Dynamics in incommensurate phases studied by NMR: Theory and relaxation measurements on ^{87}Rb satellites in Rb_2ZnCl_4

R. Walisch, J. Petersson, and D. Schüssler
Fachbereich Physik, Universität des Saarlandes, Postfach 151150, D 66041 Saarbrücken, Germany

U. Häcker and D. Michel
Fakultät für Physik und Geowissenschaften, Universität Leipzig, Linnéstrasse 5, D 04103 Leipzig, Germany

J. M. Pérez-Mato
Departamento de Fisica de la Materia Condensada, Facultad de Ciencias, Universidad del Pais Vasco, Apartado 644; 48080 Bilbao, Spain

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A general formalism is developed for describing nuclear-spin-lattice relaxation for quadrupolar perturbed nuclear magnetic resonance (NMR) in structurally incommensurately (IC) modulated crystals in terms of the elementary excitations of these systems. Our discussion deviates from previous ones as regards the identification of the amplitudon and phason induced relaxation rates $1/T_{1A}$ and $1/T_{1\phi}$ in the plane wave limit as well as the temperature dependence of $T_{1\phi}$ in the soliton limit. Measurements are reported for the spin-lattice relaxation of the ^{87}Rb satellite transitions in the normal, incommensurate, and commensurate phases of the prototype incommensurate system Rb_2ZnCl_4. At ambient temperature the variation of the nuclear magnetic relaxation rate is measured over the incommensurately broadened distribution of resonance frequencies for two crystal orientations. The T_1 model developed is applied to these data, making use of the Fourier series of the static electric field gradient determined from the NMR satellite spectra in the IC phase. A strict agreement is found. The temperature dependence of T_1 is determined in that crystal orientation where a well-defined assignment of T_{1A} and $T_{1\phi}$ can be given. In the low-temperature part of the incommensurate phase, our data reflect the local softening of phase fluctuations in the discommensurations or the flattening out of the corresponding acoustic branch what is in accordance with our theoretical prediction and in contrast to previous results. The relevance of phason gaps previously derived from NMR data is discussed.

I. INTRODUCTION

In incommensurately (IC) modulated structures the translational symmetry of the lattice is broken by a modulation, the period of which is not a rational multiple of a basic lattice vector. As a consequence, the phase of the modulation relative to the basic lattice is arbitrary or, equivalently, the IC structure is continuously degenerated with respect to a phase shift.[1] Thus, special low-energy excitations are to be expected in incommensurate systems.

Though direct experimental attempts to detect these soft phase modes by usual methods as Raman and neutron scattering failed in most cases due to the relaxatory character or overdamping of these modes, their existence is revealed quite unambiguously by the unusual short spin-lattice relaxation in NMR and NQR experiments.[2-6]

Here we are dealing with quadrupolar perturbed ^{87}Rb NMR studies of the IC prototype system rubidium tetrachlorozincate (Rb_2ZnCl_4, abbreviated as RZC). In this method the local probe consists in the interaction of the nuclear quadrupole moment of the nucleus under investigation with the electric-field gradient (EFG) at its lattice site. Because of its high NMR sensitivity and its big quadrupole moment the ^{87}Rb nucleus ($I=\frac{3}{2}$) is very suitable for these measurements.

RZC belongs to the large A_2BX_4 family and is one of the most extensively studied IC substances. The IC phase of RZC extends over a very large temperature range limited by a normal (N) phase at $T_i \approx 30\,^{\circ}C$ and a commensurate (C) phase at $T_c \approx -80\,^{\circ}C$. The structure of the N phase (which defines the basic structure of the IC phase) is orthorhombic and belongs to the space group $Pcmn$ (in this notation $a > c > b$ holds for the lattice constants). Below T_i, this basic structure is modulated along the z direction with an incommensurate periodicity close to $3c$. At T_c the modulation wave vector locks in at the commensurate value $c^*/3$ corresponding to a tripling of the unit cell along the z direction.

The dynamics in RZC has been investigated by means of ^{87}Rb NMR (Refs. 2, 3, 6, and 7) and ^{35}Cl NQR.[4,5] Until now, these NMR studies have been restricted to the ^{87}Rb $m=-\frac{1}{2}\leftrightarrow+\frac{1}{2}$ central transition[2,3,6] or to the N phase.[7] In Sec. III we present measurements of the spin-lattice relaxation time T_1 of the $m=\pm\frac{1}{2}\leftrightarrow\pm\frac{3}{2}$ ^{87}Rb satellite transitions in the N, IC, and a small part of the C phase of RZC.

The satellite transition frequencies are mainly deter-

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mined by first-order quadrupolar perturbation terms, while the central transition frequency is only affected by terms of higher order. Thus, frequency shifts are much higher and formulas much simpler for the satellites than for the central transition. In preceding works[8–13] it was shown that the statics of IC systems can be investigated with high accuracy by measuring satellite frequencies. At first sight, these advantages of satellite transition studies seem not to be important for the dynamics, since the spin-lattice relaxation is, of course, induced by the same off-diagonal elements of the quadrupolar perturbation Hamiltonian for both transitions. For a more detailed interpretation of the T_1 data, however, one has to attribute the $1/T_1$ modulation to the frequency modulation which both originate from the IC modulation of the crystal. So again the simple functional relationship between EFG and frequencies in the case of the satellite transitions is advantageous. Moreover, the phase relations between the components of the (static) EFG Fourier series needed for the interpretation of T_1 data can practically be determined only by investigating the satellite transitions.

Because of the above-mentioned disadvantages of central transition studies, in earlier NMR works an oversimplified so-called "local" model postulating simple phase relations for the EFG Fourier components in the IC phase was used and seemed to be sufficient for describing the EFG modulation. The correct treatment of the EFG in the IC phase as a complex quantity with Fourier components differing in phase, however, has important consequences for the interpretation of the spectra[9,11] and, as will be shown in Sec. II B, also of the T_1 data. So far, this property of the EFG has not been taken into account adequately, though a so-called "nonlocal" model was already presented.[3] Further essential refinements of previous theoretical descriptions of the spin-lattice relaxation in IC systems are necessary for the "soliton limit" too, as discussed in Sec. II C.

The experimental results to be presented in Sec. III will be discussed in relation to the theoretical models developed in Sec. II. In particular, the existence of soft phase fluctuations in the entire IC phase is demonstrated by our experiments. Moreover, the T_1 data presented here reflect the local softening of the phase fluctuations in the discommensurations or the flattening out of the corresponding "acoustic" branch near the IC-C phase transition.

II. THEORY

A. Basics

The basic theoretical description of T_1 in IC phases widely used is given in Refs. 3, 6, 14, and 15. As will be shown below, however, this formalism needs some corrections. As far as the procedure is similar to that of these works we shall omit details and try to focus on the essential points.

In the case of ^{87}Rb NMR experiments the dominant perturbation $\hat{H}_Q$ of the Zeeman Hamiltonian is due to the interaction of the EFG V with the nuclear quadrupole moment $Q_{\rm nuc}$, which can be treated by perturbation theory. As a result, the frequency shift of the $m=\pm\frac{1}{2}\leftrightarrow\pm\frac{3}{2}$ satellite transitions with respect to the Larmor frequency $\nu_L=\omega_L/(2\pi)$ is predominantly determined by the first-order term

$$\nu_1=\frac{eQ_{\rm nuc}}{2h}V_{zz} \tag{1}$$

of the quadrupole perturbation, which is simply proportional to the element V_{zz} of the EFG tensor given in the laboratory frame (x,y,z) with z parallel to the external static magnetic field $\mathbf{B}_0$.[16] In contrast, the frequency of the $m=+\frac{1}{2}\leftrightarrow-\frac{1}{2}$ central transition is to be calculated as a more complicated quadratic form in the EFG elements according to second-order perturbation theory.

The spin-lattice relaxation is given by the return of the nuclear-spin magnetization $M_z(t)$ back to its thermal equilibrium value after a preceding radio frequency excitation.[16] In particular, one obtains for the relaxation of a satellite line after a preceding 90° radio frequency pulse (with no further lines excited) (Ref. 17)

$$M_z(t)=M_z(t=\infty)[1-\tfrac{1}{2}(e^{-2W_1t}+e^{-(2W_1+2W_2)t})], \tag{2}$$

where W_μ stands for the probability of a quantum transition $\Delta m=\mu$, $\mu=1,2$ induced by fluctuations of $\hat{H}_Q(t)$. Note that $W_\mu=0$ for $\mu>2$. For a nucleus with spin $I=\frac{3}{2}$ as ^{87}Rb it is found[14,16,18]

$$W_1/C=J(V_{xz}^2;\omega_L)+J(V_{yz}^2;\omega_L), \tag{3a}$$

$$W_2/C=J[\tfrac{1}{4}(V_{xx}-V_{yy})^2;2\omega_L]+J(V_{xy}^2;2\omega_L), \tag{3b}$$

where

$$J(V_{ij}^2;\mu\omega_L)=\int_{-\infty}^{\infty}\langle\delta V_{ij}(0)\delta V_{ij}(t)\rangle e^{-i\mu\omega_L t}dt \tag{4}$$

is the spectral density of the EFG fluctuations δV_{ij} at the frequencies $\mu\omega_L$ ($\mu=1,2$) and $C=e^2Q_{\rm nuc}^2/(12\hbar^2)$. Here (x,y,z) again denotes the laboratory frame defined by $\mathbf{z}\|\mathbf{B}_0$.

