Low-Frequency Phason and Amplitudon Dynamics in the Incommensurate Phase of Rb_2ZnCl_4

P. Mischo, F. Decker, U. Häcker,* K.-P. Holzer, and J. Petersson
Universität des Saarlandes, Fachbereich Physik, Postfach 151150, D-66041 Saarbrücken, Germany

D. Michel
Universität Leipzig, Fakultät für Physik und Geowissenschaften, Linnéstraße 5, D-04103 Leipzig, Germany
(Received 8 November 1996)

It is shown that the phason-induced ^{87}Rb NMR spin-lattice relaxation rate in the incommensurate phase of Rb_2ZnCl_4 depends on the Larmor frequency, whereas the amplitudon-induced rate does not. The results are described consistently by relaxatory phason and amplitudon fluctuations. The relaxatory phason gap is found to be on the order of magnitude of about 10 MHz, in contrast to previous estimates from NMR studies. Our data also allow a determination of the temperature dependence of the amplitudon relaxation frequency. [S0031-9007(97)02732-4]

PACS numbers: 64.70.Rh, 64.60.Cn, 76.60.Es

Some insulating crystals pass over from a high-temperature normal (N) phase to a structurally incommensurately (IC) modulated phase at a certain temperature T_i. In the IC phase, at least one physical quantity is modulated in such a way that the characteristic wave vector $\mathbf{q}_i$ is not a rational multiple of the reciprocal lattice vectors of the N phase. As a consequence, the initial phase of the modulation wave is arbitrary, and the IC structure is continuously degenerate with respect to a phase shift [1,2]. Thus, special low-energy excitations termed "phasons" are present in IC systems. The continuum theory of IC phases predicts the existence of a gapless phason mode. It is usually assumed, however, that in a real crystal various effects lead to a nonzero gap in the phason excitation spectrum. It is this characteristic phason dynamics which is the most fascinating feature of incommensurate crystals and which is the subject of this Letter.

The incommensurate modulation wave is in most cases, at least close to T_i, a single harmonic function of space ("plane wave limit", PWL). It can be represented by an order parameter (OP) with two thermodynamic degrees of freedom, e.g., amplitude and initial phase. The normal modes of the OP are given by its longitudinal and transversal components P_1 and P_2, respectively, in the complex OP plane [2]. In first-order approximation, the fluctuations of P_1 and P_2 can be identified with those of amplitude and phase giving rise to the terms "amplitudon" and "phason" fluctuations [1,2].

In most cases, the IC phase transforms into a commensurate (C) phase at a temperature $T_c < T_i$. For the prototypic system Rb_2ZnCl_4 (RZC) the IC phase is stable between $T_i = 303$ K and $T_c = 195$ K, where a lock-in transition to a ferroelectric C phase takes place with a triplication of the unit cell with respect to the N phase [1,3]. As a characteristic precursor effect of the IC-C phase transition, a so-called soliton structure is formed. Soliton effects have been observed in RZC in a temperature region of about 40 K above T_c [3]. In the following, however, we will restrict the discussion to the PWL.

Quadrupolar perturbed nuclear magnetic resonance (NMR) has been proved to be an accurate and sensitive tool for investigating IC phases [1]. While the spectrum of NMR frequencies is determined by the static part of the electric field gradient (EFG), its fluctuating part is related to the probabilities of transitions between the nuclear spin levels. The spin-lattice relaxation rate $1/T_1$ of the nuclear magnetization is given as a linear combination of these probabilities which are a measure of the spectral density of the EFG fluctuations at the Larmor frequency ($\nu_L = \omega_L/2\pi \approx 10^8$ Hz).

It is the purpose of this Letter to demonstrate that suitable and careful NMR experiments can provide some characteristic quantitative parameters of the dynamics in incommensurately modulated crystals. In particular, it is shown for the first time that the phason-induced ^{87}Rb spin-lattice relaxation rate in RZC depends on the Larmor frequency and allows one to determine unambigously the phason gap in the IC phase. In this way, a long standing problem is solved which consists of the phason gap values which were derived by various experimental methods and which differ by some orders of magnitude [3]. Also, the time constants of the amplitudon fluctuations can be determined. Previous measurements already demonstrated the frequency dependence of the ^{1}H spin-lattice relaxation in biphenyl [4,5] and a derivation of this substance [6], resulting in an estimate for an upper bound of about 5 MHz and 500 kHz, respectively, for the phason gap.

