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NMR in substitutionally disordered incommensurate $(Rb_{1-x}K_x)_2ZnCl_4$

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The impurity-concentration dependence of the ^{87}Rb NMR line shapes and phason-induced spin-lattice relaxation rates has been studied over a wide temperature range in substitutionally disordered incommensurate $(Rb_{1-x}K_x)_2ZnCl_4$ for $x=0.00$, 0.02, and 0.06. The results yield information on the impurity-concentration dependence of the phason gap and phase fluctuations of the modulation wave as well as on the nature of the coupling of the impurities to the incommensurate modulation wave.

I. INTRODUCTION

Incommensurate phases in insulators[1] are characterized by a long-wavelength spatial distortion of the crystal lattice such that the modulation period bears no rational relation to the periodicity of the underlying lattice. Such phases are usually intermediate between a high-temperature unmodulated paraelectric (*P*) and a low-temperature commensurate (*C*) phase. In the simplest case of a one-dimensional incommensurate modulation, the order parameter has two components, the amplitude and the phase of the modulation wave. In contrast to amplitude fluctuations which are critical only close to the paraelectric-incommensurate (*P-I*) transition temperature T_I, phase fluctuations are critical over the whole incommensurate phase, since the free energy of an ideal incommensurate system is degenerate with respect to a homogeneous change in the phase: $\Phi \rightarrow \Phi + \delta\Phi$. As a result, there is a zero-frequency symmetry-recovering Goldstone mode (the phason) representing the frictionless sliding of the modulation wave. The phase change induced by an impurity decays with distance algebraically (i.e., by a power law) and not exponentially.[1] In the presence of impurities these systems thus exhibit a number of striking features not observed in the phase-transition behavior of other random solid-state systems.[2-6]

Random-field-type symmetry-breaking impurities destroy the long-range order for dimension $d \leq 4$ and smear out the *P-I* transition.[2] In improper ferroelectrics such as Rb_2ZnCl_4, such impurities have to be polar so that they couple linearly to the soft-mode eigenvector.[6]

Random-interaction-type[6] impurities, on the other hand, do not break the symmetry of the free-energy functional and thus do not discriminate between different commensurate domains. This type of disorder has been discussed[3] in connection with substitutionally disordered $(Rb_{1-x}K_x)_2ZnCl_4$, where both the Rb and the K components lead to *C* phases with the same *n* (i.e., the same type of ferroelectric commensurate phase with a tripling of the lattice parameter along the axis of modulation). Such impurities change the strength of the anisotropy term γ in the free energy[1,7] locally (i.e., $\gamma \rightarrow \gamma + \Delta\gamma$), as discussed later. Impurities which change locally the elastic constant or couple to the derivative of the phase are in the same class. The question of whether random-interaction-type impurities in general also destroy long-range order in the *I* phase for $d \leq 4$ cannot be regarded as settled.[6] Since this type of impurities also pins the phase, one would expect the same effects as for random fields.[6] On the other hand, Bak[13] argued that such defects do not necessarily destroy long-range order in three dimensions (i.e., for $d=3$).

In order to investigate effects on the modulation wave in *I* systems due to random-interaction-type impurities, we studied $(Rb_{1-x}K_x)_2ZnCl_4$ substitutionally disordered single crystals using ^{87}Rb nuclear magnetic resonance and relaxation. Rb_2ZnCl_4 exhibits successive phase transitions among four different phases:[1,8] the orthorhombic paraelectric (PE) phase ($D_{2h}^{16}-Pnma$, $z=4$), the incommensurate (*I*) phase modulated along the *a* axis, the ferroelectric commensurate (C_1) phase ($C_{2v}^{9}-Pn2_1a$, $z=12$), and the low-temperature commensurate (C_2) phase (C_s^4-Cc, $z=24$). The corresponding transition temperatures are $T_I=302$ K, $T_{C_1}=189$ K, and $T_{C_2}=74.6$ K, respectively. The phase-transition sequence in K_2ZnCl_4 is identical[1,9] to the one in Rb_2ZnCl_4 except that the transition temperatures are higher and a second incommensurate phase exists[9] in a narrow temperature interval between phases C_1 and C_2.

When a small number of Rb ions in Rb_2ZnCl_4 are replaced by K ions, the *P-I* transition temperature T_I is shifted to higher temperatures where the incommensurate to commensurate transition T_{C_1} is shifted to lower temperatures.[10,11] The cation sites are randomly occupied by the Rb^+ and K^+ ions which have different ionic radii. In crystals with $0.1 \leq x \leq 0.9$, the incommensurate-commensurate transition was found to be suppressed[10,11] and the system seems to remain in a metastable *I* state down to the lowest temperatures investigated. On cooling, the modulation vector tends to remain fixed at the value found at T_I. It is obvious that this is due to the pinning of the modulation wave by impurities which prevents the crystal from reaching thermal

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equilibrium.

Here we wish to study the effects of substitutional disorder on (a) the impurity induced gap Δ_Φ in the phason excitation spectrum,[2]

$$\omega_\Phi^2=\Delta_\Phi^2+\kappa^2k^2,\quad \mathbf{k}=\mathbf{q}-\mathbf{q}_I\ ; \tag{1}$$

(b) the NMR line shape; and (c) the phase-transition sequence in Rb_2ZnCl_4 down to liquid-helium temperatures.