In the relaxation process considered here, per quantum transition the energy of the spin system is directly transferred to a single mode of the lattice fluctuations. This direct one-phonon process is dominant, if an overdamped or relaxatory soft mode is present[14] contributing to the spectral density $J(V_{ij}^2;\mu\omega_L)$ at the comparatively low Larmor frequency $\nu_L\approx100$ MHz, and thus applies to our investigations on RZC.[19,20] The alternative relaxation process, the two-phonon (Raman) process, can be relevant for the noncritical background relaxation.[13]

As there is a dominant linear coupling of the EFG to the order parameter (see Sec. II B), the corresponding spectral densities are simply proportional. Thus, the spin-lattice relaxation is determined by the spectral densities $J(\omega,\mathbf{T})$ of the *local* fluctuations at the Larmor frequency $\omega=\omega_L$, where $\mathbf{T}$ defines the unit cell of the basic lattice. Considering normal modes $Q_{\mathbf{k}}(\mathbf{T},t)=\Psi_{\mathbf{k}}(\mathbf{T})a(\mathbf{k},t)$ separated into space-dependent eigenfunctions $\Psi_{\mathbf{k}}(\mathbf{T})$ and time-dependent normal coordinates $a(\mathbf{k},t)$ (Refs. 1, 21, and 22) and defining

$$J_a(\omega,\mathbf{k})=\int_{-\infty}^{\infty}\langle a(\mathbf{k},0)a^*(\mathbf{k},t)\rangle e^{-i\omega t}dt\ , \tag{5}$$

the spectral density $J_{\mathbf{k}}(\omega,\mathbf{T})$, i.e., the Fourier transform of the correlation function, of $Q_{\mathbf{k}}(\mathbf{T},t)$ can be written as

$$J_{\mathbf{k}}(\omega,\mathbf{T})=|\Psi_{\mathbf{k}}(\mathbf{T})|^2 J_a(\omega,\mathbf{k})\ . \tag{6}$$

$J_a(\omega,\mathbf{k})$ is related to the imaginary part of the normal mode susceptibility $\chi_a''(\omega,\mathbf{k})$ by the (classical) fluctuation-dissipation theorem as[14]

$$J_a(\omega,\mathbf{k})=2k_BT\frac{\chi_a''(\omega,\mathbf{k})}{\omega}$$

$$=2k_BT\frac{\Gamma_a}{[\omega_a^2(\mathbf{k})-\omega^2]^2+\Gamma_a^2\omega^2}\ , \tag{7a}$$

$$=2k_BT\frac{\chi_a(\omega=0,\mathbf{k})\tau_a(\mathbf{k})}{1+\omega^2\tau_a^2(\mathbf{k})}\ , \tag{7b}$$

for the damped oscillator (a) or the relaxator model (b). While $J_a(\omega,\mathbf{k})$ contains the dispersion relation of the respective branch, $|\Psi_{\mathbf{k}}(\mathbf{T})|^2$ determines the spatial distribution of the corresponding modes. The *local* spectral density $J(\omega,\mathbf{T})$ relevant for the spin-lattice relaxation is given by the *mean value*

$$J(\omega,\mathbf{T})=\frac{1}{n}\sum_{\mathbf{k}=\mathbf{k}_1,\ldots,\mathbf{k}_n}J_{\mathbf{k}}(\omega,\mathbf{T}) \tag{8}$$

taken over the respective Brillouin zone. Notice that the factor $1/n$ originates from the equipartition theorem making $J(\omega,\mathbf{T})$ independent of the crystal volume. Usually this factor is "hidden" in the normalization of $\Psi_{\mathbf{k}}(\mathbf{T})$, but here it is taken out of $\Psi_{\mathbf{k}}(\mathbf{T})$ for illustrative reasons.

As the Larmor frequency is low compared to usual modes frequencies (see above), $1/T_1\propto J(\omega,\mathbf{T})$ probes locally the softness (the susceptibility) of the present fluctuations. To see the essential point, notice that according to (7)

$$J_a(\omega=0,\mathbf{k})\propto\Gamma_a\omega_a^{-4}(\mathbf{k})=\chi_a(\omega=0,\mathbf{k})\tau_a(\mathbf{k})$$

reminding the reader that $\chi_a(\omega=0,\mathbf{k})=\omega_a^{-2}(\mathbf{k})$ and $\tau_a(\mathbf{k})$ can be formally identified with $\Gamma_a\omega_a^{-2}(\mathbf{k})$. To be more precise: T_1 decreases for softening fluctuations, as long as the fast motion condition $\omega_L\ll\omega_a(\mathbf{k})$ or $\omega_L\tau_a(\mathbf{k})\ll 1$ holds for *all* $\mathbf{k}$.[14]

B. Plane-wave limit

In the upper part of the IC phase the order parameter (OP) represents the first harmonic of the modulation (plane-wave limit, PWL):

$$\mathbf{u}_0^a(\mathbf{T})=\mathbf{e}_1^aQ_0e^{i\mathbf{q}_i\cdot\mathbf{T}}+\text{c.c.},\quad Q_0=\rho_0e^{i\Phi_0}\ . \tag{9}$$

Here $\mathbf{u}_0^a(\mathbf{T})$ is the "displacement" of the ath atom in the unit cell of the basic lattice defined by $\mathbf{T}$, and $\mathbf{e}_1^a$ is the polarization vector of the primary modulation with the modulation wave vector $\mathbf{q}_i$. The quotation marks indicate that this variable can be interpreted as well as a pseudospin of an order-disorder mechanism. The Taylor expansion of the static EFG in terms of these displacements results in a Fourier series,[8,9] reflecting the fact that the EFG must adapt, as a local quantity, to the periodicity of the lattice modulation. Restricting to the first harmonic and omitting the homogeneous, nonmodulated part, the EFG modulation is given by

$$V^a(\mathbf{T})=V_1^ae^{i\mathbf{q}_i\cdot\mathbf{T}}+\text{c.c.},\quad V_1^a=A_1^aQ_0\ . \tag{10}$$

The analogy between (9) and (10) is obvious. In this sense, the tensor A_1^a may be termed the "polarization tensor" of the EFG first harmonic. Notice that A_1^a, as well as $\mathbf{e}_1^a$, is a complex quantity containing the different phases of the different tensor components V_{1ij} with respect to the OP phase.

Disregarding the wave-vector dependence of the polarization vector, i.e., $\mathbf{e}_1^a(\mathbf{q}_i+\mathbf{k})\approx\mathbf{e}_1^a(\mathbf{q}_i)\equiv\mathbf{e}_1^a$, and thus concentrating on the long-wavelength fluctuations of the OP, the fluctuating part of $\mathbf{u}^a(\mathbf{T})$ can be written as

$$\delta\mathbf{u}^a(\mathbf{T},t)=\mathbf{e}_1^a\delta Q(\mathbf{T},t)e^{i\mathbf{q}_i\cdot\mathbf{T}}+\text{c.c.}\ , \tag{11}$$

where $\langle\delta Q(\mathbf{T},t)\rangle\equiv 0$ by definition. Again one has, now assuming $A_1^a(\mathbf{q}_i+\mathbf{k})\approx A_1^a(\mathbf{q}_i)\equiv A_1^a$, an analogous expression for the fluctuating part of the EFG:

$$\delta V^a(\mathbf{T},t)=A_1^a\delta Q(\mathbf{T},t)e^{i\mathbf{q}_i\cdot\mathbf{T}}+\text{c.c.} \tag{12}$$

Equation (12) can be derived easily from the Taylor expansion of the EFG in terms of the atomic displacements as given, e.g., in Ref. 8, but we refrain from details here, since (12) is the simple variation of the static case expressed by (10) for fluctuations of Q_0. We just note that the assumed wave-vector independence of A_1^a is based upon the wave-vector independence of the polarization vector $\mathbf{e}_1^a$ and the assumption $\delta Q(\mathbf{T}',t)\approx\delta Q(\mathbf{T},t)$ for fluctuations in the unit cells $\mathbf{T}'$ contributing significantly to $\delta V^a(\mathbf{T},t)$ in the unit cell $\mathbf{T}$.

Comparing (10) and (12) it is found that the complex tensor A_1^a coupling the EFG to the OP is the same for both the static and the dynamic part. Thus, the phase relations determined for the Fourier components of the static EFG in the IC phase can be used for the interpretation of the T_1 data. This will be demonstrated in Sec. III. In previous works[3,6] the (approximate) equality of atomic masses was supposed to be necessary for deriving this result.

It is useful to transform the complex OP $Q(\mathbf{T},t)$ into the coordinates $P_1(\mathbf{T},t)$, $P_2(\mathbf{T},t)$ defined by

$$Q(\mathbf{T},t)e^{-i\Phi_0}=P_1(\mathbf{T},t)+iP_2(\mathbf{T},t)\ , \tag{13}$$

which represent the real and imaginary parts of the order parameter rotated in the complex OP plane by $-\Phi_0$ or, in other words, the longitudinal and transverse part of the OP.[1,23,24] Accordingly, one has $\langle P_1\rangle=\rho_0$ and $\langle P_2\rangle=0$ for the static parts of P_1 and P_2 reminding $Q_0\equiv\langle Q\rangle=\rho_0\exp(i\Phi_0)$. As the static OP situated in a circle-symmetric potential defines a mirror axis along P_1 in the complex OP space, $\langle P_1P_2\rangle=-\langle P_1P_2\rangle=0$, i.e., P_1 and P_2 decouple in the PWL. (This decoupling also results from the usual Landau theory.[1,23,24])

In a linear approximation for fluctuations of $Q=\rho\exp(i\Phi)$, δP_1 and δP_2 correspond to fluctuations of the amplitude ($\delta\rho$) and phase ($\rho_0\delta\Phi$) of the OP; therefore

they are often termed "amplitudon" and "phason," which subsequently will be indicated by the indices A and ϕ, respectively.

