considering the structural bonding nature of the deep-level defect and not only the chemical species of the impurity involved.

The samples used in this investigation were fabricated by Miss P. Bradley. One of us (J.E.L.) is indebted to Philips Research Laboratories, Redhill for their hospitality and to the Council for Scientific and Industrial Research (Pretoria) for a travel grant.

[(a)]On leave from the University of Witwatersrand, Johannesburg, Union of South Africa.

[1]N. F. Mott, Solid State Electron. 21, 1275 (1978).
[2]S. D. Brotherton and J. Bicknell, J. Appl. Phys. 49, 667 (1978).
[3]S. D. Brotherton, P. Bradley, and J. Bicknell, J. Appl. Phys. 50, 3396 (1979).
[4]J. A. Pals, Solid State Electron. 17, 1139 (1974); C. T. Sah, L. Forbes, L. I. Rosier, A. F. Tasch, and A. B. Tole, Appl. Phys. Lett. 15, 5, 145 (1969).
[5]H. D. Barber, Solid State Electron. 10, 1039 (1967).
[6]J. A. Van Vechten and C. D. Thurmond, Phys. Rev. B 14, 3539 (1976).
[7]O. Engstrom and A. Alm, Solid State Electron. 21, 1571 (1978).
[8]R. A. Swalin, *Thermodynamics of Solids* (Wiley, New York, 1962), p. 49.
[9]J. A. Van Vechten and C. D. Thurmond, Phys. Rev. B 14, 3551 (1976).
[10]H. Woodbury and G. M. Ludwig, Phys. Rev. 126, 466 (1962).
[11]G. D. Watkins and J. W. Corbett, Phys. Rev. 121, 1001 (1961).
[12]W. Bludau, A. Onton, and W. Heinke, J. Appl. Phys. 45, 1846 (1974).
[13]J. E. Lowther, to be published.

^{87}Rb Spin-Lattice Relaxation in the Incommensurable Phase of Rb_2ZnCl_4

R. Blinc, S. Južnič, V. Rutar, J. Seliger, and S. Žumer
J. Stefan Institute and Department of Physics, E. Kardelj University of Ljubljana, 61001 Ljubljana, Yugoslavia
(Received 31 December 1979)

The contribution of phason and amplitudon excitations to the spin-lattice relaxation rate in structurally incommensurable (I) systems as well as the NMR line shapes in these systems have been evaluated and compared with the ^{87}Rb NMR data for Rb_2ZnCl_4. The presence of a strong, temperature-independent relaxation mechanism, which disappears below the "lockin" transition, demonstrates that in the I phase of Rb_2ZnCl_4 the spin-lattice relaxation rate is dominated by phasons.

Structurally incommensurable (I) systems[1] are characterized by the appearance of a distortion

$$u(z) = A\cos(q_s z + \varphi), \tag{1}$$

with a periodicity of $2\pi/q_s$ which is an irrational fraction of the periodicity of the underlying crystal lattice.

The excitation spectrum[2] consists of two modes: The amplitudon branch corresponds to oscillations of the amplitude of the displacement, $A = A_0 + \delta A(t)$, while the phason branch corresponds to oscillations of the phase of the displacement profile, $\varphi = \varphi_0 + \delta\varphi(t)$. The I phase represents a system with a broken continuous phase symmetry as it corresponds to a particular choice of the phase φ. According to the Goldstone theorem, the phason frequency vanishes when $\vec{k} = \vec{q} - \vec{q}_s \to 0$:

$$\omega_\varphi^2 = \kappa k^2, \tag{2a}$$

while the amplitudon frequency is finite in this limit:

$$\omega_A^2 = 2A(T_I - T) + \kappa k^2. \tag{2b}$$

Any phase-pinning perturbation will induce a gap[2] in the phason spectrum (2a). Whereas the amplitudon mode was observed[3] to follow expression (2b) over the whole I phase well into the commensurable (C) phase, there has been so far no clear evidence for the existence of a phason mode in any incommensurable system in two or three dimensions.[3,4]