The data were taken at an orientation, $\mathbf{c}\perp\mathbf{H}_0$ and $\sphericalangle(\mathbf{a},\mathbf{H}_0)=122°$, at which the linear term in the expansion of the NMR frequency in powers of the nuclear displacements is dominant.[1,8] The ^{87}Rb quadrupole perturbed NMR $\frac{1}{2}\rightarrow-\frac{1}{2}$ central transition frequencies were measured from 325 down to 6 K at $\nu_L(^{87}\mathrm{Rb})=88.4$ MHz. The doped crystals were taken from the same batch as that used previously for x-ray and dielectric studies.[10,11,7]

II. THEORY

We shall treat the K^+ ions within the Rb_2ZnCl_4 matrix as symmetry-nonbreaking defects in three dimensions.[7] The mixed system can be described by generalizing the free-energy density functional for the pure system and adding a kinetic-energy term. The complex order parameter $Q=A\exp(i\Phi)$ is assumed to vary only in the phase Φ so that the constant amplitude approximation can be used:

$$g=g_0-\delta A\frac{\partial\Phi}{\partial x}+\tfrac{1}{2}\mathcal{K}A^2|\nabla\Phi|^2-\gamma A^n\cos(n\Phi)+\tfrac{1}{2}\mu A^2\dot{\Phi}^2. \tag{2}$$

Here $n=6$ for Rb_2ZnCl_4 and K_2ZnCl_4 and μ is the effective-mass density of phase fluctuations. In the mixed system the parameters (μ, the Lifshitz parameter δ, the elastic constant $\mathcal{K}$, and the "anisotropy" parameter γ) vary in space so that the problem is of the random-interaction type. Because of the large spatial dependence of the anisotropy term [$\gamma=\gamma(\mathbf{r})$], we shall neglect the spatial variation of the other terms. We also assume that, in the absence of impurities, the system is in the plane-wave modulation regime.

Introducing small fluctuations in the phase

$$\Phi(\mathbf{r},t)\rightarrow\Phi(\mathbf{r})+\Psi(\mathbf{r},t)$$

around the stationary value $\Phi(\mathbf{r})$ and expanding in powers of Ψ, we get from (2) the dynamic Euler equation

$$\dot{\Psi}-c_0^2\nabla^2\Psi=-(\gamma/\mu)A^{n-2}n^2\cos(n\Phi)\Psi\ , \tag{3}$$

where $c_0^2=\mathcal{K}/\mu$ and $\gamma(\mathbf{r})=\gamma_0+\Delta\gamma(\mathbf{r})$. Here, $\Delta\gamma(\mathbf{r})$ represents the effect of the substitutional impurities.

We are looking for phase oscillations

$$\Psi=\tilde{\Psi}(\mathbf{r})\exp(i\omega t)\ , \tag{4}$$

where the lowest frequency represents the phason gap $\omega_g=\Delta_\Phi$. In the absence of disorder ($\gamma=\gamma_0$), the phason gap is zero ($\Delta_\Phi=0$) if soliton effects can be neglected. The effect of impurities is to induce a finite gap $\Delta_\Phi\neq0$, even in the plane-wave limit. In the weak pinning limit, we can use the variational ansatz $\tilde{\Psi}(\mathbf{r})=\Psi_0$ and obtain from Eq. (3),

$$\Delta_\Phi=[(n^2/\mu)A^{n-2}\langle\Delta\gamma(\mathbf{r})\cos(n\Phi)\rangle]^{1/2}\ . \tag{5}$$

Here the angular brackets represent the spatial average over the sample, which is nonzero because of the perturbed values of $\Phi(\mathbf{r})$ in the vicinity of the K^+ ion sites. In order to calculate this spatial average, a specific model of the effect of the impurities on the phase must be assumed. To determine $\varphi(\mathbf{r})=\Phi(\mathbf{r})-\mathbf{qr}$, the impurity-induced phase deviation from the plane-wave solution, we use the functional

$$\tilde{g}=\tilde{g}_0+\tfrac{1}{2}\mathcal{K}A^2|\nabla\varphi|^2-\Delta\gamma(\mathbf{r})A^n\cos[n(\mathbf{qr}+\varphi)]\ , \tag{6}$$

where the modulation wave vector $|q|$ equals

$$|q|=\mathcal{K}/\delta\ . \tag{7}$$

Our model[7] for calculating the effects of the impurities assumes that the substitutional K^+ defect induces a deviation $\Delta\gamma_0$ in the anisotropy term within a distance R_0 of the defect. $\Delta\gamma(\mathbf{r})$ is zero elsewhere. Thus,

$$\Delta\gamma(\mathbf{r})=\Delta\gamma_0,\quad r<R_0 \tag{8a}$$

and

$$\Delta\gamma(\mathbf{r})=0,\quad r>R_0\ . \tag{8b}$$

We also assume that the average distance between defects $l_0=n_i^{-1/3}$ is much larger than R_0:

$$l_0=n_i^{-1/3}>R_0\ . \tag{9}$$

Here, n_i is the K^+-ion defect concentration. Within the effective range of the defect ($R<R_0$), we put (Fig. 1)

$$\varphi(r)=\varphi_0,\quad r<R_0\ . \tag{10a}$$

Outside this range we assume that the defect-induced phase deviation decays algebraically with distance:

$$\varphi(r)=\varphi_0R_0/r,\quad r>R_0\ . \tag{10b}$$

For a defect, which fixes the phase at its location, the impurity-induced phase deviation must satisfy[1] the La-

