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Impurity pinning and thermally excited collective motions in incommensurately modulated structures

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Abstract. Randomly quenched impurities pin the modulation wave of incommensurate (I) structures and prevent its free motion. However, rapid thermal fluctuations reduce the pinning frequency (or, in the case of structurally incommensurate insulators (SIIs) the phason gap Δ_φ), and they have a significant effect on the spin–lattice relaxation time T_1 and the NMR and NQR lineshapes. A T_1 and lineshape model is developed for the I phase of SIIs. This model, which includes impurity pinning and thermal fluctuations, is used to explain $^{35}Cl(1)$ T_1 and experimental lineshape data for a pure Rb_2ZnCl_4 crystal. The results indicate that, while the impurities are of a strong-pinning symmetry-breaking type very close to the paraelectric-to-incommensurate transition temperature T_I, thermal fluctuations significantly reduced the impurity-induced pinning.

1. Introduction

A collective phenomenon common to many modulated systems is the motion of the modulation wave under the influence of thermal fluctuations (random motion), and/or external force coupled to the order parameter (oriented motion). Examples of such systems are structurally incommensurate insulators (SIIs) (Blinc *et al* 1982, 1983, 1984, Kogoj *et al* 1984), charge-density-wave (CDW) systems (Fukuyama 1976, Lee and Rice 1979) and, in close similarity to them, flux line lattices (FLLs) in conventional (type II) and high-T_c superconductors (Nattermann 1990, Yeshurun and Malozemoff 1988). Other collective transport phenomena which are driven by a similar mechanism are the motion of the interface between two fluids in porous media (Bruinsma and Aeppli 1984, Stokes *et al* 1986), and the motion of domain walls in disordered magnets (Villain 1984). Clearly thermal fluctuations and impurity pinning are important factors which influence both random and oriented collective motions; thus understanding their contribution to the pinning–depinning mechanism of the modulation wave in simple systems such as one-dimensional SIIs, would be helpful in understanding collective motion in more complex systems.

The possible existence of a gapless phason (Goldstone) mode, which corresponds to the fluctuations of the phase of the modulation wave, is predicted by the continuum model theory of the I phases (Bruce and Cowley 1978). However, in real I structures the free motion of the modulation wave is prohibited, either by pinning to the discrete lattice (Bruce 1983, Papavassiliou *et al* 1991a), or by pinning to the randomly distributed impurities (Prelovsek 1988). This factor induces a finite gap Δ_φ in the phason spectrum. In such case, depinning effects should be initiated only by thermal fluctuations or external forces.

In SIIs the phason gap Δ_φ has been experimentally verified to lie within the frequency range $\Delta_\varphi \simeq 10^{10}$–$10^{12}$ s^{-1} (Blinc *et al* 1986b). Contrary to these observations, the

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incommensurate phase II of biphenyl shows a nearly gapless phason mode (Cailleau 1986). Recently, NMR (Blinc *et al* 1982, 1983, 1984, Kogoj *et al* 1984), NQR (Milia *et al* 1984, Papavassiliou *et al* 1991b) and EPR (Kaziba and Fayet 1986) experiments reported unexpected deviations in the frequency lineshape and in T_1 (the spin–lattice relaxation time) behaviour close to the transition temperature T_I. These effects could be attributed to thermally induced fluctuations of the phase of the modulation wave. On the other hand, the application of an external force leads to the appearance of new effects, such as the thermally assisted flux motion and flux creep of FLLs in high-T_c superconductors (Lan *et al* 1991), and phase creep in CDWs (Segransan *et al* 1986, McCarten *et al* 1991).

A critical role in all these kinetic effects seems to be played by the kinds of impurity and the impurity pinning. Randomly quenched impurities generally tend to destroy the long-range order by creating a random field which, in the case of SIIs is coupled to the local soft mode (Prelovsek 1988). The range of this short-range order seems to be too large to be directly observed by conventional neutron scattering and x-ray spectroscopy. At the same time the impurities induce random changes in the interaction constants which would alter T_I. It is not yet clear which effect dominates: the creation of random field or the change in the random constants.

Another point is to consider the pinning of the modulation wave on the impurities (Fukuyama and Lee 1978, Prelovsek 1988); strong pinning or weak pinning should lead to totally different behaviours. In the case of strong pinning, the impurity potential is locally maximized, and any one impurity can pin the modulation wave. In the case of weak pinning, no single impurity can pin the modulation wave, but rather a large number of impurities collectively enable pinning to occur.

In this paper a model is developed which takes into consideration the influence of the thermal fluctuations, the different kinds of impurity and the impurity pinning on the phason-induced spin–lattice relaxation time $T_{1\varphi}$. In an effort to understand the role of the thermal fluctuations and the impurities in the collective motion of condensed structures, this model is used in combination with lineshape calculations, to interpret the $^{35}Cl(1)$ NQR T_1 relaxation time and frequency linewidth data of a pure Rb_2ZnCl_4 crystal.