High-quality single crystals of RZC were grown from an aqueous solution as previously described [7]. The spin-lattice relaxation rates have been measured for the upper-frequency satellite transition of ^{87}Rb in RZC for the lattice site Rb(1)—notation as in Ref. [8]—in the crystal orientation $\mathbf{b}\|\mathbf{B}_0$. The phase transition temperature T_i could be determined simply by inspecting the NMR spectra. A special spin-echo pulse sequence was used to measure the magnetization recovery with a $\pi/2$ pulse length of 2.5 μs for about 20 different magnetization recovery times. The magnetization recovery was

 0031-9007/97/78(11)/2152(4)$10.00

always found to be strictly single exponential as has been observed and explained before [9]. For measuring the Larmor frequency dependence of $1/T_1$, the magnetic field of the cryomagnet was changed.

In RZC, no soft-phonon mode could be detected above T_i by Raman or neutron scattering experiments. Consequently, and in accordance with theoretical results based on *ab initio* calculations [10], the phase transition is generally assigned to the *relaxator model* [11]. For this case of OP dynamics, a *direct process* for the relaxation of the nuclear spin system is reasonably assumed. Precise ^{87}Rb-T_1 measurements [12] indeed proved both assumptions to hold for RZC above T_i. Since the phason and amplitudon modes evolve from the relaxatory soft mode on passing from the N to the IC phase, we adopt both these assumptions as a general basis for interpreting quantitatively our experimental results in the IC phase. As will be shown, in this manner, as long as the PWL holds, a consistent description of the dynamics of the IC phase of RZC is achieved.

NMR spectra of incommensurate crystals are usually characterized by typical inhomogeneous frequency distributions with two edge singularities [1,8,13]. In general, the spin-lattice relaxation rate of any part of this distribution is given by a superposition of two contributions which are proportional to the spectral densities J_1 and J_2 of the OP normal modes δP_1 and δP_2, respectively. The correct assignment of the experimental T_1 data to these spectral densities requires the knowledge of the spatial modulation functions of the NMR frequencies and of the transition probabilities W_μ between the nuclear spin levels $|m\rangle$ and $|m + \mu\rangle$ with $\mu = 1, 2$. Following the procedure given in Ref. [9], it can be shown that for the lattice site Rb(1) of RZC in the special crystal orientation $\mathbf{b} \| \mathbf{B}_0$ the relaxation rates are simply given by

$$1/T_1 = DJ_1(\omega_L), \qquad 1/T_1 = DJ_2(\omega_L) \tag{1}$$

for the lower-frequency and upper-frequency edge singularity, respectively. Here D is a constant, and $J_1(\omega_L)$ and $J_2(\omega_L)$ are the amplitudon and phason spectral densities, respectively, at Larmor frequency. In the frequency region between the edge singularities, the relaxation rate was predicted to vary linearly with the NMR satellite frequency (in contrast to other crystal orientations) [9]. This linear variation of $1/T_1$ over the frequency distribution, which is also a criterion for the validity of Eq. (1), is confirmed by careful well-resolved spin-lattice relaxation measurements (Fig. 1) in which the recovery of the magnetization was monitored at each frequency after the whole frequency distribution was saturated.

For estimating the characteristic time scale of the OP fluctuations, we measured the dependence of $J_1(\omega_L)$ and $J_2(\omega_L)$ on the Larmor frequency. The results are shown in Fig. 2. In all three cases, the spectral density $J_2(\omega_L)$ shows a distinct Larmor frequency dependence according to a square root law while $J_1(\omega_L)$ is obviously independent of frequency. Already, this qualitative result is a look-and-see proof for the fact that the time constants of the phason fluctuations are obviously of the order of magnitude of at least 10^{-8} s and, on the other hand, that those of the amplitudon fluctuations are considerably smaller. Besides, the different Larmor frequency dependences, in turn, demonstrate that the contributions proportional to $J_1(\omega_L)$ and $J_2(\omega_L)$ are actually decomposed at the edge singularities.