Combining (12) and (13), δV^a can be described in terms of δP_1 and δP_2. Thus, the transition probabilities W_μ, $\mu=1,2$, given in Eqs. (3a) and (3b) can be related to the spectral densities J_1 and J_2 of δP_1 and δP_2, respectively, defined analogously to (4) according to

$$W_\mu(v)/C = D_\mu[J_1+J_2] + E_\mu[J_1-J_2]\cos[2(v+\Phi_0+\varphi_\mu)] , \tag{14}$$

where $v=\mathbf{q}_i\cdot\mathbf{T}$, $J_\beta\equiv J_\beta(\mu\omega_L)$, $\beta=1,2$, and

$$\begin{aligned} D_1 &= |A_{1xz}|^2+|A_{1yz}|^2 , \\ D_2 &= \tfrac{1}{4}|A_{1xx}-A_{1yy}|^2+|A_{1xy}|^2 , \\ (A_{1xz})^2+(A_{1yz})^2 &= E_1 e^{2i\varphi_1} , \\ \tfrac{1}{4}(A_{1xx}-A_{1yy})^2+(A_{1xy})^2 &= E_2 e^{2i\varphi_2} . \end{aligned} \tag{15}$$

The index a specifying the atom or nucleus is dropped for simplicity. Note that the spatial dependence of $W_\mu(v)$ in (14) does not originate from J_1 and J_2, which are spatially independent according to (6) and (8) as the eigenfunctions $\Psi_{\mathbf{k}}(\mathbf{T})$ are simple harmonic plane waves of the form $\exp(i\mathbf{k}\cdot\mathbf{T})$. The variable v reduced to the interval $[0,2\pi)$ is a continuous one because of the incommensurability of $\mathbf{q}_i$ with respect to the basic lattice.[8,9] A more detailed derivation of (14) including the explicit definition of J_1 and J_2 is given in the Appendix.

In the N phase, the P_1 and P_2 coordinates degenerate as transverse and longitudinal coordinates are not defined, and (14) applies with $J_1=J_2$. Consequently the modulated term disappears. Below T_i this term rapidly grows: the P_1 fluctuations harden like the OP fluctuations for a usual commensurate lower symmetry phase, while the P_2 fluctuations retain the soft-mode susceptibility at T_i.[1,15,23,24] Thus, J_1 decreases while J_2 is expected to be nearly temperature independent, i.e., proportional to the absolute temperature T according to the fluctuation-dissipation theorem [cf. Eq. (7)]. Notice the unusual softness of the P_2 (phase) fluctuations, which is a direct consequence of the incommensurate structure resulting in the arbitrariness of the phase Φ_0 of the static OP.[1]

For $D_\mu=E_\mu$, Eq. (14) can be rewritten as

$$W_\mu(v)/C = 2D_\mu[J_1\cos^2(v+\Phi_0+\varphi_\mu) + J_2\sin^2(v+\Phi_0+\varphi_\mu)] . \tag{16}$$

This special case corresponds to the result given in previous works [e.g., Eq. (39) in Ref. 3 or Eq. (3.82) in Ref. 6], though the general case was assumed explicitly by the authors. According to equations such as (16) used previously, J_1 and J_2 are directly given by the minimum and maximum, respectively, of $W_\mu(v)$ reminding $J_1<J_2$. However, from (14) one derives

$$\begin{aligned} \max[W_\mu(v)/C] &= (D_\mu-E_\mu)J_1+(D_\mu+E_\mu)J_2 , \\ \min[W_\mu(v)/C] &= (D_\mu+E_\mu)J_1+(D_\mu-E_\mu)J_2 , \end{aligned} \tag{17}$$

with $D_\mu\neq E_\mu$ in the general case. [Considering for instance $W_1(v)$, the special case $D_\mu=E_\mu$ is only realized, if the phases of A_{1xz} and A_{1yz}, i.e., the phases of the first harmonics of $V_{xz}(v)$ and $V_{yz}(v)$, are equal or shifted by π.] Therefore, in general, the "phason" and "amplitudon" contributions are mixed in the extrema of $W_\mu(v)$. Notice that W_μ is not modulated at all if $E_\mu=0$. [This case occurs, e.g., for E_1 if $A_{1xz}=\pm iA_{1yz}$.]

Evidently, because of $J_2\gg J_1$ for bigger T_i-T, the influence of J_2 on the minimum of $W_\mu(v)$ is considerably higher than vice versa that of J_1 on the maximum. Accordingly, the use of equations such as (16) may have lead to "amplitudon" contributions $1/T_{1A}\propto J_1$ which are too high since "contaminated" by the large "phason" spectral density. Indeed, there are some indications for too high "amplitudon" contributions $1/T_{1A}$ given in previous publications. We shall come back to this point in Sec. III.

C. Soliton limit

In the lower part of the IC phase the so-called soliton limit (SL) holds, where the primary modulation can no longer be described by a simple harmonic plane wave and thus by the OP $Q\equiv Q(\mathbf{q}_i)$ used above. Rather it is useful to introduce an OP $Q(\mathbf{T})$ expressing the modulation with respect to the commensurate modulation $\exp(i\mathbf{q}_c\cdot\mathbf{T})$ of the commensurate phase. The displacement of the atom a is then written as

$$\mathbf{u}_0^a(\mathbf{T})+\delta\mathbf{u}^a(\mathbf{T},t)=\mathbf{e}_1^a[Q_0(\mathbf{T})+\delta Q(\mathbf{T},t)]e^{i\mathbf{q}_c\cdot\mathbf{T}}+\text{c.c.} \tag{18}$$

As usual, we introduce polar coordinates (ρ,θ) in the OP space by

$$Q_0(\mathbf{T})+\delta Q(\mathbf{T},t)=[\rho_0(\mathbf{T})+\delta\rho(\mathbf{T},t)]e^{i[\theta_0(\mathbf{T})+\delta\theta(\mathbf{T},t)]} . \tag{19}$$

In the PWL the relation $Q_0(\mathbf{T})=Q_0^{\mathrm{PWL}}\exp(i\delta\cdot\mathbf{T})$ with $\delta=\mathbf{q}_i-\mathbf{q}_c$ holds, where the spatially independent OP used in Sec. II A was labeled explicitly. On approaching T_c, this linear relationship between the T component in modulation direction (for RZC the z direction using *Pcmn* notation) and the OP phase θ_0 is deformed to a periodic function of increasing steplike character,[6,15,23,25,26] where strongly T-dependent regions separate regions with weak T dependence. As the OP $Q(\mathbf{T})$ now expresses the modulation with respect to the commensurate phase (see above), the latter correspond to nearly commensurate regions (C regions) while the former are called discommensurations (DC's) or solitons. Because of the regular periodic arrangement the resulting structure is called the soliton lattice. For systems with a small anisotropy parameter in the Landau expansion (such as RZC) as reflected by a large temperature range of the IC phase, the OP amplitude ρ_0 can be assumed to be only weakly modulated for $T\to T_c$ with a smaller value in the DC's as in the C regions.

On approaching T_c (phase) fluctuations soften locally

in the DC's reflecting the beginning instability or softening of the soliton lattice, whereas fluctuations harden locally in the C regions reflecting the approach to the commensurate structure for which the softness of the phase fluctuations disappears. As T_1 locally probes the softness of the present fluctuations getting shorter with increasing softness (see Sec. II A), T_1 can be expected to decrease locally in the DC's and to increase locally in the C regions. Essentially this is the whole story. However, previous works[6,14,27,28] came to a different result predicting an increase of T_1 for the DC's. So we feel obliged to explain the qualitative argument just given more extensively.

As in the PWL, in the SL one can distinguish between the spectral densities of the amplitude (longitudinal) fluctuations J_ρ and the phase (transversal) fluctuations J_θ corresponding to J_1 and J_2 in the PWL. Restricting to terms coupling linearly to the OP, the transition probability W_μ of the spin-lattice relaxation can be represented on the complete analogy of (14) as the modulation

$$W_\mu(v)/C = D_\mu(J_\rho + J_\theta) + E_\mu(J_\rho - J_\theta)\cos\{2[\theta_I(v)+\varphi_\mu]\}\ , \qquad (20)$$

where $\theta_I(v) \equiv \theta_0(\mathbf{T}) + \mathbf{q}_c \cdot \mathbf{T}$ as well as the modulation variable v are appropriately reduced to the interval $[0, 2\pi)$.[8] The coefficients E_μ and D_μ were defined in (15).

The amplitude fluctuations may be assumed to be only weakly affected by the soliton structure for the weak anisotropy system under consideration[22] (on the analogy of the statics) and, moreover, to be comparatively hard and therefore of minor relevance for the spin-lattice relaxation. Just the opposite is true for the phase fluctuations: they are soft—yielding relevant contributions to $J(\omega, \mathbf{T})$ at the Larmor frequency—and strongly influenced by the IC-C phase transition and the soliton structure. So we will focus on these phase fluctuations in the following.