In this Letter we report the first direct observation of the phason mode in the incommensurable phase[3,5] of Rb_2ZnCl_4 by ^{87}Rb quadrupole-perturbed spin-lattice relaxation. The characteristic ^{87}Rb ($I = \frac{3}{2}$) NMR line shape in the I phase —measured at $\nu_L = 29.5$ MHz and at $\nu_L = 88.5$ MHz by Fourier-transform NMR—further shows that the "plane-wave[2] limit" is a rather good description of the I phase and that soliton effects[2] may be important only close to T_c. Quadrupole-perturbed NMR thus provides one of the most sensitive means to study the local arrangement and the phase fluctuation spectrum of structurally incommensurate systems.

The temperature dependence of the second-order quadrupole shifts of the central $\frac{1}{2} \rightarrow -\frac{1}{2}$ ^{87}Rb NMR lines of Rb_2ZnCl_4 is presented in Fig. 1 for $\vec{b} \perp \vec{H}_0$, $\sphericalangle(\vec{a}, \vec{H}_0) = 120°$ at $\nu_L = 29.5$ MHz. The paraelectric lines split and broaden at T_I but can be followed through the whole I phase into the C phase. Satellites are generally too broad to be observable. The change in the line shape on going into the I phase is illustrated in Fig. 2. Below T_I each paraelectric line broadens into a continuum which is limited by two edge singularities. The frequency separation between the two edge singularities increases with decreasing temperature (Fig. 1) as $(T_I - T)^{1/2}$. Close to T_c an additional structure appears (Fig. 1) which changes only little on going into the C phase. The characteristic line shape consisting of the broad continuum and the edge singularities disappears below T_c. It is replaced by a series of sharp lines the multiplicity of which is determined by the tripling[5] of the unit cell in the C phase of Rb_2ZnCl_4.

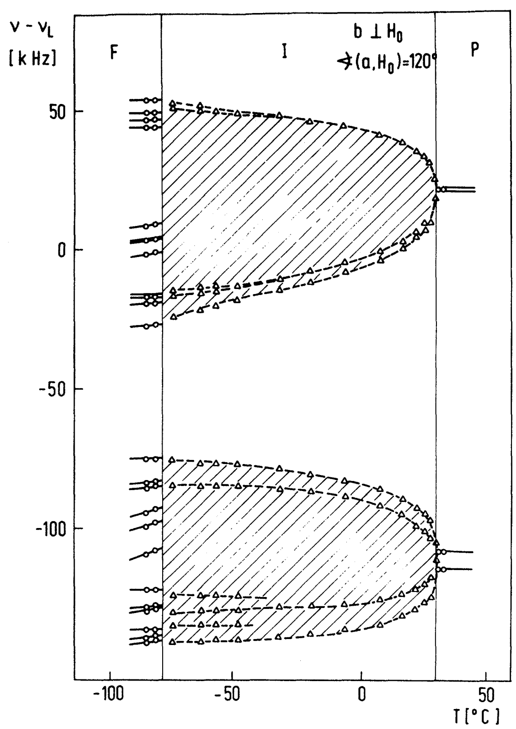

FIG. 1. Temperature dependence of the second-order quadrupole shifts of the $\frac{1}{2} \rightarrow -\frac{1}{2}$ ^{87}Rb NMR lines of Rb_2ZnCl_4 at $\nu_L = 29.5$ MHz. In the hatched region, which is limited by two edge singularities, there is a continuum distribution of resonance lines.

The observed NMR line shape in the I phase (Fig. 2) reflects the distribution of the electric field gradients (EFG) due to the incommensurability of the order parameter (i.e., the frozen-in displacement wave) with the underlying crystal lattice. If we expand the EFG tensors at the Rb sites in powers of lattice displacements, the second-order quadrupole shift of a given ^{87}Rb $\frac{1}{2} \rightarrow -\frac{1}{2}$ transition can be expressed in the "plane-wave limit" as

$$\Delta\nu_i \approx \Delta\nu_{i0} + \Delta\nu_{i1}\cos(q_s z_i + \varphi_0) + \dots, \tag{3}$$