2. Theory

2.1. T_1 model

In the case of a SII and a pinned modulation wave, the displacement of a nucleus from its position in the paraphase can be described as

$$u(r, t) = u_0 \cos(q_s \cdot r) + \delta u(r, t) \tag{1}$$

where q_s is the wavevector of the I modulation, u_0 is the amplitude of the modulation wave given by $u_0 \propto (T_I - T)^\beta$, and $\beta \simeq \frac{1}{3}$ is the critical exponent of the amplitude of the I modulation wave, which is in agreement with the $d = 3$, $n = 2$ Heisenberg model (Bruce and Cowley 1978). The inclusion of thermal fluctuation is described in equation (1) by the very small, rapidly fluctuating part $\delta u(r, t)$. By decomposing this term into a phase-fluctuating term and an amplitude-fluctuating term, one obtains the familiar expression for the spin–lattice relaxation rate in I systems (Blinc *et al* 1986b):

$$T_1^{-1} \propto J_A \cos^2(q_s \cdot r) + J_\varphi \sin^2(q_s \cdot r). \tag{2}$$

J_A and J_φ are the spectral densities for the amplitude and phase fluctuations which in the plane-wave model limit are given by Blinc *et al* (1986b)

$$J_\beta = C\Gamma_\beta/\Delta_\beta \qquad \beta = \varphi, A. \tag{3}$$

Here, C is a constant proportional to the square of the fluctuating electric-field-gradient tensor components, Δ_β is the phason–amplitudon energy gap and Γ_β are the corresponding damping constants. The contributions of the amplitudon and phason fluctuations are thus, according to equation (2), 90° out of phase. If we take into consideration that the NMR and NQR frequency spectra of I systems are inhomogeneously distributed between two edge singularities, as given by

$$\nu(\phi, t) = \nu_0 + \alpha_1 u_0 \cos(q_s \cdot r) + \alpha_2 u_0^2 \cos^2(q_s \cdot r) \tag{4}$$

the phason contributions to the relaxation mechanism can be monitored at the positions of the spectra which are relaxing via a pure phason mechanism, corresponding to $\cos(q_s \cdot r) = 0$, whereas the amplitudon contributions can be monitored at the positions which are relaxing via a pure amplitudon mechanism, i.e. where $\sin(q_s \cdot r) = 0$.

Recent experimental and theoretical work on both the impurity (Blinc *et al* 1986a) and the discrete lattice pinning (Papavassiliou *et al* 1991a), have shown that the phason gap Δ_φ, close to T_I, is proportional to a relatively high power of the amplitude of the modulation wave u_0 and thus to the temperature ($u_0 \simeq T_I - T$ as referred to before). In the weak-impurity-pinning case for example,

$$\Delta_\varphi \propto |T_I - T|^{\beta(n-2)} \tag{5}$$

while, in the discrete-lattice-pinning case,

$$\Delta_\varphi^2 \propto |T_I - T|^{\beta(n-2)} \exp[-C/(T_I - T)^{2\beta}]. \tag{6}$$

Here n is the commensurability index, equal to the number of commensurate regions of the modulation wave with a phase equal to $2\pi/n$ (in the case of Rb_2ZnCl_4 which we study below, $n = 6$).

One may thus expect that, since Δ_φ decreases rapidly close to T_I, the thermally induced phase fluctuations play a significant role close to T_I. As a consequence, equation (1) is no longer a valid approximation, and the complete expression for the nuclear displacement must be used (Bruce and Cowley 1978):

$$u(r, t) = [u_0 + \delta u_0(r, t)] \cos[q_s \cdot r + \delta\phi(r, t)]. \tag{7}$$

The influence of the phase fluctuations of the modulation wave on the NMR and NQR frequency lineshapes has been evaluated for several models of the motion of the modulation wave (Blinc *et al* 1983, Kogoj *et al* 1984). A reasonable model is that phase fluctuations can be represented by standing waves within an average coherence volume V_c (Blinc *et al* 1982, 1984):

$$\begin{aligned} \delta\phi(r, t) &= \sum_k \delta\phi_k(r, t) \\ \delta\phi_k(r, t) &= \phi_{0_k} \sin(\omega_{\phi_k} t) \sin(k_x x) \sin(k_y y) \sin(k_z z). \end{aligned} \tag{8}$$

The coherence volume V_c must be defined differently in extreme cases of strong and weak pinning. In the strong-pinning regime, where the modulation wave can be assumed to be pinned by very strong impurities, and where the phase of the modulation wave in each segment between the pinning centres can fluctuate freely, the wave behaves much like a string with fixed ends. In this case, the coherence volume V_c is defined as $V_c \simeq 1/n_i$. In the second case, i.e. the weak-pinning regime, the system is assumed to separate into domains (Fukuyama and Lee 1978). Within each of these domains the impurity-induced phase distortion varies slowly, while it takes random values in different domains. This allows us to consider that the phase of the modulation wave is still fluctuating freely within each domain, and to identify the coherence volume V_c with the domain volume. Here (unlike the strong-pinning regime), V_c proves to be temperature dependent, according to the relation $V_c \simeq [1/(u_0^{2m-4} n_i)]^3$ (Prelovsek 1988).