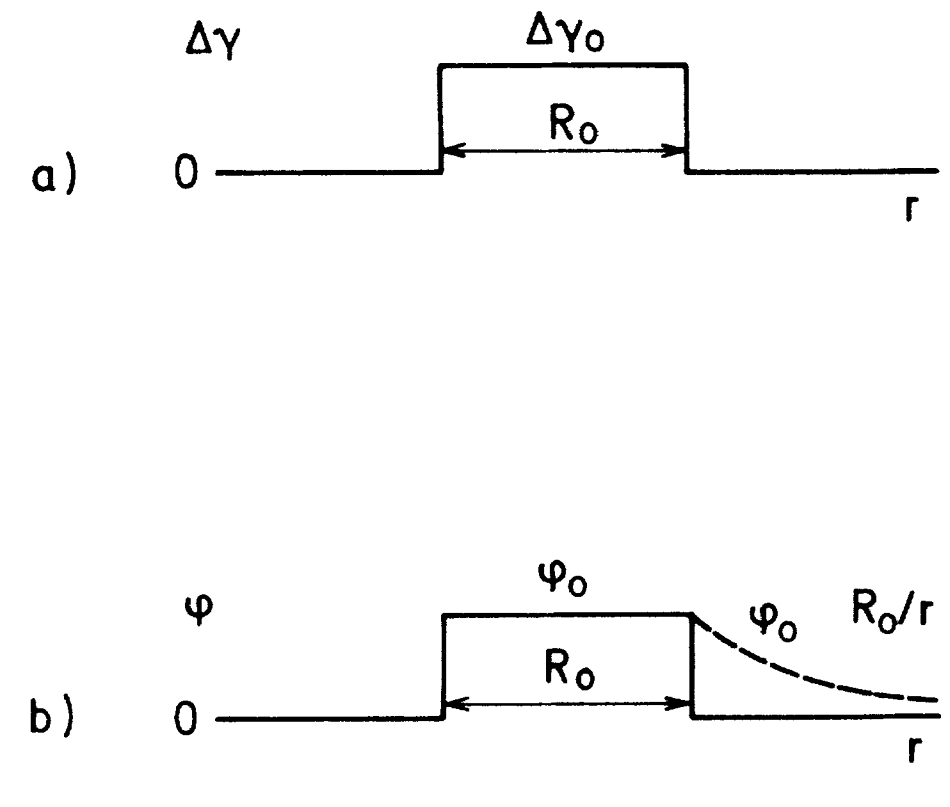

FIG. 1. (a) Impurity-induced anisotropy coupling variation and (b) impurity-induced phase deviation from the plane-wave solution in the vicinity of a substitutional K^+-ion impurity in $(Rb_{1-x}K_x)_2ZnCl_4$.

place equation

$$\nabla^2\varphi=0 . \tag{11}$$

It can be shown that, for $\Delta\gamma/\gamma \ll 1$, the phase deviation induced by the defect remains small, so that $\varphi_0 < \pi/n$ over the whole I phase.

With this ansatz the free-energy difference per defect, following from Eq. (6), becomes

$$\begin{aligned}\Delta\tilde{F}&=\int_{R_0}^{\infty}(\tilde{g}-\tilde{g}_0)d^3r\\ &=\mathcal{K}A^2R_0 2\pi\varphi_0^2+nA^n\Delta\gamma_0V_0\sin(n\mathbf{q}\cdot\mathbf{r})\varphi_0 ,\end{aligned} \tag{12}$$

where $V_0=4\pi R_0^3/3$. Minimizing $\Delta\tilde{F}$ with respect to φ_0, $\partial(\Delta\tilde{F})/\partial\varphi_0=0$, we get

$$\varphi_0=-A^{n-2}n\Delta\gamma_0V_0\sin(n\mathbf{q}\cdot\mathbf{r})/(4\pi R_0\mathcal{K}) . \tag{13}$$

With the help of expression (13), we now evaluate the spatial average in expression (5). Using the fact that up to first order

$$\langle\Delta\gamma(r)\cos[n(\mathbf{q}\cdot\mathbf{r}+\varphi)]\rangle=-nn_iV_0\Delta\gamma_0\langle\sin(n\mathbf{q}\cdot\mathbf{r})\varphi_0\rangle , \tag{14}$$

we get the phason gap after performing the spatial average as

$$\Delta_\Phi=\left[\frac{n^4n_i}{8\pi R_0\mathcal{K}\mu}\right]^{1/2}\Delta\gamma_0V_0A^{n-2} . \tag{15}$$

Since the amplitude of the modulation wave varies with temperature as $A\propto|T_I-T|^\beta$, where $\beta=\frac{1}{3}$, Eq. (15) predicts a temperature dependence of the phason gap as[2]

$$\Delta_\Phi\propto|T_I-T|^{\beta(n-2)}\sqrt{n_i} , \tag{16}$$

where, for Rb_2ZnCl_4, $\beta=\frac{1}{3}$ and $n=6$, so that $\beta(n-2)=\frac{4}{3}$.

The above temperature and impurity-concentration dependence of the phason gap is completely different from the one expected for the case of strong random-field-like pinning[7] where

$$\Psi(r\le R_0)=0 , \tag{17}$$

within the defect range. Here the gap frequency is obtained as

$$\Delta_\Phi=C_0\pi/l_0=(\mathcal{K}/\mu)^{1/2}\pi n_i^{1/3} \tag{18}$$

and is independent of temperature.