provided that the wavelength of the incommensurable modulation is large compared to the radius of the region where the dominant contribution to the EFG tensor comes from and that terms linear in the order parameter are allowed by symmetry. Here $\Delta\nu_{i0}$ is the second-order quadrupole shift in the P phase and $\Delta\nu_{i1}$ is proportional to the order parameter: $A_0 \propto (T - T_I)^{1/2}$. In the C phase below T_c, $\cos(q_s z_i + \varphi_0)$ takes on a discrete value, while in the I phase the whole crystal is a unit cell and $\cos(q_s z_i + \varphi_0)$ takes on nearly continuously all values between $+1$ and -1 as z_i runs over all equivalent Rb sites. Reducing the phases $\varphi = q_s z_i + \varphi_0$ to the interval $(0, 2\pi)$, one can introduce the phase density $\rho(\varphi)$ which

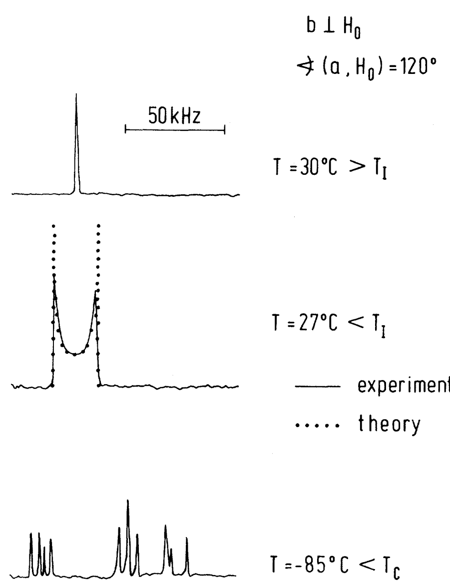

FIG. 2. ^{87}Rb quadrupole-perturbed $\frac{1}{2} \rightarrow -\frac{1}{2}$ NMR line shapes in the paraelectric ($T > T_I$), incommensurable ($T < T_I$), and commensurable ($T < T_c$) phases.

is constant within this interval and zero outside. The frequency distribution $f(\nu)$ of the second-order shifts in the I phase is thus obtained from

$$f(\nu)\,d\nu = \rho(\varphi)\,d\varphi, \tag{4a}$$

as[6]

$$f(\nu) = 1/(2\pi|d\nu/d\varphi|), \tag{4b}$$

where $\int f(\nu)d\nu = 1$. In the "plane-wave" limit, the frequency distribution will be given by

$$f(\nu) = [2\pi\Delta\nu_1(1-x^2)^{1/2}]^{-1}, \tag{4c}$$

where $x = (\Delta\nu - \Delta\nu_0)/\Delta\nu_1$. The edge singularities corresponding to $x = \pm 1$ will occur at $\Delta\nu = \Delta\nu_0 + \Delta\nu_1$ and $\Delta\nu = \Delta\nu_0 - \Delta\nu_1$, where $d\nu/d\varphi = 0$. The frequency separation will be proportional to $(T - T_I)^{1/2}$. The extension of the above analysis to the case where the leading term in the expansion (3) is quadratic is straightforward.[7]

In the "soliton[2] limit", on the other hand, one would expect to see in the I phase sharp "commensurable" lines superimposed on a broad background originating from the incommensurable domain walls. The sharp "commensurable" lines would be practically unchanged at T_c where the broad domain-wall lines would vanish.

The observed ^{87}Rb line shapes in the I phase can be quantitatively (Fig. 2) described by expression (4c) predicted by the "plane-wave" modulation model. The agreement between the theoretical and experimental line shapes is excellent over most of the I phase. Higher-order terms in the expansion (3) have to be taken into account close to T_c. The temperature dependence of the frequency separation between the edge singularities (Fig. 1) and the change in the spectrum on going to the C phase can be as well quantitatively accounted for by the above model and the assumption that the soft-mode eigenvectors are analogous to the ones in K_2SeO_4.[8] The "plane-wave" limit thus provides a surprisingly good description of the I phase. Soliton effects may be important only close to T_c.