In the PWL, eigenfunctions $\Psi_{\mathbf{k}}(\mathbf{T})$ are simple harmonic plane waves of the form $\exp(i\mathbf{k}\cdot\mathbf{T})$ resulting in spatially independent spectral densities $J_{\mathbf{k}}(\omega, \mathbf{T})$ according to (6). This, of course, no longer holds in the SL. There, eigenfunctions are given by more complicated Bloch functions adapted to the periodicity L of the soliton lattice: The eigenfunctions and eigenfrequencies obey an equation corresponding to the Schrödinger equation of a particle moving in a periodic potential.[1,21,29,22] Under the influence of the periodic potential (defined by the soliton lattice), essentially the phase fluctuations split into two branches separated by a large gap at the boundary of the Brillouin zone of the soliton lattice ($k_z = \pi/L = p\delta/2$, $p = 6$ for RZC), as shown in Fig. 1. The soft, lower-frequency ("acoustic") branch represents phase fluctuations concentrated in the DC's. These phase fluctuations correspond to oscillations (or relaxations) of the DC's in the modulation ($\mathbf{q}_c$) direction, and the dynamics is that of a linear chain with a next-neighbor DC interaction decreasing as $\exp(-\alpha L)$ with increasing soliton distance L.[1,21] This branch vanishes as the soliton lattice periodicity disappears at the transition into the C phase. In an ideal incommensurate crystal, the nonmodulated ($\mathbf{k}=0$) mode of this branch is completely soft or gapless in analogy to the phase fluctuations in the PWL. Lattice defects

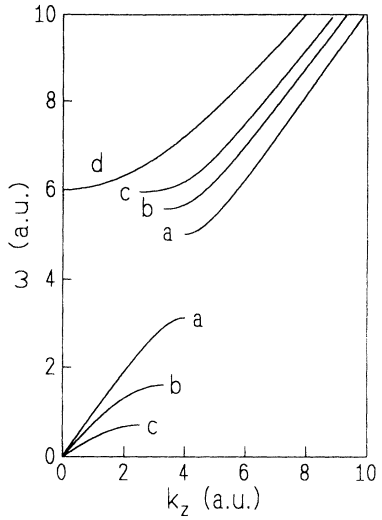

FIG. 1. Schematic plot of the dispersion $\omega(k_z) \propto \chi^{-1/2}(k_z) \propto \tau^{-1/2}(k_z)$ along the modulation direction of the "acoustic" (lower) branch and the "optic" (upper) branch of the phase fluctuations in the soliton limit given in the cases a,b,c for three different temperatures on approaching T_c from above. The line indicated by d represents the corresponding dispersion remaining in the commensurate phase below T_c. The gap between both branches appears at the wave vector $k_z = \pi/L$ (Brillouin zone boundary of the soliton lattice) decreasing for $T \to T_c$ as L increases. According to Ref. 25.

as well as a (high) commensurability of the basic and the soliton lattice can pin the soliton lattice in the real crystal thus producing a gap for $\mathbf{k}=0$. The second branch represents comparatively hard, high-frequency ("optic") phase fluctuations concentrated in the C regions. Accordingly, this is the branch persisting in the C phase.

Now, according to the general arguments given in Sec. II A in context with Eqs. (5)–(8), a local softening means that the *mean value* of $J_a(\omega, \mathbf{k})$ which is to be taken over the dispersion of the respective branch becomes higher at small frequencies such as the Larmor frequency. Corresponding, on approaching T_c the phase fluctuations soften locally in the DC's as the slope of the "acoustic" branch decreases, reflecting the decreasing DC interaction mentioned above and so simply the softening of the soliton lattice itself. This is also revealed experimentally for RZC by dielectric measurements, which can be described, in a good approximation, by a simple monodispersive Debye relaxator[30,31] (apart from a small temperature range $\Delta T < 0.5$ K close to T_c). These measurements, coupling to the fluctuations of the "acoustic" branch at the boundary $\mathbf{k}_z = \pi/L$ of the Brillouin zone of the soliton lattice,[29] show a decrease of the relaxation rate $1/[2\pi\tau(\mathbf{k}_z = \pi/L)]$ from about 2500 MHz at $T - T_c = 19$ K down to about 100 MHz at $T \approx T_c$.[30,31] It is well known, however, that crystal quality is important in this context. As demonstrated by other dielectric constant studies on RZC,[32] the decrease of the relaxation rates on approaching T_c is diminished for poor quality crystals and the deviations from monodispersive relaxation behavior increase.

On the other hand, the hardening of phase fluctuations

in the C regions is to be attributed to the gap of the "optic" branch reflecting the approach to commensurability of these regions. The corresponding eigenfunctions $\Psi_{\mathbf{k}}(\mathbf{T})$ concentrate the respective behavior locally to the DC's for the "acoustic" branch and to the C regions for the "optic" branch.

Reminding the reader that $1/T_1 \propto J(\omega,\mathbf{T})$, we conclude that the "phason"-induced T_1 is expected to *decrease* for nuclei located *in the DC's* and to *increase* for nuclei located *in the C regions* on passing from the PWL to the SL (i.e., on approaching T_c). As already mentioned after Eq.(8) for the general case, the decrease of the T_1 of nuclei located in the DC's would come to an end, if $\omega_L \gg \omega_a(\mathbf{k})$ or $\omega_L \tau_a(\mathbf{k}) \gg 1$ for *all* $\mathbf{k}$ of the acoustic branch. But this is a theoretical case.

In contrast, previous publications[6,14,27,28] predicted an increase of the T_1 in the DC's on approaching T_c from above proportional to the soliton distance $L \propto 1/N_s$ with N_s denoting the number of solitons or DC's. However, as far as we see it, therein the local spectral density $J(\omega,\mathbf{T}) \propto 1/T_1$ was taken as the *sum* of $J_{\mathbf{k}}(\omega,\mathbf{T})$ over the "acoustic" branch and not as the *mean value* as expressed by (8). As a consequence, a factor L is overseen which cancels the $1/L$ behavior of $1/T_1$ predicted in the works cited. We remind that the "acoustic" branch represents the oscillation or relaxation of the DC's. Consequently, for these modes, the reference lattice is the soliton lattice with the lattice constant L (in the z direction) and thus $n = N_x N_y N_s$ in Eq. (8), while for the normal modes in the PWL $n = N_x N_y N_z = N$ [cf. Eq. (A5)] referring to the basic lattice, where N_x gives the number of basic lattice cells in the x direction, etc. The same result is obtained by the correct normalization of the corresponding eigenfunctions $\Psi_{\mathbf{k}}(T)$.[33] Applying the argument given in previous works to a usual lattice (no soliton lattice) would mean that $1/T_1$ would decrease with a decreasing number of unit cells, what cannot be true. The (local) DC fluctuations and thus the corresponding spin-lattice relaxation depend on N_s or L only in that sense that the DC interaction decreases with increasing L resulting in a softening of the DC fluctuations and thus in a decrease of the corresponding T_1. Of course, a decreasing number of solitons $N_s \propto 1/L$ results in a decrease of the *intensity* of those parts representing the DC's in the NMR spectrum.

In addition, in the works cited the gap $\omega_a(\mathbf{k}=0)$ of the eigenfrequencies of the "acoustic" branch is assumed to be so large that the whole dispersion $\omega_a(\mathbf{k})$ is practically constant even for $\mathbf{k} \perp \mathbf{q}_c$, i.e., *perpendicular* to the modulation direction. Of course, on this condition, any flattening out of the branch along $\mathbf{q}_c$ becomes irrelevant. The mentioned assumption presupposes an extreme hardening in particular for the $\mathbf{k}=0$ mode and consequently for the whole "acoustic" branch and thus conflicts with the dielectric measurements on RZC mentioned above. Moreover, it could be asked, if, under this condition, the "acoustic" branch would give any detectable contribution to the direct process of the spin-lattice relaxation at all.

III. EXPERIMENTAL RESULTS AND DISCUSSION

The spin-lattice relaxation of the upper-frequency satellite line of ^{87}Rb in RZC was measured for Rb(1) (as defined in Ref. 9) in the crystal orientations $\mathbf{b} \| \mathbf{B}_0$ and $\mathbf{c} \| \mathbf{B}_0$ using a Bruker CXP 300 NMR spectrometer operating at a frequency $\nu_L = 98.2$ MHz. In general the standard $(90°)_x - \tau - (90°)_x$ pulse sequence was applied. When detecting the whole IC spectrum and not only its singularities, however, a $(90°)_x - \tau - (90°)_x - \delta - (90°)_\alpha$ pulse sequence with an echo pulse distance $\delta = 250\ \mu$s and an alternating pulse phase $\alpha = \pm x$ (suppression of stimulated echoes) was used. The samples investigated were cut from the same crystal grown from aqueous solution of RbCl and $ZnCl_2$ with a molar ratio of 2:1. Further experimental details were already described in Refs. 9, 10, and 13.

The temperature dependence of the ^{87}Rb(1) satellite spectrum in the N, IC, and C phase of RZC is shown exemplarily in Fig. 2 for the crystal orientation $\mathbf{b} \| \mathbf{B}_0$. The frequencies of the discrete NMR lines in the N and C phases and those of the edge singularities in the IC phase were measured[33] for both satellites ($m = +\frac{3}{2} \leftrightarrow +\frac{1}{2}$ and $m = -\frac{3}{2} \leftrightarrow -\frac{1}{2}$) on stepwise heating above $T \approx 11$ °C and stepwise cooling below this temperature.

Because of crystal symmetry, in the orientations $\mathbf{b} \| \mathbf{B}_0$ and $\mathbf{c} \| \mathbf{B}_0$ investigated one obtains per each Rb kind Rb(1,2) and satellite transition one discrete line in the N phase and three discrete lines in the C phase reflecting the tripling of the unit cell.[9] On passing from the N into the IC phase, the discrete line of the N phase splits into a frequency distribution limited by two edge singularities. The width of this distribution (i.e., the edge singularity distance) increases on lowering the temperature as the amplitude of the modulation increases.[8-13]

In the vicinity of the IC-C phase transition, the ^{87}Rb satellite spectra were measured for the upper-frequency satellite on stepwise heating. The spectra obtained are shown in Fig. 3. The marked changes in line shape and amplitude between $T = -78.1$°C and -77.6°C reflect the IC-C phase transition. From our measurements the difference ΔT_c for T_c obtained on heating and cooling

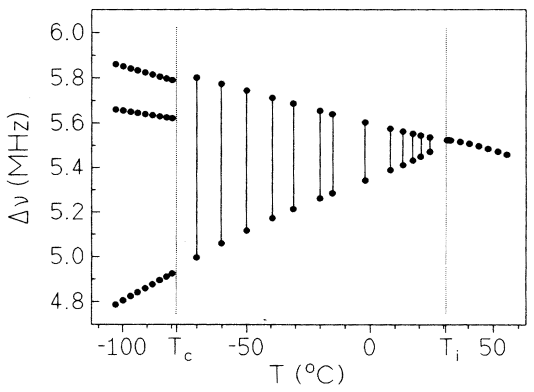

FIG. 2. Temperature dependence of the quadrupolar splittings $\Delta\nu$ of the edge singularities (IC phase) and discrete lines (N and C phase) of the ^{87}Rb satellite spectrum of Rb(1) in RZC in the crystal orientation $\mathbf{b} \| \mathbf{B}_0$. Disregarding second-order effects, the corresponding frequencies $\nu_\pm$ of the upper and lower frequency satellite transition are given by $\nu_\pm = \nu_L \pm \Delta\nu/2$ with $\nu_L = 98.2$ MHz.