The phason-induced spin-lattice relaxation rate contribution $T_{1\Phi}^{-1}$ varies with the phason gap as

$$T_{1\Phi}^{-1}=C\Gamma_\Phi/\Delta_\Phi \tag{19}$$

if the phason gap exceeds the nuclear Larmor frequency. Experimentally, a measurement of $T_{1\Phi}^{-1}$ can thus easily discriminate between the cases described by Eqs. (16) and (18), respectively.

Let us now try to estimate the effects of substitutional impurities on the NMR line shape for nonzero quadrupolar coupling. In the simplest case the NMR frequency ν at a given site is linearly related to the nuclear displacement $u(x)$ due to the modulation wave at this site:[1]

$$\nu(x)=\nu_0+au(x)=\nu_0+\nu_1\cos\Phi(x) , \tag{20a}$$

where

$$\nu_1=aA\propto|T_I-T|^\beta . \tag{20b}$$

The NMR frequencies thus vary sinusoidally in space between $\pm\nu_1$. The inhomogeneous incommensurate frequency distribution $f(\nu)$ is obtained[1] for a pure crystal in the plane-wave modulation limit $\Phi=qx$ from

$$f(\nu)d\nu=\text{const}\,dx \tag{21a}$$

as

$$f(\nu)=\frac{\text{const}}{\dfrac{d\nu}{d\Phi}\dfrac{d\Phi}{dx}}=\frac{C}{\left[1-\left[\dfrac{\nu-\nu_0}{\nu_1}\right]^2\right]^{1/2}} . \tag{21b}$$

The actual line shape $F(\nu)$ is a convolution of $f(\nu)$ with the nonzero width of the individual lines $L(\nu)$, as narrowed, for example, by thermal fluctuations

$$F(\nu)=\int_{-\infty}^{+\infty}L(\nu-\nu_0)f(\nu)d\nu . \tag{21c}$$

The presence of a small concentration of substitutional random impurities induces a random strain as well as random fluctuations of the phase around the plane-wave modulation value at a given nuclear site. Both will affect the electric-field-gradient (EFG) tensor and thus the NMR frequency. As a result, the shape of the individual lines is expected to be Gaussian:

$$L(\nu-\nu_0)=C\exp[-(\nu-\nu_0)^2/2\sigma^2] . \tag{22}$$

The broadening due to phase fluctuations will be superimposed on the broadening due to dislocations and other crystal imperfections present already in the paraelectric phase. Since these effects are uncorrelated, we expect

$$\sigma^2=\sigma_0^2+\sigma_{\text{ph}}^2 . \tag{23a}$$

σ_0^2 describes the strain contribution to the line broadening which varies linearly with temperature due to thermal expansion. σ_{ph}^2 describes the phase-fluctuation contribution

$$\sigma_{\text{ph}}^2=\overline{\delta\nu^2}=\tfrac{1}{2}\nu_1^2\overline{\delta\Phi^2} . \tag{23b}$$

The mean-square phase fluctuation $\overline{\delta\Phi^2}$ is

$$\overline{\delta\Phi^2}=Kn_i\overline{\varphi_0^2} , \tag{23c}$$

with φ_0 being given by expression (13) and K being a numerical factor of the order of 1. For Rb_2ZnCl_4, σ_{ph}^2 should thus increase with decreasing temperature as

$$\sigma_{\text{ph}}^2\propto|T_I-T|^{(2n-2\beta)}\propto|T_I-T|^{10/3} \tag{23d}$$

in the immediate vicinity of T_I.

The shape of the spectrum is now given by Eq. (21c) using Eqs. (22) and (21b). The increased width of the individual components should thus mask the fine structure of the incommensurate frequency distribution and prevent the observation of soliton effects[1] if the defect concentration is large enough. It should also make the observation of the fine structure due to the presence of commensurate lines in phases C_1 and C_2 nearly impossible. The total width of the I spectrum $\Delta\nu=2\nu_1$ should, however, not be affected by the impurities.

III. RESULTS AND DISCUSSION

A. NMR line shape

The ^{87}Rb $\frac{1}{2}\rightarrow-\frac{1}{2}$ NMR spectra of pure ($x=0$) and substitutionally disordered $(\mathrm{Rb}_{1-x}\mathrm{K}_x)_2\mathrm{ZnCl}_4$ single crystals with $x=0.06$ are shown in Fig. 2 for various selected temperatures between 320 and 10 K. In the doped system with $x=0.06$, the P-I transition is clearly seen for this orientation $[\mathbf{a}\perp\mathbf{H}_0 \sphericalangle(\mathbf{c},\mathbf{H}_0)=122°]$ only in the first Rb line around $\nu-\nu_0\approx 0$. In contrast, the second Rb line around $\nu-\nu_0\approx -40$ kHz is too broad to show a splitting at T_I. The soliton and commensurate lines at lower temperatures, which are clearly observable in the pure system, are likewise smeared out in the doped system.

The temperature dependence of the incommensurate splitting between the edge singularities, $\delta\nu=2\nu_1 \propto |T_I-T|^{\beta}$, is compared in Fig. 3 for $x=0.00$, 0.02, and 0.06. As expected, the P-I transition temperatures T_I are shifted to higher temperatures with increasing K^+ concentration. The critical exponent β for determining the T dependence of the amplitude of the modulation wave is, however, unaffected[7] by the K^+ doping for $x\leq 0.06$ and its value ($\beta=0.35\pm0.03$) agrees with that determined from the x-ray data.[4] The total width of the I spectrum is also unaffected by K^+ doping, in agreement with the model derived in Sec. II.