Taking the above into consideration, the phason-induced spin–lattice relaxation time $T_{1\varphi}^{-1}$ can be calculated from

$$T_{1\varphi}^{-1} \propto J_\varphi(\omega) \propto \int_{-\infty}^{\infty} G_\varphi(t) \exp(i\omega t)\, dt \tag{9}$$

where $J_\varphi(\omega)$ is the spectral density of the phason-induced thermal fluctuations, and

$$G_\varphi(t) = u_0^2 \langle \cos[q_s \cdot r + \delta\phi(r,0)] \cos[q_s \cdot r + \delta\phi(r,t)] \rangle. \tag{10}$$

In a way similar to that discussed for equation (2), at the positions of a spectrum where $\cos(q_s \cdot r) = 0$ the excited $^{35}Cl(1)$ nuclei are still relaxing via a pure phason mechanism, and the autocorrelation function $G_\varphi(t)$ is for those spectral positions given by

$$\begin{aligned} G_\varphi(t) = u_0^2 \langle \sin[\delta\phi(r,0)] \sin[\delta\phi(r,t)] \rangle &= \tfrac{1}{4} u_0^2 [\![\langle \exp\{i[\delta\phi(r,0) - \delta\phi(r,t)]\} \rangle \\ &\quad - \langle \exp\{i[\delta\phi(r,0) + \delta\phi(r,t)]\} \rangle + \text{cc}]\!]. \end{aligned} \tag{11}$$

Using the Gaussian-averaging theorem (Baeriswyl and Bishop 1980) we obtain, after separating the diagonal terms,

$$\begin{aligned} G_\varphi(t) &= \tfrac{1}{2} u_0^2 [\![\exp\{-\tfrac{1}{2} \langle [\delta\phi(r,0) - \delta\phi(r,t)]^2 \rangle\} - \exp\{-\tfrac{1}{2} \langle [\delta\phi(r,0) + \delta\phi(r,t)]^2 \rangle\}]\!] \\ &= \tfrac{1}{2} u_0^2 \exp[-\tfrac{1}{2} \{ \langle \delta^2\phi(r,0) \rangle + \langle \delta^2\phi(r,t) \rangle \}] \{ \exp[\langle \delta\phi(r,0)\, \delta\phi(r,t) \rangle] \\ &\quad - \exp[-\langle \delta\phi(r,0)\, \delta\phi(r,t) \rangle] \} \end{aligned} \tag{12}$$

where we can define $\langle \delta^2\phi(r,0) \rangle$ and $\langle \delta^2\phi(r,t) \rangle$ with the help of (8) as

$$\langle \delta^2\phi(r,0) \rangle = \langle \delta^2\phi(r,t) \rangle = \sum_k \frac{\langle \phi_{0k}^2 \rangle}{16} \propto \frac{1}{V_c u_0^2} \sum_k \frac{1}{\omega_{\phi_k}^2}. \tag{13}$$

From (12) we observe that the autocorrelation function decays to zero (as it should do) for $t \to \infty$, because the term $\exp[\langle \delta\phi(r,0)\, \delta\phi(r,t) \rangle] - \exp[-\langle \delta\phi(r,0)\, \delta\phi(r,t) \rangle] \to 0$ when $\langle \delta\phi(t)\, \delta\phi(0) \rangle \to 0$. The last step of equation (13) has been calculated by applying the equipartition theorem after summing over all nuclei (Blinc *et al* 1984). If we take into consideration that (Blinc 1986b)

$$\omega_{\varphi k}^2 = \Delta_\varphi^2 + \kappa k^2$$

$$k = q - q_s \qquad \kappa = \text{constant}$$

we obtain, by replacing the summation over k by an integration up to a cut-off frequency Λ,

$$\frac{1}{V_c u_0^2}\frac{V}{2\pi}\int_0^{\Lambda}\frac{k^2\,dk}{\Delta_\varphi^2+\kappa k^2}=\frac{V\Lambda}{2\pi\kappa V_c u_0^2}[1-\epsilon(T)] \tag{14}$$

$$\epsilon(T)=[\Delta_\varphi(T)/\kappa^{1/2}\Lambda]\tan^{-1}[\kappa^{1/2}\Lambda/\Delta_\varphi(T)]. \tag{15}$$

Equation (13) can be put, with the help of equations (14) and (15), in the more convenient form

$$\langle\delta^2\phi(r,0)\rangle=\langle\delta^2\phi(r,t)\rangle=\alpha(T)/V_c u_0^2 \tag{16}$$

where the parameter $\alpha(T)\propto 1-\epsilon(T)$ is a measure of the influence of the thermal fluctuations. In the case where thermal fluctuations play a significant role, and the phason gap is small, the thermal-fluctuations parameter $\alpha(T)\neq 0$. However, in the case of very small thermal fluctuations and high Δ_φ-values ($\Delta_\varphi\gg\kappa^{1/2}\Lambda$) we obtain $\sum_k 1/\omega_{\varphi_k}^2\simeq 0$ and thus $\alpha(T)=0$.