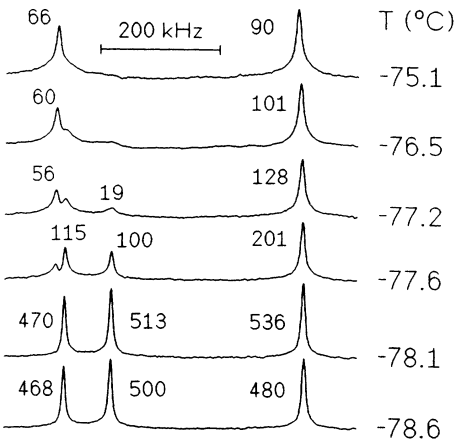

FIG. 3. Spectra of the upper frequency ^{87}Rb satellite transition of Rb(1) in RZC obtained in the crystal orientation $\mathbf{b}\|\mathbf{B}_0$ near $T_c \approx -78\,^{\circ}\mathrm{C}$ by stepwise heating. The numbers give the amplitude (height) of the respective line or singularity when normalizing the spectra relative to each other. The frequency increases from right to left. Phase distortions are eliminated by "magnitude calculation" leading to a broadening of the lines by a factor of about 1.7 compared to the absorption spectra.

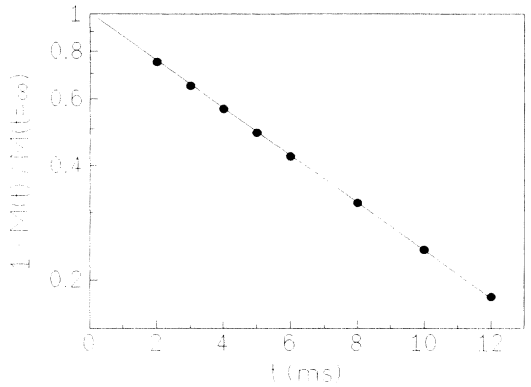

FIG. 4. Magnetization recovery of the upper frequency ^{87}Rb satellite transition of Rb(1) in RZC measured in the N phase at $T = 34\,^{\circ}\mathrm{C}$ (i.e., $T - T_i \approx 3$ K) in the crystal orientation $\mathbf{b}\|\mathbf{B}_0$.

was determined to be $\Delta T_c \leq 1$ K. The smallness of this value as well as the sharpness of the ^{87}Rb satellite lines and singularities demonstrate the high quality of the samples investigated. Note that the linewidths of the spectra presented in Fig. 3 are even broadened compared to the absorption spectra by use of "magnitude calculation" (cf. caption of Fig. 3). We shall come back to Fig. 3 later on.

A. Variations of transition probabilities along frequency

1. *Crystal orientation* $\boldsymbol{b}\|\boldsymbol{B}_0$

For the description of the experimental results, the formalism described in Sec. II is to be applied to the special case considered here: For ^{87}Rb in RZC symmetry imposes [cf., e.g., Eqs. (2)–(4) in Ref. 9]

$$A_{1ij}=0 \quad \text{or} \quad V_{1ij}=0 \tag{21}$$

for the components $ij = aa$, bb, cc, and ac of the tensors defined by (10) and (12) now given in the orthorhombic crystal frame (a,b,c). Restricting, according to Sec. II, to the dominant EFG fluctuations coupling linear to the OP, thus the only EFG spectral densities left are those of V_{ab} and V_{bc}. Equation (3) transformed from the laboratory frame ($\mathbf{z}\|\mathbf{B}_0$) to the crystal frame ($\mathbf{b}\|\mathbf{B}_0$) reduces to

$$W_1/C = J(V_{ab}^2;\omega_L) + J(V_{bc}^2;\omega_L), \quad W_2 \approx 0 . \tag{22}$$

According to (2), Eq. (22) means that the time dependence of the magnetization recovery is single exponential and thus the relaxation time T_1 is well defined by $1/T_1 = 2W_1$. The corresponding magnetization recovery obtained in the N phase is shown in Fig. 4.

Let ψ_{nij} denote the phase of the complex A_{nij} and thus the phase of the nth harmonic of the EFG component ij.[8,9] Relations between these phases can be determined from the orientational dependences of the satellite IC spectra.[9,11] For the phases appearing in (22) we obtained[33] $|\psi_{1ab} - \psi_{1bc}| \leq 5°$. To calculate from (14) and (15) the modulation $W_1(v)$ corresponding to (22) we put $\varphi_1 = \psi_{1ab} = \psi_{1bc}$ resulting in

$$W_1(v) = K_b\{(J_1+J_2) + (J_1-J_2)\cos[2(v+\Phi_0+\psi_{1ab})]\} , \tag{23}$$

where $K_b/C = |A_{1ab}|^2 + |A_{1bc}|^2$, $J_{1,2} = J_{1,2}(\omega_L)$. Thus we obtain in this special case (to a good approximation) a transition probability modulation of the special type of (16). In view of the discussion in Sec. II B it has to be noted that this is a consequence of the symmetry condition (21) and the phase relation $\psi_{1ab} \approx \psi_{1bc}$ determined for Rb(1). Considering Rb(2) instead of Rb(1) would be sufficient to make this type of $W(v)$ inapplicable.

According to (1), the frequency modulation $\nu(v)$ of the ^{87}Rb upper-frequency satellite in the IC phase is determined for $\mathbf{b}\|\mathbf{B}_0$ by the modulation of $U_{bb} \equiv V_{bb} eQ_{\mathrm{nuc}}/h$ and thus given by[8,9]

$$\nu(v) = \nu_b + \tfrac{1}{2}U_{2bb}\cos(2v + 2\Phi_0 + \psi_{2bb}) , \tag{24}$$

as the first harmonic vanishes by the symmetry condition (21). The resulting NMR frequency distribution typical for IC systems is characterized by two edge singularities occurring for $d\nu(v)/dv = 0$, i.e., at the frequencies $\nu(v_{s2;s1}) = \nu_b \pm \frac{1}{2}U_{2bb}$ at the edges of this distribution.[8,9]

Comparing (23) and (24) and using the relation $\psi_{2bb} - 2\psi_{1ab} = \pm 183° \approx 180°$ determined previously[33] it is found that the modulations of $W_1(v)$ and $\nu(v)$ are *equal in period and phase* ($J_2 > J_1$). Thus, the combination of these two equations leads to a linear relation describing the W_1 variation over the frequencies ν of the IC spectrum

$$W_1(\nu) = K_b\left[(J_1+J_2) + (J_2-J_1)\left(\frac{\nu-\nu_b}{\frac{1}{2}U_{2bb}}\right)\right] . \tag{25}$$

The variation of the spin-lattice relaxation rate $1/T_1(\nu)$ over the distribution of frequencies ν was measured in the upper part of the IC phase at $T = 15\,^{\circ}\mathrm{C}$ in

the crystal orientation discussed here. The obtained $1/T_1$ values are presented in Fig. 5. The linear variation of $W_1(\nu)$ predicted by (25) is actually found here. As also observed in the N phase[13] (Fig. 4) and as predicted, the relaxation behavior is single exponential over the whole IC spectrum (inset of Fig. 5) within the limits of experimental accuracy.

2. *Crystal orientation* $\mathbf{c}\|\mathbf{B}_0$

Proceeding as in the case $\mathbf{b}\|\mathbf{B}_0$ now yields for the transition probabilities determining the spin-lattice relaxation in the crystal orientation $\mathbf{c}\|\mathbf{B}_0$

$$W_1(v)/C=|A_{1bc}|^2\{(J_1+J_2)+(J_1-J_2)\times\cos[2(v+\Phi_0+\psi_{1bc})]\}\ , \tag{26a}$$

$$W_2(v)/C=|A_{1ab}|^2\{(J_1+J_2)+(J_1-J_2)\times\cos[2(v+\Phi_0+\psi_{1ab})]\}\ . \tag{26b}$$

From the measurements[33] referred to in front of (23), we know $\psi_{1ab}\approx\psi_{1bc}$ and $|A_{1ab}|^2/|A_{1bc}|^2=1.34$. Note that now $W_2(v)\neq 0$. Consequently, according to (2), a double-exponential relaxation of the magnetization with the rates $2(W_1+W_2)$ and $2W_1$ is expected.

However, as shown in Fig. 6, no distinct deviation from a single-exponential behavior of the magnetization was found for the singularities of the ^{87}Rb satellite frequency distribution of Rb(1) in the upper IC phase at $T=15\,^{\circ}$C. On the other hand, the corresponding plot for the center of the frequency distribution also presented in Fig. 6 exhibits a curvature expected for double-exponential relaxation.