The above conclusion is further supported by the ^{87}Rb spin-lattice relaxation data. On approaching T_I from above, T_1—as measured on the $\frac{1}{2} \to -\frac{1}{2}$ lines—exhibits a typical soft-mode behavior (Fig. 3) with T_1 decreasing as $T \to T_I^+$. This is analogous to what is observed in other structural phase transitions. In the I phase, on the other hand, the behavior of T_1 is highly anomalous. T_1 is anomalously short, does not depend on the Larmor frequency, and is—except close to T_I—nearly temperature independent. On closer inspection it turns out that T_1 varies over the I line, i.e., it varies with x and is significantly longer at the edge singularities ($x = \pm 1$) than at the center ($x = 0$) of the frequency distribution (4c). For $x = \pm 1$, T_1 exhibits the normal soft-mode behavior and increases with increasing $(T_I - T)^{1/2}$ whereas it is nearly temperature independent for $x = 0$ (inset to Fig. 3). On cooling below T_c, T_1 sharply increases by an order of magnitude. In the C phase it slowly increases with decreasing temperature. On heating through T_c, there is a small temperature hysteresis of about 2 K.

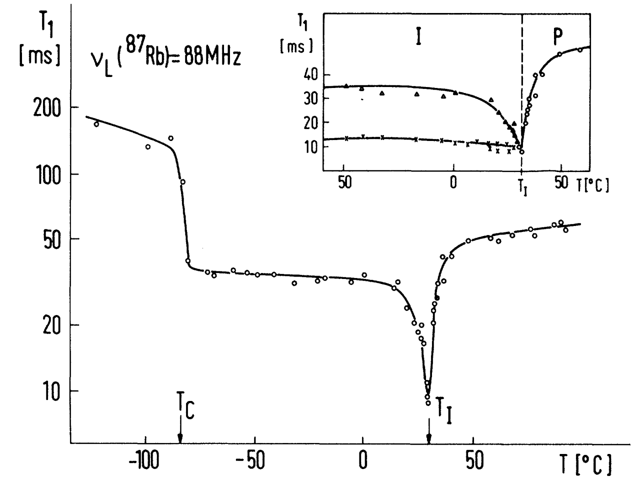

FIG. 3. Temperature dependence of the ^{87}Rb spin-lattice relaxation time in Rb_2ZnCl_4 as measured on a relatively sharp $\frac{1}{2} \to -\frac{1}{2}$ line. The inset shows the temperature dependence of T_1 at the edge singularity (crosses), where $x = \pm 1$, and at the center (triangles) of the incommensurable frequency distribution where $x = 0$. In view of the finite width (Δx) of the signal there is a small phason contribution to T_1^{-1} even at the edge singularity.

The anomalously strong, nearly temperature-independent mechanism which dominates T_1 in the I phase and which disappears on going to the C phase can be most easily explained as being due to the phason branch of the order-parameter excitation spectrum.

The ^{87}Rb relaxation rate in the I phase may be dominated either by direct processes if the phase and amplitude fluctuations are overdamped or by Raman processes if the excitations are underdamped. For direct processes one finds

$$T_1^{-1}(x) \propto x^2 I_A + (1-x^2) I_\varphi, \tag{5a}$$

where I_A and I_φ are the spectral densities of the amplitude (P_{Ak}) and phase ($P_{\varphi k}$) fluctuations of the incommensurable displacement profile (1):

$$I_\alpha \propto \sum_k \int_{-\infty}^{+\infty} \langle P_{\alpha\vec{k}}(0) P_{\alpha\vec{k}}(t)\rangle e^{i\omega t} dt, \quad \alpha = A, \varphi. \tag{5b}$$