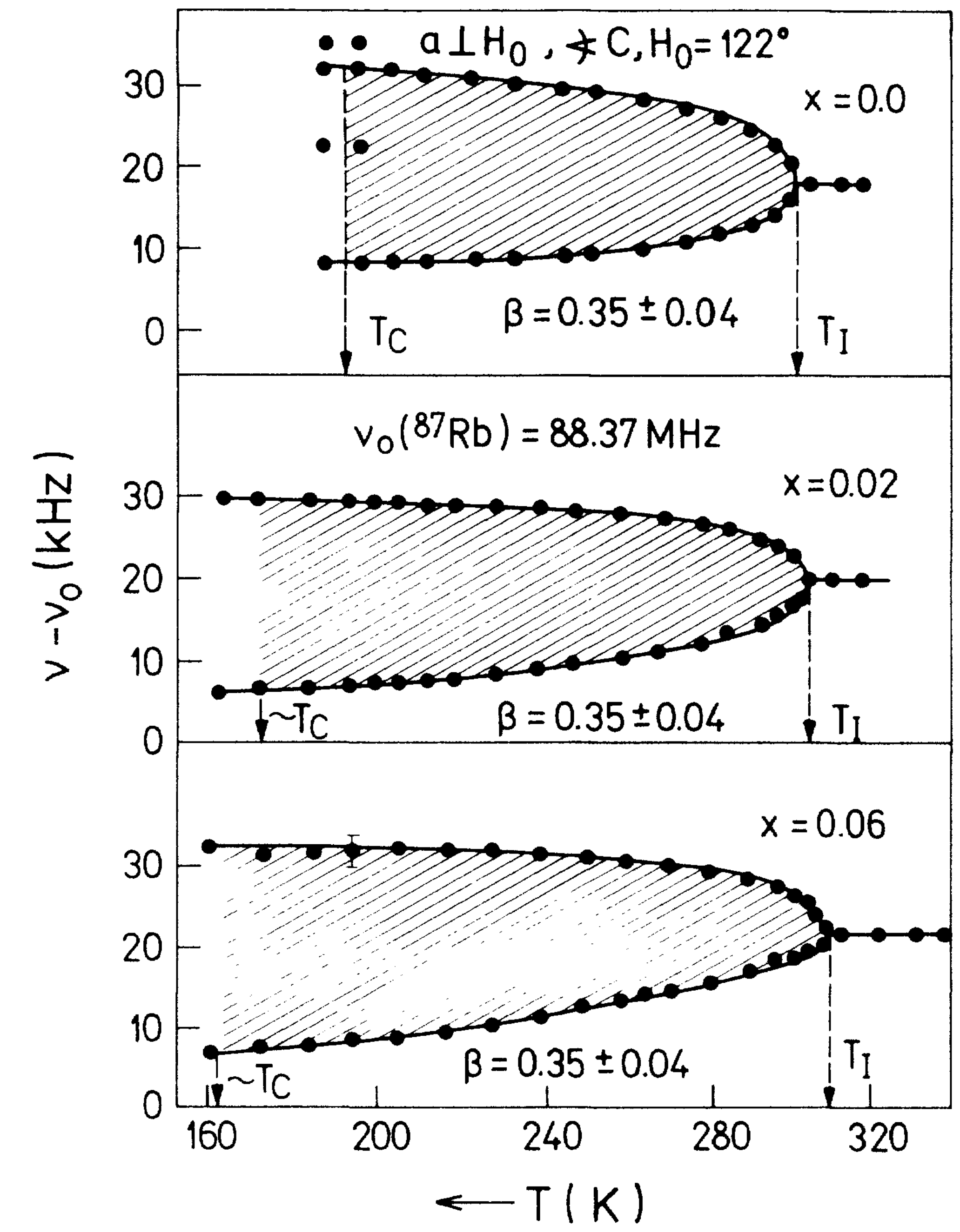

FIG. 3. Temperature dependence of the incommensurate splitting $\Delta\nu=2\nu_1\propto|T_I-T|^{\beta}$ of the ^{87}Rb $\frac{1}{2}\rightarrow-\frac{1}{2}$ NMR line for $x=0.00$, 0.02, and 0.06.

