman processes in the spin-lattice relaxation of ^{35}Cl nuclei. A plot T_1^{-1} versus T in Fig. 4 shows that Raman processes proportional to T^2 become important below 60 K. Between 70 and 110 K T_1^{-1} is proportional to T as expected for direct processes whereas between 110 and 140 K T_1^{-1} is nearly independent of T. This seems to show that the phason gap is not temperature independent but varies with temperature in a relatively complicated way. A similar temperature independence of T_1^{-1} at high temperatures—where direct processes are expected to dominate the nuclear spin lattice relaxation rate—has been also observed in incommensurate Rb_2ZnCl_4.[3] Further investigations are necessary to understand the microscopic nature of this effect.

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