Equation (12) thus becomes

$$G_\varphi(t)=\tfrac{1}{2}u_0^2\exp[-\alpha(T)/V_c u_0^2]\{\exp[\langle\delta\phi(r,0)\,\delta\phi(r,t)\rangle]-\exp[-\langle\delta\phi(r,0)\,\delta\phi(r,t)\rangle]\}. \tag{17}$$

If we expand the term in curly brackets we obtain a series of n-phason contributions. However, by assuming a high damping constant Γ_φ for the phason mode, we can examine the one-phonon contribution, so that

$$G_\varphi(t)=u_0^2\exp[-\alpha(T)/V_c u_0^2]\langle\delta\phi(r,0)\,\delta\phi(r,t)\rangle. \tag{18}$$

The multi-phason contributions should only introduce small corrections which can be neglected. This assumption is indeed experimentally justified. Inelastic neutron-scattering experiments in K_2SeO_4, for example, have been consistently interpreted by considering a value $\Gamma_\varphi\simeq 3\times 10^{11}$ s^{-1} (Kaziba and Fayet 1986). The phason-induced spin–lattice relaxation rate $T_{1\varphi}^{-1}$ thus becomes

$$\frac{1}{T_{1\varphi}}\propto u_0^2\exp\left(-\frac{\alpha(T)}{V_c u_0^2}\right)\int_{-\infty}^{\infty}\sum_k\langle\delta\phi_k(r,0)\,\delta\phi_k(r,t)\rangle\exp(i\omega t)\,dt \tag{19}$$

where we have assumed that the phase fluctuations are uncorrelated for different k-values so that $\langle\delta\phi(r,0)\,\delta\phi(r,t)\rangle=\sum_k\langle\delta\phi_k(r,0)\,\delta\phi_k(r,t)\rangle$.

Using the classical fluctuation–dissipation theorem we obtain

$$\frac{1}{T_{1\varphi}}\propto u_0^2\exp\left(-\frac{\alpha(T)}{V_c u_0^2}\right)\frac{2kT}{\omega}\sum_k\chi_\varphi''(k,\omega). \tag{20}$$

If we describe the susceptibilities by damped harmonic oscillator-type susceptibilities (Blinc *et al* 1986b), i.e.

$$\chi_\varphi''(k,\omega)=\Gamma_\varphi\omega/(\omega^2-\omega_{\varphi_k}^2)^2+\Gamma_\varphi^2\omega^2 \tag{21}$$

we obtain in the plane-wave limit, after replacing the summation over $\boldsymbol{k}$ by an integration over half the Brillouin zone,

$$1/T_{1\varphi} \propto u_0^2 \exp(-\alpha/V_c u_0^2)\Delta_\varphi^{-1}. \tag{22}$$

In the case of small thermal fluctuations $\alpha(T) \simeq 0$ we obtain the well known phason-induced relaxation rate (the phason part of equation (2)).

Equation (22) indicates that $T_{1\varphi}$ is influenced by the additional temperature dependence of the phason gap Δ_φ. The dynamics of the phason mode have been studied by Okabe and Fukuyama (1976), using the impurity-averaged phase mode Green function $D(q; i\omega)$. The standard treatment of the problem is to introduce the self-energy function so that

$$D(q; i\omega) = [\tfrac{1}{2}\mu u_0^2(\omega^2 + c^2q^2) - \Gamma_1(t)] \tag{23}$$

where $\Gamma_1(t)$ is the self-energy function in its lowest-order approximation (Prelovsek 1988). Equation (23) implies a pole at frequency $\omega = [2\Gamma_1(t)/\mu u_0^2]^{1/2}$ which is defined as the phason gap Δ_φ.

The self-energy function is found to be equal to (Prelovsek 1988)

$$\Gamma_1(t) \propto m^2 U u_0^m \left\langle \sum_j \cos\left(m\boldsymbol{q}_s \cdot \boldsymbol{r}_j + m\,\delta\phi_{\text{imp}}(\boldsymbol{r}_j) + m\sum_k \phi_k(\boldsymbol{r}, t)\right)\right\rangle \tag{24}$$

where U is the impurity-potential strength and $\delta\phi_{\text{imp}}(\boldsymbol{r})$ is the impurity-induced phase deviation. In the case of random interactions, $m = n$ whereas, in the case of random fields, $m < n$ (Prelovsek 1988); here m represents the symmetry properties of the impurities relative to the symmetry of the n-domain commensurate (C) phase. When $m = n$, the impurities will not break the symmetry of the C phase (random interactions) while, when $m < n$ they will discriminate between the n possible C domains (random fields).

The key assumption in introducing thermal fluctuations in the phason gap is that, in a way similar to the calculations in equation (11), and using also here the Gaussian averaging theorem, the self-energy $\Gamma_1(t)$ should be replaced by

$$\begin{aligned} \Gamma_1(t) &= \Gamma_{10} \exp\left(-\tfrac{1}{2}m^2 \sum_k \langle \phi_k^2(t)\rangle \right) \\ \Gamma_{10} &\propto m^2 U u_0^m \left\langle \sum_j \cos[m\boldsymbol{q}_s \cdot \boldsymbol{r}_j + m\,\delta\phi_{\text{imp}}(\boldsymbol{r}_j)] \right\rangle. \end{aligned} \tag{25}$$

Here we have as before assumed that the phase fluctuations are uncorrelated for different k-values. Equation (25) is in accordance with other approximations (see, e.g., Okabe and Fukuyama (1976) and Maki (1986)) where the influence of thermal fluctuations is incorporated by applying the self-consistent field approximation to the effective Hamiltonians.