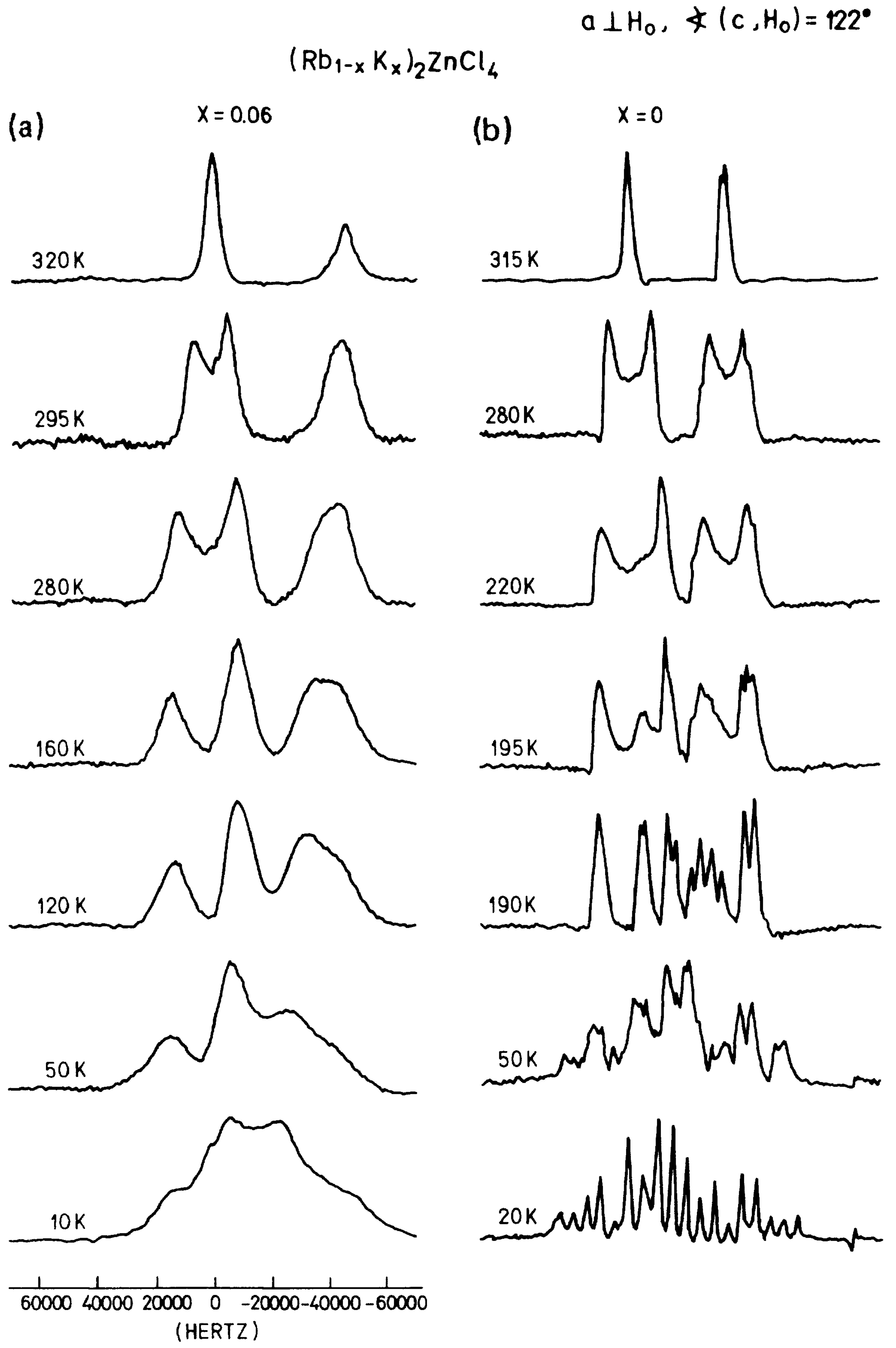

FIG. 2. ^{87}Rb $\frac{1}{2}\rightarrow-\frac{1}{2}$ NMR spectra of $(\mathrm{Rb}_{1-x}\mathrm{K}_x)_2\mathrm{ZnCl}_4$ at various temperatures for $x=$ (a) 0.06 and (b) 0.00.

A comparison of the NMR spectra of pure ($x=0$) and doped ($x=0.06$) $(\mathrm{Rb}_{1-x}\mathrm{K}_x)_2\mathrm{ZnCl}_4$ shows (Fig. 2) that the ^{87}Rb NMR lines in the substitutionally disordered system are significantly broader than in the pure system. As can be seen from Fig. 4, the experimental spectra can be reproduced by a convolution of the frequency distribution (21b) with a Gaussian having a temperature-dependent width. The width σ^2 can be decomposed in two parts: (i) a part (σ_0^2) which is present already in the paraelectric phase and which increases linearly with decreasing T down to the lowest temperatures investigated (i.e., down to 5 K) and (ii) another part (σ_{ph}^2) which is specific for the I phase (Fig. 5). This part starts to increase at T_I according to expression (23d) and decreases to zero below the I-C transition. We believe that σ_0^2 is due to random strains and has a linear temperature dependence due to lattice contraction. On the other hand, σ_{ph}^2 seems to reflect random phase fluctuations around the plane-wave value induced by weak, randomly distributed substitutional impurities (Fig. 6).

B. Spin-lattice relaxation

The average value of the spin-lattice relaxation time T_1 (Fig. 7) for $x=0.06$ shows a dip only at T_I and no anom-