On the basis of the general assumptions formulated above, it can be shown that the frequency dependence of the phason spectral density $J_2(\omega)$ can be written as [5,12]

$$J_2(\omega) = J_2(0)F(\omega\tau_2), \tag{2}$$

where $J_2(0)$ depends only on temperature and where the frequency dependence is given by

$$F(\omega\tau_2) = \sqrt{2} \Big/ \sqrt{\sqrt{1 + (\omega\tau_2)^2} + 1}\,. \tag{3}$$

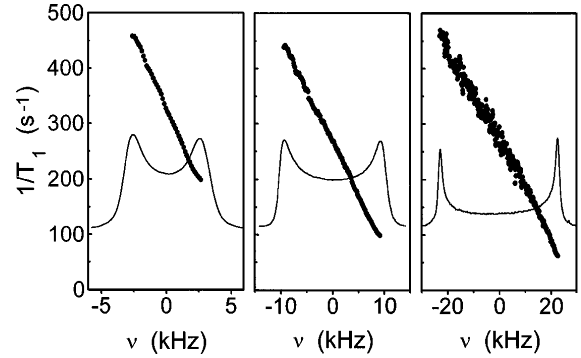

FIG. 1. Variation of the spin-lattice relaxation rate $1/T_1$ over the frequency distribution of the upper-frequency ^{87}Rb NMR satellite transition of Rb(1) in RZC at the temperatures $T_i - T = 0.8$ K (left), $T_i - T = 3.5$ K (center), $T_i - T = 9.6$ K (right). The line shape functions of the frequency distribution at the respective temperatures are also shown (frequency increases from right to left). The spectra (not normalized) were obtained from spin-echo experiments.

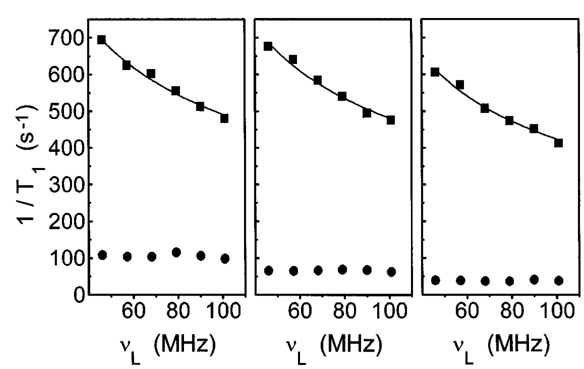

FIG. 2. Larmor frequency dependence of the spin-lattice relaxation rates $1/T_1$ at the temperatures $T_i - T = 3.5$ K (left), $T_i - T = 9.6$ K (center), $T_i - T = 38.7$ K (right). Results are shown for the upper- (■) and lower-frequency (●) edge singularities of the ^{87}Rb NMR satellite frequency distributions which are proportional to the phason (■) and amplitudon (●) spectral densities J_2 and J_1, respectively. The curves correspond to the square root law discussed in context with Eq. (3).

The function $F(\omega_L\tau_2)$ depends only on the ratio of the Larmor frequency ν_L to the relaxatory phason gap $1/2\pi\tau_2 \equiv 1/2\pi\tau_2(\mathbf{q}_i)$. For a relaxatory phason gap which is large compared to the employed frequencies, $F(\omega_L\tau_2)$ is equal to unity and the relaxation rate is, of course, frequency independent. However, a phason gap with $\omega_L\tau_2 \gg 1$ leads approximately to a behavior $J_2(\omega_L) \propto 1/\sqrt{\omega_L}$ as derived previously [13]. As can be inferred from Fig. 2, this is actually fulfilled for the spin-lattice relaxation times pertinent to the phason-induced contribution. Thus, the phason gap $1/2\pi\tau_2$ in the IC phase of RZC must be smaller than the lowest Larmor frequency in our experiments, i.e., it can be estimated as $1/2\pi\tau_2 < 40$ MHz.