Using the fluctuation-dissipation theorem, one finds the amplitudon contribution I_A as

$$I_A \propto \frac{kT}{\kappa^{3/2}} \frac{\Gamma_A}{[2A(T_I - T)]^{1/2}}, \quad T < T_I, \tag{5c}$$

and the phason contribution $I_\varphi > I_A$ as

$$I_\varphi \propto (kT)\kappa^{-3/2}\Gamma_\varphi/\Delta. \tag{5d}$$

Here Δ = const is the gap in the phason spectrum, and Γ_α the damping of the harmonic-oscillator-like phason and amplitudon modes. We assumed that $\omega_A(\vec{k}=0)$ and Δ are much larger than the nuclear Larmor frequency ω_L. If, however, $\Delta < \omega_L$ one finds $I_\varphi \propto \omega_L^{-1/2}$. For Raman processes, on the other hand, we have

$$T_1^{-1}(x) \propto [x^4 J_A + (1-x^2)^2 J_\varphi], \tag{6a}$$

where the spectral densities J_α are always independent of ω_L:

$$J_\alpha \propto \frac{(kT)^2}{\kappa^{5/2}}\left[1 - 2\left(\frac{\omega_\alpha(\vec{k}=0)}{\omega_\alpha(\vec{k}_{max})}\right)^{1/2} + \dots\right], \quad \alpha = A, \varphi, \tag{6b}$$

and where the frequencies ω_α are given by expressions (2a) and (2b). Here too J_A decreases with increasing $(T_I - T)^{1/2}$ whereas J_φ is not critically temperature dependent and—except at $T = T_I$—is larger than J_A.

The observed x dependence of T_1 seems to give a better fit with the "direct" than the "Raman" mechanism though no definite conclusions can be made.

The x dependence of T_1 also allows us to determine I_A and I_φ separately. I_A continuously decreases on cooling from T_I into the C phase, whereas I_φ is temperature independent in the I phase and changes discontinuously at T_c. A comparison between the experimental and theoretical ^{87}Rb T_1 data in the I phase of Rb_2ZnCl_4 thus demonstrates the existence of a phason contribution which is—for $x = 0$—rate determining over the whole I phase. The Larmor frequency independence of T_1 shows the presence of a small gap Δ—which is somewhat larger than ω_L—in the phason spectrum. An analogous phason mode has been observed by ^{87}Rb spin-lattice relaxation as well in Rb_2SnBr_4.[7]

[1]A. Janner and T. Janssen, Phys. Rev. B 15, 643 (1977); P. M. de Wolf, Acta Crystallogr. A33, 493 (1977).

[2]A. D. Bruce and R. A. Cowley, J. Phys. C 11, 3609 (1978).

[3]M. Wada, A. Sawada, and Y. Ishibashi, J. Phys. Soc. Jpn. 45, 1429 (1979).

[4]R. A. Cowley, in *Proceedings of the Fourth European Physical Society General Conference; Trends in Physics, York, England, 1978* (European Physical Society, London, 1979), Chap. 3, p. 176.

[5]K. Gesi and M. Iizumi, J. Phys. Soc. Jpn. 46, 697 (1979).

[6]R. Osredkar, S. Južnič, V. Rutar, J. Seliger, and R. Blinc, to be published.

[7]R. Blinc, V. Rutar, J. Seliger, S. Žumer, Th. Rasing, and I. P. Aleksandrova, to be published.

[8]M. Iizumi, J. D. Axe, G. Shirane, and K. Shimaoka, Phys. Rev. B 15, 4329 (1977).

Photoemission Observation of the Formation of Pd(111) Surface States (Surface Resonances) and Resonant *d* Levels for Pd Overlayers on Nb

Shang-Lin Weng and M. El-Batanouny
Physics Department, Brookhaven National Laboratory, Upton, New York 11973
(Received 13 November 1979)

Photoemission indicates that the formation of the surface states (surface resonances) on the (111) face of ultrathin Pd overlayers on a recrystallized Nb foil commences with the deposition of the third atomic layer and is completely established at the full fourth layer. It also shows the formation of two resonant *d* states at submonolayer coverages, corresponding to the interaction of Pd *d* levels with the Nb bulk bands and to the Pd bulk *d*-band resonance, respectively.

The observation of intrinsic surface states (surface resonances) has become fairly common on metals[1-4] as well as on semiconductors.[5] To date, by the use of advanced experimental and theoretical techniques, much progress has been made in understanding the origin and character