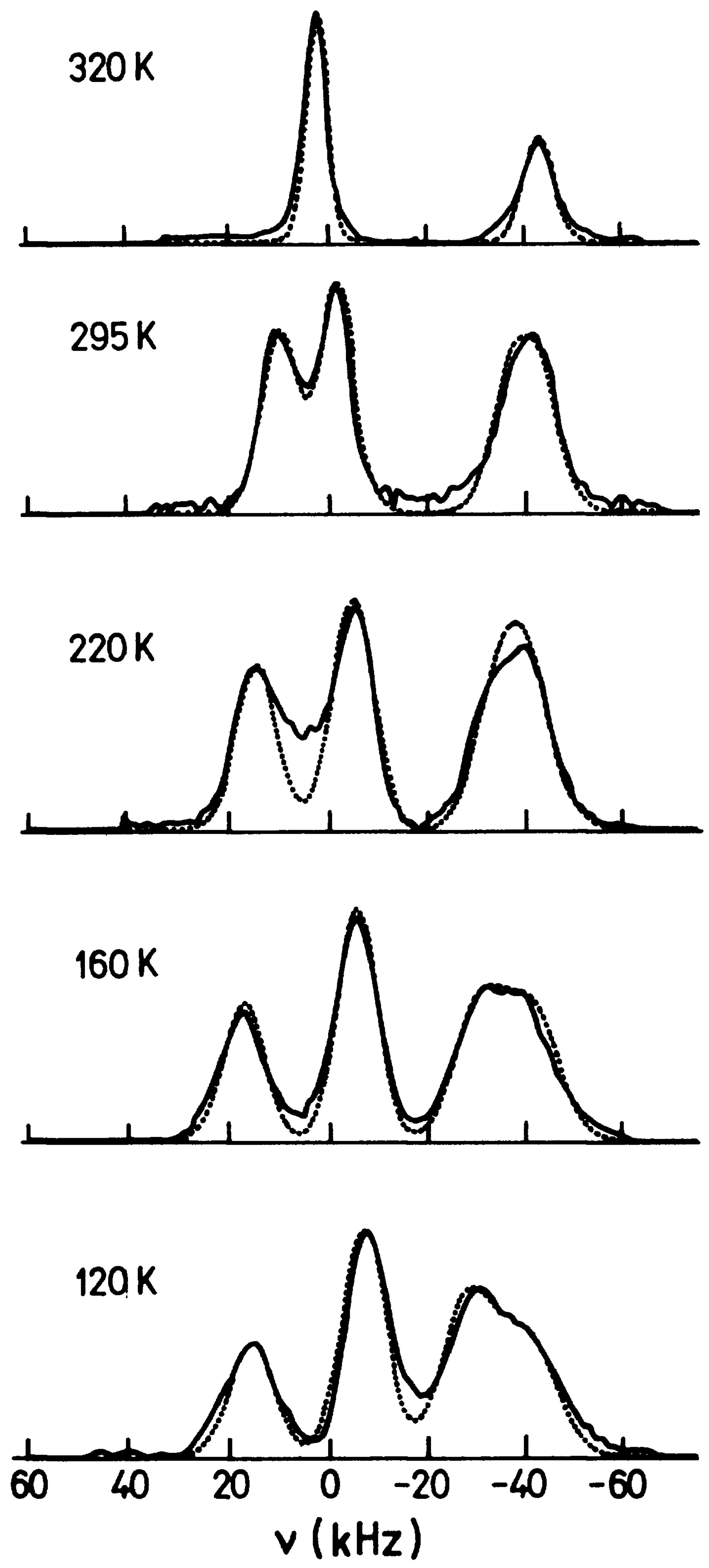

FIG. 4. Comparison between experimental and theoretical ^{87}Rb $\frac{1}{2}\rightarrow-\frac{1}{2}$ NMR line shapes in $(Rb_{1-x}K_x)_2ZnCl_4$ for $x=0.06$ at various temperatures.

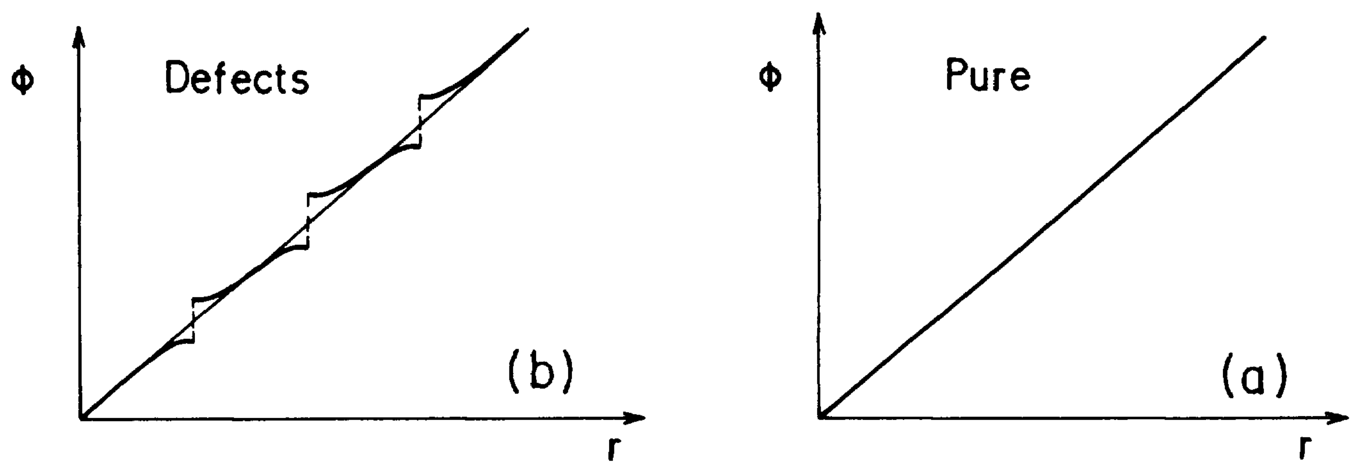

FIG. 6. Schematic spatial dependence of the phase of the modulation wave in (a) pure Rb_2ZnCl_4 and (b) substitutionally disordered $(Rb_{1-x}K_x)_2ZnCl_4$.

aly at T_{C_1} or T_{C_2}. In the C_2 phase it increases strongly as $T\rightarrow 0$. The absence of a T_1 anomaly at T_{C_1} and T_{C_2} may be due to the large phason gap induced by impurities which masks the commensurability induced gap. The variation of the effective T_1 over the NMR line allows the determination of the phason contribution $T_{1\Phi}^{-1}$ to T_1^{-1}. The phason-induced spin-lattice relaxation time $T_{1\Phi}$, which is proportional to the phason gap Δ_Φ, is drastically affected by K^+ doping (Fig. 8). In pure Rb_2ZnCl_4, $T_{1\Phi}$ is temperature independent and equals 10 ms from $+25\,^\circ C$ to $-60\,^\circ C$. For $x=0.02$, on the other hand, $T_{1\Phi}$ increases with decreasing temperature from 10 ms at $34\,^\circ C$ to 36 ms at $-80\,^\circ C$. For $x=0.06$, the effect of K^+ doping is even more pronounced. $T_{1\Phi}$ increases from 20 ms at $T=40\,^\circ C$ to $T_{1\Phi}=50$ ms at $T=-80\,^\circ C$.