To explain this seeming conflict, we first remind the reader that, while the final slope of $M_z(t)$ logarithmically

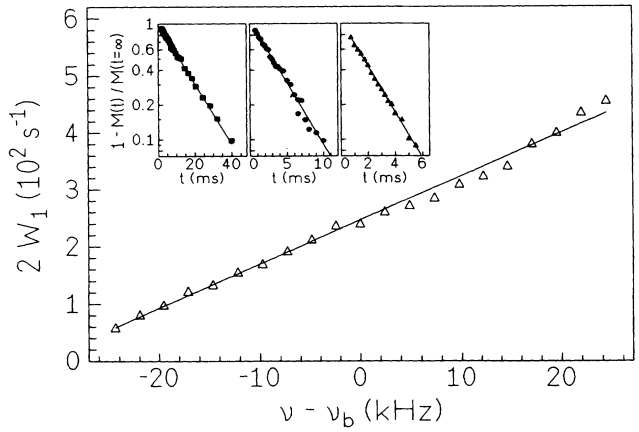

FIG. 5. Variation of the inverse spin-lattice relaxation time $1/T_1=2W_1$ over the frequency distribution of the upper frequency ^{87}Rb satellite transition of Rb(1) in RZC measured in the IC phase at $T\approx 15\,^{\circ}$C in the crystal orientation $\mathbf{b}\|\mathbf{B}_0$. The line describes the linear relationship expected from (25). The inset demonstrates the single-exponential magnetization recovery measured at the singularities (■, ▲) and in the center of the frequency distribution (●).

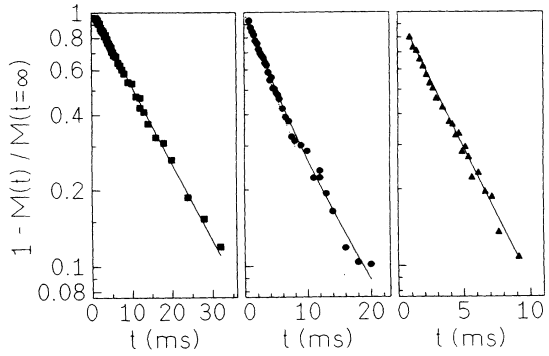

FIG. 6. Magnetization recovery measured for different parts of the frequency distribution belonging to the upper frequency ^{87}Rb satellite transition of Rb(1) in RZC in the crystal orientation $\mathbf{c}\|\mathbf{B}_0$ in the IC phase at $T\approx 15\,^{\circ}$C: edge singularities (■, ▲) with single-exponential relaxation, center of the frequency distribution (●) with double-exponential relaxation (the straight line here gives the initial slope).

scaled is determined by the smaller relaxation rate ($2W_1$), the initial slope is given by the mean value $2W_e=2W_1+W_2$ of the two different relaxation rates. Thus, the deviation from the single-exponential behavior essentially depends on the ratio W_2/W_1. Here we note that close above T_i we found fluctuations with relaxation frequencies of the order of the Larmor frequency, i.e., a violation of the fast-motion condition. While the ratio W_2/W_1 equals $|A_{1ab}|^2/|A_{1bc}|^2=1.34$ in the fast-motion limit, outside this limit this ratio has to be multiplied by a factor $1/\sqrt{2}$ reflecting the fact that W_2 detects the spectral density of the fluctuations at double the frequency as W_1 does. A more extensive discussion will be given elsewhere.[34] Since the phase fluctuations preserve the softness or susceptibility of the soft mode at T_i—as predicted by theory and shown experimentally, e.g., by T_1 data presented in Fig. 8—the same argument applies in the IC phase to the phase fluctuations dominating the spin-lattice relaxation. Thus, the ratio W_2/W_1 is reduced giving rise to only a slight curvature in a semilogarithmic plot of $M_z(t)$ which cannot be detected within the limits of accuracy of our measurement.

In this sense, reminding $\psi_{1ab}\approx\psi_{1bc}$, we write in analogy to (23) for the experimentally relevant transition probability W_e

$$W_e(v)=K_c\{(J_1+J_2)+(J_1-J_2)\cos[2(v+\Phi_0+\psi_{1ab})]\}\ , \tag{27}$$

where, when applying the above arguments, $K_c/C=|A_{1bc}|^2+\frac{1}{2}|A_{1ab}|^2/\sqrt{2}$. As for the frequency modulation

$$\nu(v)=\nu_c+\tfrac{1}{2}U_{2cc}\cos(2v+2\Phi_0+\psi_{2cc}) \tag{28}$$

holds analogously to (24), W_e is related to the frequency ν by

$$W_e^{\pm}(\nu)=K_c\{(J_1+J_2)+(J_1-J_2)\cos(\Delta\varphi_c)X(\nu) \pm(J_1-J_2)\sin(\Delta\varphi_c)[1-X^2(\nu)]^{1/2}\}\ , \quad (29)$$

$$X(\nu)=\frac{\nu-\nu_c}{\frac{1}{2}U_{2cc}},\quad \Delta\varphi_c=2\psi_{1ab}-\psi_{2cc}\ .$$

In Ref. 33 a value $\Delta\varphi_c=140°$ was determined from the static EFG Fourier series. Equation (29) describes an ellipse and, accordingly, there are two transition probabilities or relaxation rates $2W_e^{\pm}$ for each ν of the frequency distribution except for the edge singularities where $X(\nu_s)=\pm1$. This explains the different behavior of $M_z(t)$ in Fig. 6 already mentioned, i.e., the (effective) single-exponential time dependence for the edges with $X(\nu_s)=\pm1$ and the double-exponential one for the center of the frequency distribution with $X(\nu_c)=0$. The ellipse degenerates to a straight line, if the phase shift $\Delta\varphi$ between the modulation of the transition probability and that of the frequency equals 0° or 180°. This special case actually occurs for Rb(1), $\mathbf{b}\|\mathbf{B}_0$.

The ellipse obtained experimentally for $\mathbf{c}\|\mathbf{B}_0$ is shown in Fig. 7. The most reliable data, however, are not obtained for the two relaxation rates $W_e^{\pm}$ but for their mean value

$$\overline{W}_e(\nu)=K_c[(J_1+J_2)+(J_1-J_2)\cos(\Delta\varphi_c)X(\nu)] \quad (30)$$

which can be determined directly and accurately from the initial slope of the magnetization recovery $M_z(t)$ in a semilogarithmic plot. Equations (29) and (30) show, provided $\Delta\varphi_c$ is given, that all relevant parameters (K_cJ_1 and K_cJ_2) can be derived from this straight line $\overline{W}_e(\nu)$ according to (30). The ellipse given in Fig. 7 was calculated using these parameters.

This result offers the possibility to check the consistency of our T_1 study. We use two characteristics of the linear $\overline{W}_e(\nu)$ dependence expressed by (30). First, we take its center value $K_c(J_1+J_2)$ obtained for $X(\nu_c)=0$ and, second, its slope with respect to $X(\nu)$, which equals $K_c(J_1-J_2)\cos(\Delta\varphi_c)$. Calculating the ratio to the corresponding values obtained in Sec. III A 1 for Rb(1), $\mathbf{b}\|\mathbf{B}_0$ [cf. Eq. (25) and Fig. 5], the former yields $K_b/K_c=1.60$ and the latter $K_b/K_c=1.54$ demonstrating a nice agreement. Moreover, the ratio K_b/K_c can be obtained theoretically from

$$\frac{K_b}{K_c}=\frac{|A_{1bc}|^2+|A_{1ab}|^2}{|A_{1bc}|^2+\frac{1}{2}|A_{1ab}|^2/\sqrt{2}} \quad (31)$$

yielding $K_b/K_c=1.59$ in accordance with the above results.

It should be noted that so far the linear $W_1(\nu)$ variation observed for $\mathbf{b}\|\mathbf{B}_0$ has been attributed to the "local case" while the elliptic $W_1(\nu)$ variation found for $\mathbf{c}\|\mathbf{B}_0$ in principle corresponds to the "nonlocal case."[3] Since these qualitatively different results for $W_1(\nu)$ were obtained here by measurements on the same nucleus ^{87}Rb(1), their assignment to "local" or "nonlocal cases" is not physically adequate. Instead, they can be derived directly from the model presented here.

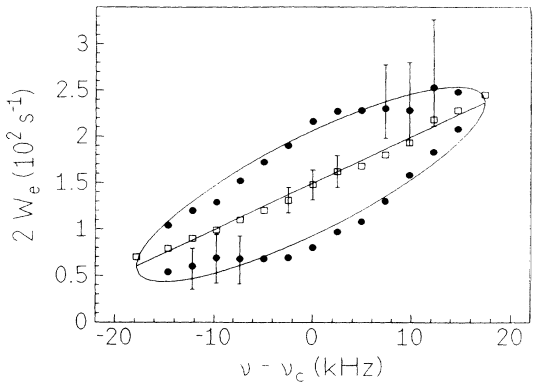

FIG. 7. Variation of the transition probability $2W_e$ [cf. Eq. (27)] over the frequency distribution of the upper frequency ^{87}Rb satellite transition of Rb(1) in RZC measured in the crystal orientation $\mathbf{c}\|\mathbf{B}_0$ in the IC phase at $T\approx15$ °C (●). The open square data points ($2\overline{W}_e$) were determined from the initial slopes of the magnetization recovery (see text) and can be fitted by a straight line according to (30). The other data points ($2W_e^{\pm}$) were derived from a fit of the magnetization recovery with two time constants $2W_e^{+}$ and $2W_e^{-}$. The fit corresponds to the ellipse predicted by (29).

B. Temperature dependence of T_1 in the crystal orientation $\mathbf{b}\|\mathbf{B}_0$

In the previous section the consistency of the model used has been shown. This model predicts, according to (24) and (25), $W_1(\upsilon_{s1})=2K_bJ_1$ and $W_1(\upsilon_{s2})=2K_bJ_2$ with $1/T_1=2W_1$ [cf. Eq. (22) ff.] for the edge singularities at $\nu(\upsilon_{s2,s1})=\nu_b\pm\frac{1}{2}U_{2bb}$. Consequently, the spectral densities J_1 and J_2 of the longitudinal (amplitude) and transverse (phase) fluctuations can be inspected by studying the spin-lattice relaxation of the edge singularities only. From the experimental point of view this is very advantageous, since the edge singularities naturally provide the best signal-noise ratio of the frequency distribution.