When these assumptions are taken into consideration and equations (13) and (16) are used, Δ_φ proves to be

$$\Delta_\varphi = \Delta_{\varphi_0} \exp(-m^2\alpha/2V_c u_0^2) \tag{26}$$

where, in the weak-pinning regime (Prelovsek 1988),

$$\Delta_{\varphi_0} \simeq u_0^{m-2}\sqrt{n_i} \tag{27}$$

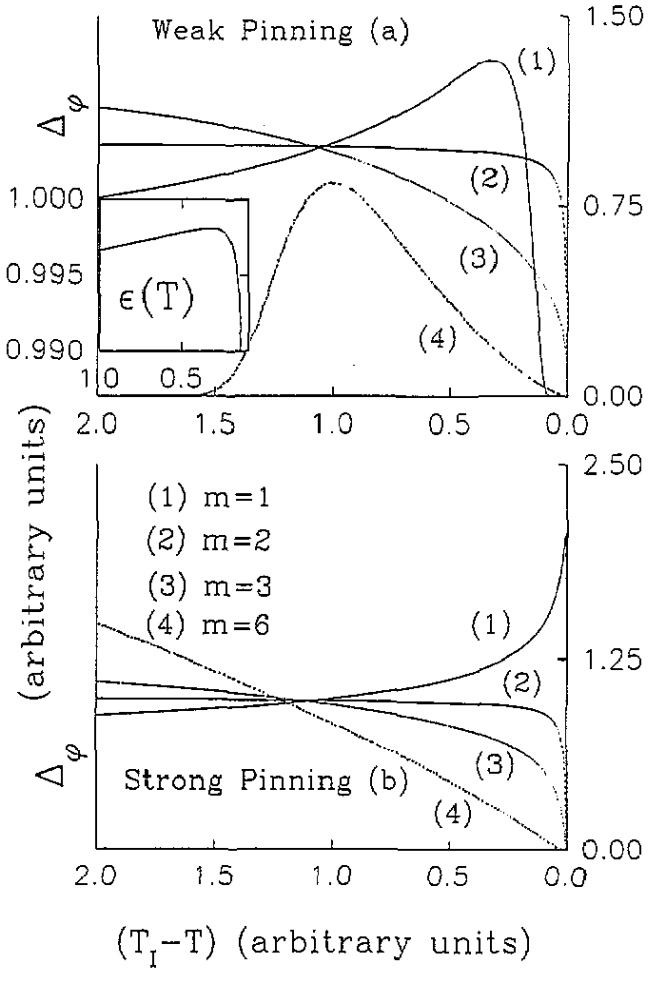

Figure 1. The phason gap Δ_φ as a function of temperature close to T_I: (*a*) in the weak-pinning limit; (*b*) in the strong-pinning limit. The inset exhibits the function $\epsilon(T)$ (equation (15)) for $m = 1$ in the weak-pinning limit.

and, in the strong-pinning regime,

$$\Delta_{\varphi_0} \approx u_0^{(m-2)/2} n_i^{1/3}. \tag{28}$$

The phason gap Δ_φ versus T very close to the transition temperature T_I is shown in figures 1(*a*) and 1(*b*). The parameter α is considered, as explained below, to be temperature independent, thus giving a slight modification of the $\Delta_\varphi(T)$ curves.

We observe that $\Delta_\varphi \to 0$ as $T \to T_I$ for all m-values. What thermal fluctuations really influence is the strength of the impurity potential at all impurity sites. This is best seen in the $m = 1$ case (weak-pinning limit) where, by omitting thermal fluctuations, $\Delta_\varphi \to \infty$ as $T \to T_I$. However, the coherence volume $V_c \to 0$ as $T \to T_I$, so that the thermal fluctuations have a diverging amplitude $\phi_k \to \infty$ (Blinc *et al* 1982, 1984), thus forcing the impurity potential strength U and the phason gap Δ_φ to go to zero. By lowering the temperature we observe a different behaviour of Δ_φ versus T for different kinds of pinning

and different m-values. What is remarkable is that, by studying the limiting behaviour of equation (26), we observe the existence of cases ($m = 1$ in both the strong- and the weak-pinning limits, and $m > 2$ in the weak-pinning limit) where, after reaching a maximum, Δ_φ decreases with decreasing temperature. However, one should expect such effects to be extremely difficult to observe experimentally; deeper inside the I phase, discrete-lattice pinning effects dominate, thus masking impurity-induced pinning effects (Papavassiliou *et al* 1991a). In all cases, Δ_φ versus $T_I - T$ increases rapidly very close to T_I, within a few tenths of 1 °C. After this small temperature interval, the thermal-fluctuations parameter $\alpha(T)$ which is greatly reduced (but non-zero) can be assumed to be temperature independent. This approximation is permissible if we take into consideration that the variation in Δ_φ is smoothed out owing to the function $\epsilon(T)$ (see inset of figure 1(a)).