It is generally assumed that the phason gap is practically temperature independent in the whole IC phase [1,2]. Thus, at a given Larmor frequency, the function $F(\omega_L\tau_2)$ should be constant below T_i, and only the "static" spectral density $J_2(0)$ should show a weak temperature variation according to $J_2(0) \propto T$ [9], except for the soliton regime. Consequently, for the PWL, the frequency dependence of the squared spin-lattice relaxation time $T_1^2(\omega_L)$ can be given in a normalized representation by writing

$$T^2T_1^2(\omega_L) = T^2/D^2J_2^2(0)F^2(\omega_L\tau_2) = C\left(\sqrt{1 + (\omega_L\tau_2)^2} + 1\right), \quad (4)$$

where C is a constant. The corresponding plot for temperatures between T_i and about $T_i - 40$ K is shown in Fig. 3. A remarkable consistency within the experimental data is found. The asymptotic behavior of Eq. (4) for large arguments, i.e., for the limit $\omega_L \gg 1/2\pi\tau_2$, is given by a straight line according to

$$A(\omega_L) = C(1 + \omega_L\tau_2) \quad (5)$$

which intersects with the frequency axis just at the (negative) phason gap. Thus, the plot of $T^2T_1^2(\omega_L)$ in Fig. 3 allows one to derive the phason gap in a simple geometric way, as it is demonstrated in the diagram. From this procedure we obtain $1/2\pi\tau_2 = 10$ MHz, where the experimental errors are still consistent with a value of 15 MHz. A plausible lower bound for this quantity is 1 MHz.

A value for the relaxatory phason gap in the order of some MHz agrees with the results of measurements of the dielectric behavior in the lower part of the IC phase of RZC [3]. In this context we also refer to recent ^{87}Rb spin-lattice relaxation measurements in the N phase of RZC [12]. In this work, the critical temperature dependence of T_1 on approaching the N-IC phase transition was analyzed, resulting in a relaxatory soft-mode frequency of the order of 10 MHz very close to T_i. This is in excellent agreement with the results of acoustic investigations [14] and Brillouin scattering studies in the N phase of RZC [3,15]. Note that the analysis of our NMR data in the IC phase is completely independent from that in Ref. [12]. Thus, our experimental results above and below T_i are fully consistent and, moreover, confirm the fact that the phason dynamics in the IC phase preserves the soft-mode dynamics at the N-IC phase transition at T_i.

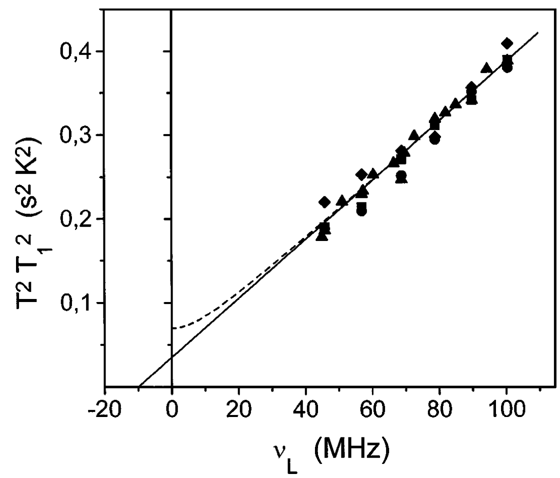

FIG. 3. Normalized representation of the squared phason-induced ^{87}Rb spin-lattice relaxation time in the IC phase of RZC [cf., Eq. (4)]. Data points are given for the temperatures $T \cong T_i$ (◆), $T_i - T = 3.5$ K (▲), $T_i - T = 9.6$ K (●), $T_i - T = 38.7$ K (■). The broken curve corresponds to Eq. (4) and the straight line to the asymptote given by Eq. (5) with a phason gap of $1/2\pi\tau_2 = 10$ MHz.