The T_1 data obtained for the two edge singularities in the IC phase as well as those of the corresponding discrete satellite lines in the N and C phases are given as a function of temperature in Fig. 8. In the temperature range between T_c and about −70 °C the relaxation time was measured on stepwise heating, after the crystal has been orientated for practical reasons in the C phase just below T_c. Except from this temperature range, T_1 was measured below $T\approx11$ °C as a rule on stepwise cooling and above $T\approx11$ °C predominantly on stepwise heating. Thermal hysteresis of T_1 data was not investigated here.

On approaching $T_i\approx31$ °C the T_1 values obtained in the N phase decrease from about 30 ms down to 2 ms. As explained in Sec. II A, this behavior reflects the softening of the critical fluctuations in the N phase near the phase transition. The spin-lattice relaxation time of the higher-frequency singularity stays in the whole IC phase nearly at the value attained at T_i, increasing only slightly on decreasing temperature. In contrast, T_1 of the other singularity increases distinctly below T_i up to values approaching those measured in the N phase at higher temperatures. In the lower part of the IC phase, however,

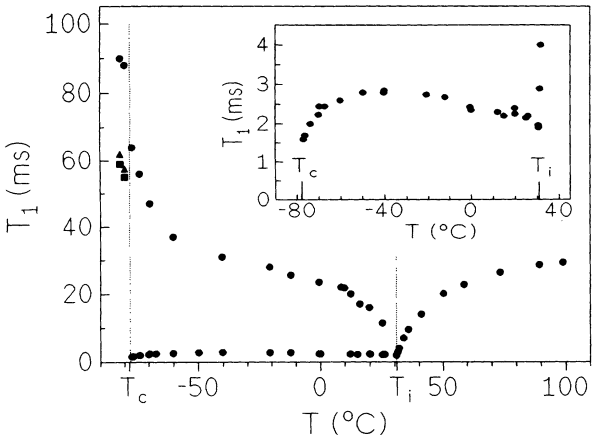

FIG. 8. Temperature dependence of the spin-lattice relaxation time T_1 of the upper frequency ^{87}Rb satellite transition of Rb(1) in RZC measured in the crystal orientation $\mathbf{b}\|\mathbf{B}_0$. In the N and IC phases, the data points mark T_1 of the discrete lines and of the edge singularities, respectively. In the C phase, the T_1 values of the three discrete lines belonging to the Rb(1) kind in the N phase are given, from higher to lower frequencies, by triangles, squares, and points (cf. Fig. 2). The inset shows the short T_1 values of the edge singularity relaxing fast on an enlarged scale.

the tendencies of these temperature dependences change: On decreasing temperature T_1 of the singularity relaxing fast gets smaller, while T_1 of the singularity relaxing slowly bends to higher values and approaches the long relaxation times measured below T_c.

The temperature dependence of the short T_1 corresponds, except for the lower temperature range of the IC phase, essentially to the $1/T$ behavior resulting from the fluctuation-dissipation theorem for a temperature-independent susceptibility [cf. Eq. (7)] identical with that of the soft mode at T_i, which is usually assumed for the "phason" branch. It reflects the extreme softness of the IC structure with respect to a phase shift of the modulation wave, i.e., it is a consequence of the special symmetry of an IC phase. Accordingly, the soft phase fluctuations disappear below the transition into the commensurate phase, and the T_1 values increase strongly. Thus, the experimental results are in nice accordance with our T_1 model predicting a purely "phason"-induced spin-lattice relaxation for just this higher-frequency singularity according to (25). The same model attributes the longer, temperature-dependent T_1 of the other singularity to the longitudinal OP modes ("amplitudon" modes).

It should be emphasized that such a well-defined assignment of "phason" and "amplitudon" contributions to the relaxation of the singularities of an IC spectrum requires the use of phase relations of the static EFG Fourier series obtained experimentally.[33] A correct determination of these phase relations is only possible by studying the orientational dependence of the satellite transitions in the IC phase.[9,11] In previous works, this methodical necessity has not been taken into account adequately.

As explained in Sec. II B in context with (17), the "amplitudon" induced relaxation rate identified by means of previous models can be "contaminated" severely by "phason" contributions. In fact, the ratio of the "amplitudon" and "phason" spin-lattice relaxation times $T_{1A}/T_{1\phi}$ determined previously from NMR studies of the ^{87}Rb central transition in RZC (Refs. 6 and 35) is about 1 at 25 °C and 1.5 at −40 °C and thus significantly smaller than the corresponding values 5 and 11 resulting from our data. Nearly the same holds for further T_1 data reported in Ref. 6 and for earlier measurements on the ^{87}Rb central transition in RZC.[36] Also the "amplitudon" induced relaxation time T_{1A} determined from ^{39}K NMR measurements in K_2SeO_4 previously[37] is presumably strongly "contaminated" by "phason" contributions, since T_{1A} is much shorter than the soft-mode induced T_1 above T_i for the same temperature distance $|T-T_i|$.

In a recent work[2] dealing with ^{87}Rb NMR central line investigations on RZC, the unusual shortness of the T_1 values identified with T_{1A} was attributed to some nonspecified "cross-relaxation" between those parts of the spectrum with "amplitudon"- and "phason"-induced relaxation. Such an effect, however, should also show up in our ^{87}Rb NMR studies on satellite lines. Obviously this is not the case, as clearly demonstrated both by the much higher $T_{1A}/T_{1\phi}$ values obtained here compared to those given in Ref. 2 and by the linear variation of $2W_1(\nu)$ found here given in Fig. 5.

As already mentioned, in the lower part of the IC phase marked changes in the temperature dependences of T_1 can be observed for both edge singularities. It is reasonable to relate these changes to the formation of the soliton lattice in this temperature region.

From the arguments given in Sec. II C we concluded that T_1 can be expected to increase for nuclei located in the nearly commensurate regions (C regions) and to decrease for nuclei located in the discommensurations (DC's). C regions and DC's can be assigned to certain parts of the frequency distribution by inspecting the temperature dependences of the satellite spectra near T_c as presented in Fig. 3. For simplicity we call the corresponding intensity maxima of the frequency distribution C intensities and DC intensities. While the C intensities merge continuously into the discrete lines obtained below T_c with amplitudes increasing on approaching T_c, the opposite holds for the DC intensities. Consequently, the low-frequency (right-hand side in Fig. 3) edge singularity (the outermost intensity maximum), coincides with a C intensity, whereas the high-frequency edge singularity, appearing just beside a C intensity, has to be attributed to the DC's.

Thus, the theoretical prediction of Sec. II C repeated above is actually reflected by T_1 of the two edge singularities measured in the lower part of the IC phase, as T_1 of the lower-frequency singularity relaxing slowly increases and T_1 of the higher-frequency singularity relaxing fast decreases on approaching T_c. Referring to the discussion in Sec. II C, this decrease of the short T_1 of the DC intensity reflects the softening of the phase fluctuations $[\delta\Phi(t)]$ in the DC's or, equivalently, the flatten-

ing out of the corresponding branch on approaching T_c. This behavior is in accordance with frequency-dependent dielectric measurements[30,31] discussed already in Sec. II C. Notice that the increase of the longer T_1 of the C intensity has to be put down essentially to the hardening of *phase* fluctuations in the C regions on the usual assumption that the fluctuations of the OP amplitude $[\delta\rho(t)]$ are not significantly affected by the formation of the soliton lattice and the IC-C phase transition (see Sec. II C). Reminding the reader that the relaxation of this edge singularity was attributed to the "amplitudon" in the PWL, we refer to Sec. III C for reasons explaining this conflict.

In contrast to our result, previous T_1 data obtained on RZC by ^{87}Rb NMR at the central transition[6,28,35] and by ^{35}Cl NQR (Ref. 5) show in the lower part of the IC phase an increase of the T_1 attributed to the "phason" on decreasing temperature, though these data are restricted in most cases to very few points. Provided the abovementioned T_1 results really reflect the spin-lattice relaxation of nuclei located in the DC's and not that one of nuclei located in the C regions for which T_1 is expected to increase, then this might indicate an increasing hardening of the corresponding modes for $T\rightarrow T_c$ due to a particular pinning of the soliton lattice as a consequence of a poor crystal quality.

Discommensurations in the IC phase of RZC have been observed by TEM studies[38] in a temperature range between T_c and about $-50\,^{\circ}$C. This range agrees fairly well with the temperature range in which the influence of the soliton lattice on the spin-lattice relaxation has been found according to the interpretation given above.

C. Phason gap and spin-lattice relaxation

In many works[4–6,35,37] usually a "phason gap" $\omega_\phi(\mathbf{k}=0)$ is determined from the ratio $T_{1A}/T_{1\phi}$ of "amplitudon" and "phason"-induced relaxation times. On several assumptions, the relation

$$\frac{T_{1A}}{T_{1\phi}}=\frac{\omega_A(\mathbf{k}=0)}{\omega_\phi(\mathbf{k}=0)} \tag{32}$$

has been derived.[14,27,37] Identifying T_{1A} and $T_{1\phi}$ with the spin-lattice relaxation time of certain intensities in the frequency distribution and using the "amplitudon" frequency $\omega_A(\mathbf{k}=0)$ determined by Raman or neutron scattering,[39–41] a "phason gap" $\omega_\phi(\mathbf{k}=0)$ can be obtained from (32). Applying this usual procedure to our T_1 data taking $\omega_A(\mathbf{k}=0)=6\times10^{11}\ \mathrm{s}^{-1}$ at $T\approx-45\,^{\circ}$C (for higher temperatures the relevant modes cannot be observed) (Refs. 39 and 40) yields $\omega_\phi(\mathbf{k}=0)=5\times10^{10}\ \mathrm{s}^{-1}$, where T_{1A} is identified with T_1 of the edge singularity relaxing slowly in the case of ^{87}Rb(1), $\mathbf{b}\|\mathbf{B}_0$ as given in Sec. III B. However, as will be argued in the following, the relevance of this value can be doubted. The same holds, in our opinion, for "phason gaps" given previously.[4–6,35,37]

The temperature dependence of T_1 of the edge singularity relaxing slowly significantly differs from the temperature dependence of the frequencies $\omega_A(\mathbf{k}=0)$ assigned to the amplitudon mode observed in Raman studies.[39–41] While the former temperature dependence is markedly affected by the IC-C phase transition, the latter is not. Consequently, it is problematic to relate both quantities as it is done in the "phason gap" determination $[T_{1A}\propto\omega_A(\mathbf{k}=0)$ according to (32)].