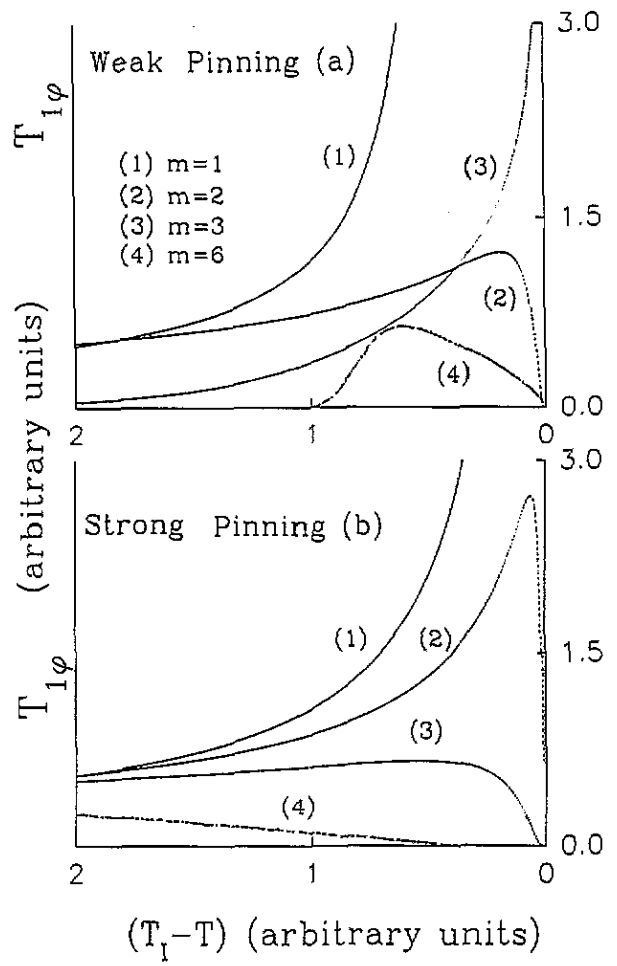

Figure 2. The phason-induced spin–lattice relaxation time $T_{1\varphi}$ as a function of temperature very close to T_I: (a) in the weak-pinning limit; (b) in the strong-pinning limit.

In figures 2(a) and 2(b) we see the phason-induced spin–lattice relaxation time $T_{1\varphi}$ versus temperature, very close to T_I and for different impurities and pinning types. It is

assumed that, in this temperature region, thermally induced phase fluctuations significantly influence the phason mode ($\alpha \neq 0$). The great differences between the plots for the different kinds of impurity and pinning indicate that $T_{1\varphi}$ could be an excellent tool for the investigation of the pinning–depinning mechanism and the motion of the modulation wave under the influence of thermal fluctuations.

In order to check the validity of our calculations, we performed high-temperature-resolution NQR spin–lattice relaxation time T_1 measurements on a pure crystal of Rb_2ZnCl_4 ($n = 6$) and compared the experimental data with the model. As the results must also be consistent with corresponding NMR and NQR lineshape calculations, the theory has been extended to the lineshape calculations versus T or the Cl(1) nucleus of Rb_2ZnCl_4. This lineshape model can be easily applied to other cases.

2.2. *Lineshape model*

The NQR frequency of the Cl(1) nuclear site of Rb_2ZnCl_4, very close to T_I, depends quadratically on the I displacement (Papavassiliou *et al* 1991b):

$$\nu(\phi, t) = \nu_0 + \nu_2 \cos^2[\phi + \delta\phi(r, t)]. \tag{29}$$

Here $\nu_2 \propto u_0^2, \phi$ is given by $\phi = q_s \cdot r$ and $\delta\phi(r, t)$ depends on time according to equation (8). We assumed that the amplitude fluctuations can, to a first approximation, be ignored, as they are very small in comparison with the phase fluctuations (Blinc *et al* 1984).

The adiabatic NMR and NQR lineshapes are given by (Blinc *et al* 1983, Kogoj *et al* 1984)

$$f(\nu) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} G_f(t) \exp(\mathrm{i}2\pi\nu t)\, \mathrm{d}t \tag{30}$$

where $G_f(t)$ is the autocorrelation function:

$$G_f(t) = \left\langle \frac{1}{2\pi} \int_0^{2\pi} \mathrm{d}\phi \exp\left(\mathrm{i}2\pi \int_0^t \nu(\phi, t')\, \mathrm{d}t'\right)\right\rangle_t . \tag{31}$$

By inserting equation (29) into equation (31), rewriting $\cos^2[\phi + \sum_k \delta\phi_k(r, t)]$ as $\frac{1}{2}[[1 + \cos\{2[\phi + \sum_k \delta\phi_k(r, t)]\}]]$ and expanding the cos term into a Fourier series, in case of fast oscillations ($\omega_k/2\pi a u_0^2 \gg 1$), we obtain the following autocorrelation function:

$$G_f(t) = \frac{1}{2\pi} \int_0^{2\pi} \mathrm{d}\phi \exp\{\mathrm{i}2\pi t[\nu_0 + \tfrac{1}{2}\nu_2 + \tfrac{1}{2}\nu_2 \cos(2\phi) J_0(\tau)]\}. \tag{32}$$

Here $\tau = 2\sum_k \delta\phi_k(r, t)$, and $J_0(\tau)$ is a zeroth-order Bessel function. Near to T_I the thermal-fluctuations parameter α takes, as already stated, a small value and $J_0(\tau)$ can be approximated by $J_0(\tau) \propto \exp(-\frac{1}{4}\tau^2) \propto \exp(-\alpha/V_c u_0^2)$, where τ^2 has been replaced by its average as obtained by equation (16). This last approximation is not valid infinitely close to T_I, where $\Delta_\varphi \to 0$.