Contrary to this description, previous attempts to derive the phason gap from NMR data were made on the basis of an oscillatory model using the ratio of putative amplitudon- and phason-induced relaxation rates [16–18]. In the case of RZC, they led to phason gaps in the order of 10–100 GHz [16]. Among others, the analysis in these works rests on the assumptions that (i) the amplitudon and phason spectral densities J_1 and J_2 are related to a direct (one-phonon) relaxation process with overdamped oscillatory modes [13], and (ii) the amplitudon modes responsible for J_1 can be identified with some modes detected by Raman or neutron scattering experiments in the lower part of the IC phase and which were assigned to the OP fluctuations. As can be inferred directly from the smooth temperature dependence of the amplitudon frequencies determined this way at the IC-C phase transition [19,20] and the completely different behavior of the NMR relaxation rates pertinent to J_1 close to T_c [9,13,16], the latter assumption is hardly justified. Besides, the first assumption contradicts the neutron scattering experiments which detect underdamped modes. The phason gap values derived in the NMR works cited do not differ very much from the corresponding amplitudon frequencies obtained from neutron or Raman scattering studies, and one should wonder why they cannot be observed in the same scattering studies. Thus, the relevance of the phason gaps determined this way from NMR data has been questioned severely, emphasizing the overdamped character of the phason fluctuations [5,9,21]. In any case, this discussion demonstrates that in these NMR works several assumptions are needed, the basis and consequences of which are not well justified. On the contrary, the conclusions we draw are much more direct and essentially rest on the characteristic frequency dependence of T_1 which is an unambiguous proof for the existence of low-frequency excitations in the MHz region.

Moreover, our data also allow one to determine the temperature dependence of the amplitudon relaxation frequency from the spin-lattice relaxation rates pertinent to the amplitudon spectral density J_1. The experimental data for the amplitudon- and phason-induced relaxation times $T_{1(1)}$ and $T_{1(2)}$, respectively, are shown in Fig. 4. Applying the formalism given in [13] for oscillatory modes to the present case of pure relaxatory modes and assuming the fast-motion limit $\omega_L \tau_\beta \ll 1$ to hold for both amplitudons and phasons, we find

$$\frac{\tau_1}{\tau_2} = \left(\frac{J_1(0)}{J_2(0)}\right)^2 = \left(\frac{T_{1(2)}}{T_{1(1)}}\right)^2. \tag{6}$$

In our case the fast-motion limit is valid only for the amplitudon spectral density, i.e., $1/T_{1(1)} = DJ_1(0)$, but not for the phason spectral density, as demonstrated in Fig. 2. Thus, inserting Eqs. (3) and (4) into Eq. (6), we arrive at

$$\tau_1 = 2C\tau_2/(T_{1(1)}T)^2. \tag{7}$$

Since C and τ_2 are practically constant in the IC phase, the squared amplitudon-induced relaxation rate $1/T_{1(1)}^2$ directly reflects the behavior of the relaxatory amplitudon gap. Note that the quantity $C\tau_2$ is nothing but the slope of the straight line in Fig. 3 whose relative error is therefore considerably smaller than that of τ_2 and C themselves. The result is shown in the inset of Fig. 4. The relaxatory amplitudon gap increases from about 10 MHz at T_i up to values of some GHz within an interval of about 70 K below T_i. We stress that this analysis cannot be continued simply to the region of the soliton regime since the OP dynamics and its influence on the relaxation rates are more complicated here than in the PWL [22].