First of all, according to the assessment of Poulet and Pick,[42] the identification of the "amplitudon" in the case of Raman studies on RZC is "not unambiguous." Besides, there is a principal conflict when assigning Raman frequencies to T_1 data of a direct relaxation process presupposed on deriving (32): The direct T_1 process generally is induced by strongly damped modes [cf. Sec. II A after (4)] which may give no distinct frequencies in a Raman experiment.

Moreover, the NMR/NQR quantity can be severely disturbed by the influence of phase fluctuations for the following reasons: As already discussed in Secs. II B and III B, in general T_{1A} cannot be obtained by taking simply the maximum of the T_1 variation measured over the IC frequency distribution—as it has been done in previous works. Second, higher-order coupling to the OP beside the linear one considered in our and other models may also give rise to some "phason contamination" of the putative T_{1A} especially in the lower part of the IC phase, where the "phason gap" has to be determined because Raman data are only available in this temperature range. According to the discussion by Bruce and Cowley,[1] the influence of gapless phase fluctuations in an ideal IC structure leads to a gapless dispersion with $\omega^2(\mathbf{k})\propto k$ for small k for the longitudinal fluctuations. Surprisingly, this argument was not taken up later on. We remind that the modes which, in the ideal case, can be separated in the T_1 experiment are the longitudinal and transverse OP fluctuations. Thus, even in the case of a complete separation of the corresponding contributions the influence of the soft phase fluctuations on the longitudinal ("amplitudon") fluctuations has to be taken into consideration. In fact, assuming that our T_1 model is appropriate for the T_{1A} assignment at least down to $T=0\,^{\circ}$C or $-10\,^{\circ}$C, the smallness of the corresponding T_{1A} values compared to the T_1 values obtained below T_c may indicate such an influence.

Finally, one could ask what is the physical relevance of a gap frequency $\omega_\phi(\mathbf{k}=0)$ when dealing with relaxatory or overdamped modes?

IV. CONCLUSIONS

In the present work the nuclear-spin-lattice relaxation for quadrupolar perturbed NMR in structurally incommensurately (IC) modulated systems was investigated. A general formalism for describing the spin-lattice relaxation time T_1 was developed on the basis of the dynamics of these systems.

On the usual assumption of dominating contributions of local and long-wavelength fluctuations, the complex tensor coupling the complex order parameter linearly to the electric-field gradient (EFG) tensor is the same for both the static and the fluctuating part. The presupposition of equal atomic masses applied in previous works is not necessary.[3,6] As a consequence, phase relations

determined for the Fourier compounds of the static EFG in the IC phase can be used for the interpretation of the T_1 data. It has been shown that the identification of "amplitudon" and "phason" contributions T_{1A} and $T_{1\phi}$ assumed in previous works[3,6] is justified only in special cases. This may explain some too low T_{1A} values thus determined.[6,35–37]

According to our discussion, $T_{1\phi}$ can be expected to decrease for nuclei located in the discommensurations (DC's) reflecting the softening of the soliton lattice or the flattening out of the corresponding "acoustic" branch. This is similar to the well-known decrease of T_1 in an ordinary (nonmodulated) softening lattice with the difference that in the soliton lattice the effect is locally restricted to the DC's since the softening is locally restricted to the DC's. In contrast, previous works[6,14,27,28] predicted an increase of $T_{1\phi}$ in the soliton regime of the IC phase on approaching T_c.

Measurements were reported for the spin-lattice relaxation of the satellite transitions of ^{87}Rb in Rb_2ZnCl_4. At ambient temperature the variation of the relaxation rate was measured over the IC frequency distribution for two crystal orientations. The T_1 model developed could be proved to be consistent with these data. The procedure requires the knowledge of the Fourier series of the static EFG which can practically be determined only by investigating satellite spectra (quadrupole effects of first order).

The temperature dependence of T_1 was measured in that crystal orientation specially chosen on the basis of this model, where T_{1A} and $T_{1\phi}$ could be assigned to the lower and upper frequency edge singularity, respectively, of the satellite frequency distribution. The unusual short $T_{1\phi}$ determined this way demonstrates the particular softness of the phase fluctuations in the IC phase expected due to the broken translational symmetry of the lattice. In contrast to previous results,[5,6,28,35] in the lower part of the IC phase we found a decrease of $T_{1\phi}$ on approaching T_c for nuclei located in the DC's in accordance with our theoretical prediction.

In previous works[4–6,35,37] a frequency gap for the phason modes was determined by comparison of T_1 and Raman data. We discuss a number of reasons why we doubt the relevance of phason gaps obtained by this procedure.

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APPENDIX

From (12) one obtains for the EFG correlation function

$$\langle \delta V_{ij}(\mathbf{T},0)\delta V^*_{lm}(\mathbf{T},t)\rangle = \{ A_{1ij}A_{1lm}\langle \delta Q(\mathbf{T},0)\delta Q(\mathbf{T},t)\rangle e^{2i\mathbf{q}_i\cdot\mathbf{T}} + A_{1ij}A^*_{1lm}\langle \delta Q(\mathbf{T},0)\delta Q^*(\mathbf{T},t)\rangle\} + \text{c.c.} \quad \text{(A1)}$$

For simplicity the atom index a is dropped here and below. Introducing the longitudinal and transverse OP coordinates P_1, P_2 according to (13) and taking into account $\langle P_1P_2\rangle = 0$ yields for the EFG correlation functions of (A1):

$$\langle \delta Q(\mathbf{T},0)\delta Q(\mathbf{T},t)\rangle e^{-2i\Phi_0} = \langle \delta P_1(\mathbf{T},0)\delta P_1(\mathbf{T},t)\rangle - \langle \delta P_2(\mathbf{T},0)\delta P_2(\mathbf{T},t)\rangle , \quad \text{(A2)}$$

$$\langle \delta Q(\mathbf{T},0)\delta Q^*(\mathbf{T},t)\rangle = \langle \delta P_1(\mathbf{T},0)\delta P_1(\mathbf{T},t)\rangle + \langle \delta P_2(\mathbf{T},0)\delta P_2(\mathbf{T},t)\rangle . \quad \text{(A3)}$$

Thus, for the spectral densities of the EFG fluctuations

$$J(V_{ij}V_{lm};\omega) = \int_{-\infty}^{\infty} \langle \delta V_{ij}(\mathbf{T},0)\delta V^*_{lm}(\mathbf{T},t)\rangle e^{-i\omega t}dt \quad \text{(A4)}$$

and those of the longitudinal (J_1) and transverse (J_2) OP fluctuations

$$J_\beta(\omega) = 2\int_{-\infty}^{\infty} \langle \delta P_\beta(\mathbf{T},0)\delta P_\beta(\mathbf{T},t)\rangle e^{-i\omega t}dt = \frac{1}{N}\sum_{\mathbf{k}} \int_{-\infty}^{\infty} \langle \delta P_\beta(\mathbf{k},0)\delta P^*_\beta(\mathbf{k},t)\rangle e^{-i\omega t}dt \quad (\beta = 1,2 \text{ or } A,\phi) , \quad \text{(A5)}$$

where N denotes the number of unit cells, one obtains from (A1) with (A2) and (A3)

$$J(V_{ij}V_{lm};\omega) = \{ A_{1ij}A_{1lm}e^{2i(\Phi_0+\mathbf{q}_i\cdot\mathbf{T})} + \text{c.c.}\}\tfrac{1}{2}[J_1(\omega)-J_2(\omega)] + \{ A_{1ij}A^*_{1lm} + \text{c.c.}\}\tfrac{1}{2}[J_1(\omega)+J_2(\omega)] . \quad \text{(A6)}$$

Consequently, inserting the spectral densities of (A6) into (3), one finds for the transition probabilities W_1, W_2 relevant for the spin-lattice relaxation

$$W_\mu(v)/C = (a_\mu + \text{c.c.})\tfrac{1}{2}[J_1(\mu\omega_L)+J_2(\mu\omega_L)] + (b_\mu e^{2i(\Phi_0+v)} + \text{c.c.}) \times \tfrac{1}{2}[J_1(\mu\omega_L)-J_2(\mu\omega_L)] , \quad \text{(A7)}$$

where

$$a_1 = |A_{1xz}|^2 + |A_{1yz}|^2 ,$$
$$a_2 = \tfrac{1}{4}|A_{1xx} - A_{1yy}|^2 + |A_{1xy}|^2 ,$$
$$b_1 = (A_{1xz})^2 + (A_{1yz})^2 ,$$
$$b_2 = \tfrac{1}{4}(A_{1xx} - A_{1yy})^2 + (A_{1xy})^2 ,$$

and where we used the internal coordinate $v = \mathbf{q}_i\cdot\mathbf{T}$ which is reduced to the interval $[0,2\pi)$. Note that (A7) also holds for the N phase where the term modulated by $\exp(2iv)$ is to be canceled due to the degeneracy of P_1 and P_2 [i.e., $J_1(\omega) = J_2(\omega)$]. Rewriting (A7) in terms of real expressions leads to (14) and (15).

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