Taking into consideration the above and equations (30) and (32) we obtain the following lineshape formula:

$$f(\nu) = \{[\tfrac{1}{2}\nu_2 \exp(-\alpha/V_c u_0^2)]^2 - (\nu - \nu_0 - \tfrac{1}{2}\nu_2)^2\}^{-1/2}. \tag{33}$$

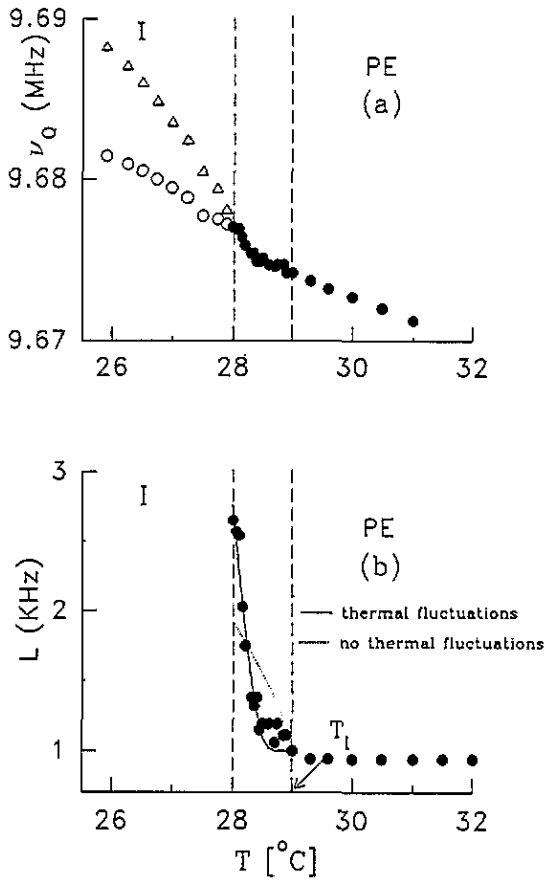

Figure 3. (*a*) Temperature dependence of (*a*) the Cl(1) NQR frequency ν_Q and (*b*) the HHFW, close to T_l for a pure Rb_2ZnCl_4 crystal: ——, theoretical fit of equation (34) to the experimental data points for $\alpha \neq 0$; ·····, fit for $\alpha = 0$. For both α-values, $m = 1$ in the strong-pinning regime.

The half-height full width (HHFW) L of the inhomogeneous I line is in that case given by

$$L = \nu_2 \exp(-\alpha / V_c u_0^2) + L_0 \tag{34}$$

where L_0 is the HHFW of the paraelectric line.

In the case of negligible thermal fluctuations, $\alpha = 0$ so that $J_0 = 1$ and equation (33) reduces to the well known incommensurate static frequency distribution

$$f(\nu) = [(\nu - \nu_0)(\nu_2 + \nu_0 - \nu)]^{-1/2}. \tag{35}$$

3. Experimental details

The pure crystal of Rb_2ZnCl_4 was prepared from an aqueous solution of RbCl and $ZnCl_2$ in a 2:1 molar ratio, and the method of repeated crystallization was used. Fourier-transformed

^{35}Cl NQR spin echo spectra were recorded of the Cl(1) nucleus, which lies on a mirror plane. T_1 was obtained by the inversion recovery spin-echo pulse sequence. Calibrated chromel–constantan thermocouples were used and temperature regulation provided a stability of better than 0.02 K over the measuring period.

4. Results and discussion

The temperature dependence of Cl(1) NQR frequency ν_Q in the vicinity of T_I is shown in figure 3(*a*). We observe that ν_Q slowly increases with decreasing temperature from 31 °C down to T_I at 29 °C. At T_I, inhomogeneous broadening of the NQR line sets (figure 3(*b*)) which evolves in a way that can be explained only if we take into consideration the dominating role of thermal fluctuations. The full curve in figure 3(*b*) represents the theoretical fit of equation (34) to the experimental data by taking into consideration the influence of thermal fluctuations ($\alpha \neq 0$), whereas the dotted curve corresponds to no thermal fluctuations ($\alpha = 0$). Equation (34) gives an excellent fit to the experimental data if we consider that firstly $\alpha \neq 0$ and symmetry-breaking impurities with $m = 1$ in the weak-pinning limit (in the case of Rb_2ZnCl_4 $n = 6$ (Prelovsek and Blinc 1984)) or secondly $\alpha \neq 0$ and $m < 6$ in the strong-pinning limit. We may thus say that, in the temperature region very close to T_I, strong thermal fluctuations exist, which motionally narrow the I NQR splitting. Under the condition that the two edge singularities are very close to each other, only a single line is observed. Thus it is clear that the change in the slope of the ν_Q versus T at T_I (figure 3(*a*)) is a result of the shift in the centre of gravity of the NQR line from ν_0 towards $\nu_2 + \nu_0$. The real T_I is not the temperature where the I split is observed (Blinc *et al* 1986b), but the temperature where the ν_Q line versus T changes slope. The temperature region between the broken vertical lines in figure 3 thus belongs to the I phase and not to the P phase as believed until now.