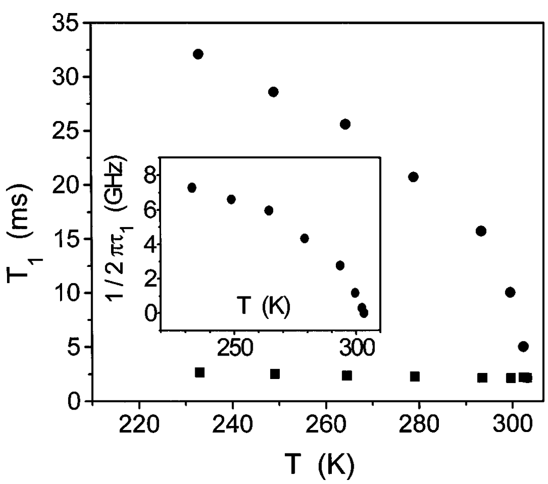

FIG. 4. Temperature dependences of the phason- and amplitudon-induced ^{87}Rb spin-lattice relaxation times T_1 measured for $\nu_L \cong 98$ MHz at the respective edge singularities with $1/T_1 \propto J_2$ (■) and with $1/T_1 \propto J_1$ (●). The inset shows the temperature dependence of the relaxatory amplitudon gap $1/2\pi\tau_1$ derived via Eq. (7) from the experimental data.

The authors are indebted to A. Klöpperpieper and K. Kretsch for growing and characterizing the high-quality crystal samples. Financial support from the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

*Permanent address: Universität Leipzig, Fakultät für Physik und Geowissenschaften, Linnéstraße 5, D-04103 Leipzig, Germany.

[1] See *Incommensurate Phases in Dielectrics*, edited by R. Blinc and A. P. Levanyuk (North-Holland, Amsterdam, 1986), Vol. 1 and 2.
[2] A. D. Bruce and R. A. Cowley, J. Phys. C **11**, 3609 (1978).
[3] H. Z. Cummins, Phys. Rep. **185**, 211 (1990).
[4] S.-B. Liu and M. S. Conradi, Phys. Rev. Lett. **54**, 1287 (1985).
[5] L. von Laue, F. Ermark, A. Gölzhäuser, U. Haeberlen, and U. Häcker, J. Phys. Condens. Matter **8**, 3977 (1996).
[6] R. E. de Souza, M. Engelsberg, and D. J. Pusiol, Phys. Rev. Lett. **66**, 1505 (1991).
[7] J. Petersson and E. Schneider, Z. Phys. B **61**, 33 (1985).
[8] R. Walisch, J. Petersson, and J. M. Perez-Mato, Phys. Rev. B **35**, 6538 (1987).
[9] R. Walisch, J. Petersson, D. Schüßler, U. Häcker, D. Michel, and J. M. Perez-Mato, Phys. Rev. B **50**, 16 192 (1994).
[10] V. Katkanant *et al.*, Phys. Rev. Lett. **57**, 2033 (1986).
[11] See J. D. Axe, M. Iizumi, and G. Shirane, in Ref. [1].
[12] K.-P. Holzer, J. Petersson, D. Schüssler, R. Walisch, U. Häcker, and D. Michel, Europhys. Lett. **31**, 213 (1995).
[13] R. Blinc, Phys. Rep. **79**, 331 (1981).
[14] Z. Hu, C. W. Garland, and S. Hirotsu, Phys. Rev. B **42**, 8305 (1990).
[15] Y. Luspin, M. Chabin, G. Hauret, and F. Gilletta, J. Phys. C **15**, 1581 (1982).
[16] S. Chen and D. C. Ailion, Solid State Commun. **69**, 1041 (1989); F. Milia and G. Papavassiliou, Phys. Rev. B **39**, 4467 (1989); J. Dolinsek, T. Apih, and R. Blinc, J. Phys. Condens. Matter **4**, 7203 (1992); D. C. Ailion and S. Chen, Solid State Commun. **92**, 835 (1994).
[17] R. Blinc, D. C. Ailion, J. Dolinsek, and S. Zumer, Phys. Rev. Lett. **54**, 79 (1985).
[18] B. Topic, U. Haeberlen, and R. Blinc, Phys. Rev. B **40**, 799 (1989).
[19] M. Wada, A. Sawada, and Y. Ishibashi, J. Phys. Soc. Jpn. **50**, 531 (1981).
[20] M. Quilichini, J. P. Mathieu, M. Le Postollec, and N. Toupry, J. Phys. (France) **43**, 787 (1982).
[21] J. Etrillard, B. Toudic, H. Cailleau, and G. Coddens, Phys. Rev. B **51**, 8753 (1995).
[22] U. Häcker, J. Petersson, R. Walisch, and D. Michel, Z. Phys. B **100**, 441 (1996).