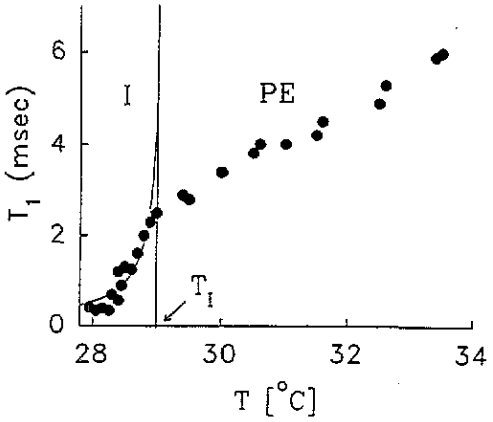

Figure 4. Temperature dependence of the phason-induced spin–lattice relaxation time $T_{1\varphi}$ very close to T_I, for pure Rb_2ZnCl_4: ——, theoretical fit of equation (22) to the experimental data points.

In figure 4 we see T_1 experimental data as a function of temperature in both the P and I phases, very close to the transition temperature T_I. We observe that T_1 decreases on

approaching T_I from above, as expected for a spin–lattice relaxation mechanism dominated by soft-mode fluctuations. The interesting point is that T_1 continues to decrease with decreasing temperature below T_I. Since only one frequency line is observed, it is not possible to separate the amplitudon and phason contributions to the relaxation mechanism, and the effective relaxation rate will be determined by the faster process, i.e. by the thermal phase fluctuations. In accordance with this, we try to fit the spin–lattice relaxation data to equation (22) (full curve in figure 4). In the case of Rb_2ZnCl_4 both $m = 1$ cases (symmetry-breaking impurities), in the weak- and strong-pinning regimes under the presence of thermal fluctuations, fit the experimental data quite well (figure 4). However, only the fit for $m = 1$ in the strong-pinning regime gives comparable α-values for both the HHFW and the T_1 fit.

A combination thus of both NQR HHFW lineshape and T_1 measurements leads to the following conclusions. In pure Rb_2ZnCl_4 and very close to T_I, thermally excited fluctuations of the phase of the modulation wave seem to play a predominant role in the motion (depinning effects) of the modulation wave. The small amount of impurities seem to be of strong-pinning and of the random-field type (with $m = 1$), linearly coupled to the local soft-mode.

A similar analysis could be equally well applied to CDW systems. Further experiments on both doped and pure crystals are needed to obtain a better understanding of the pinning–depinning mechanism.

References

Baeriswyl D and Bishop A R 1980 *J. Phys. C: Solid State Phys.* **13** 1403

Blinc R, Ailion D C, Prelovsek P and Rutar V 1983 *Phys. Rev. Lett.* **50** 67

Blinc R, Dolinsek J, Prelovsek P and Hamano K 1986a *Phys. Rev. Lett.* **56** 2387

Blinc R, Milia F, Rutar V and Zumer S 1982 *Phys. Rev. Lett.* **48** 47

Blinc R, Milia F, Topic B and Zumer S 1984 *Phys. Rev.* B **29** 4173

Blinc R, Prelovsek P, Rutar V, Seliger J and Zumer S 1986b *Incommensurate Phases in Dielectrics* vol I, ed R Blinc and A P Levanyuk (Amsterdam: North-Holland) pp 146–276

Bruce A D 1983 *J. Physique* **44** 147

Bruce A D and Cowley R A 1978 *J. Phys. C: Solid State Phys.* **11** 3609

Bruinsma G and Aeppli G 1984 *Phys. Rev. Lett.* **52** 1547

Cailleau H 1986 *Incommensurate Phases in Dielectrics* vol II, ed R Blinc and A P Levanyuk (Amsterdam: North-Holland)

Fukuyama H 1976 *J. Phys. Soc. Japan* **41** 513

Fukuyama H and Lee P A 1978 *Phys. Rev.* B **17** 535

Kaziba A and Fayet J C 1986 *J. Physique* **47** 239

Kogoj M, Zumer S and Blinc R 1984 *J. Phys. C: Solid State Phys.* **17** 2415

Lan M D, Liu J Z and Shelton R N 1991 *Phys. Rev.* B **44** 2751

Lee P A and Rice T M 1979 *Phys. Rev.* B **19** 3970

Maki K 1986 *Phys. Rev.* B **33** 2852

McCarten J, Maher M, Adelman T L, DiCarlo D A and Thorne R E 1991 *Phys. Rev.* B **43** 6800

Milia F, Blinc R and Zumer S 1984 *Solid State Commun.* **50** 1019

Nattermann Th 1990 *Phys. Rev. Lett.* **64** 2454

Okabe Y and Fukuyama H 1976 *Solid State Commun.* **20** 345

Papavassiliou G, Anagnostopoulos A, Milia F, Blinc R and Kotsios S 1991a *Phys. Rev.* B **44** 7283

Papavassiliou G, Milia F, Blinc R and Zumer S 1991b *Solid State Commun.* **77** 891

Prelovsek P 1988 *Phase Transitions* **11** 203

Prelovsek P and Blinc R 1984 *J. Phys. C: Solid State Phys.* **17** 577

Segransan P, Jannossy A, Berthier C, Marais J and Butanol P 1986 *Phys. Rev. Lett.* **56** 1854

Stokes J B, Weitz D A, Gollub J P, Dougherty A, Robbins M O, Chaikin P M and Lindsay H M 1986 *Phys. Rev. Lett.* **57** 1718

Villain J 1984 *Phys. Rev. Lett.* **52** 1543

Yeshurun Y and Malozemoff A P 1988 *Phys. Rev. Lett.* **60** 2202