The phason gap is thus larger in K^+ doped samples and strongly increases with decreasing temperature, whereas it is small and temperature independent in nominally pure Rb_2ZnCl_4.

If one now assumes that the phason gap frequency is a sum of (1) a part that is independent of both temperature and K^+-ion concentration and is present in nominally pure Rb_2ZnCl_4 and (2) a K^+-ion-induced part, the experimental results for $x=0.02$ and 0.06 are in reasonable

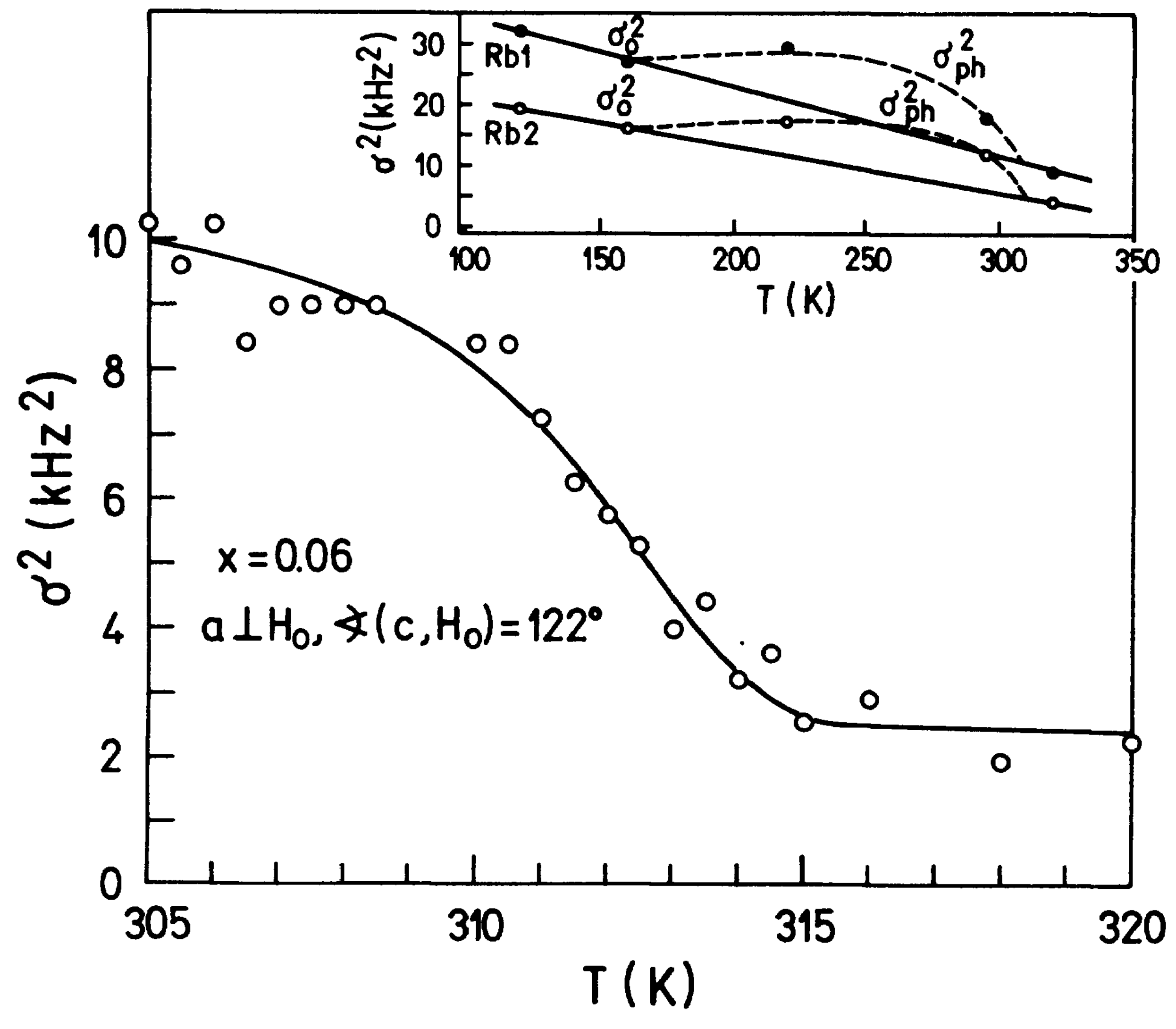

FIG. 5. Temperature dependence of the Gaussian half-width $\sigma^2=\sigma_0^2+\sigma_{ph}^2$ in $(Rb_{1-x}K_x)_2ZnCl_4$ for $x=0.06$ for the two inequivalent Rb sites 1 and 2 in $(Rb_{1-x}K_x)_2ZnCl_4$.

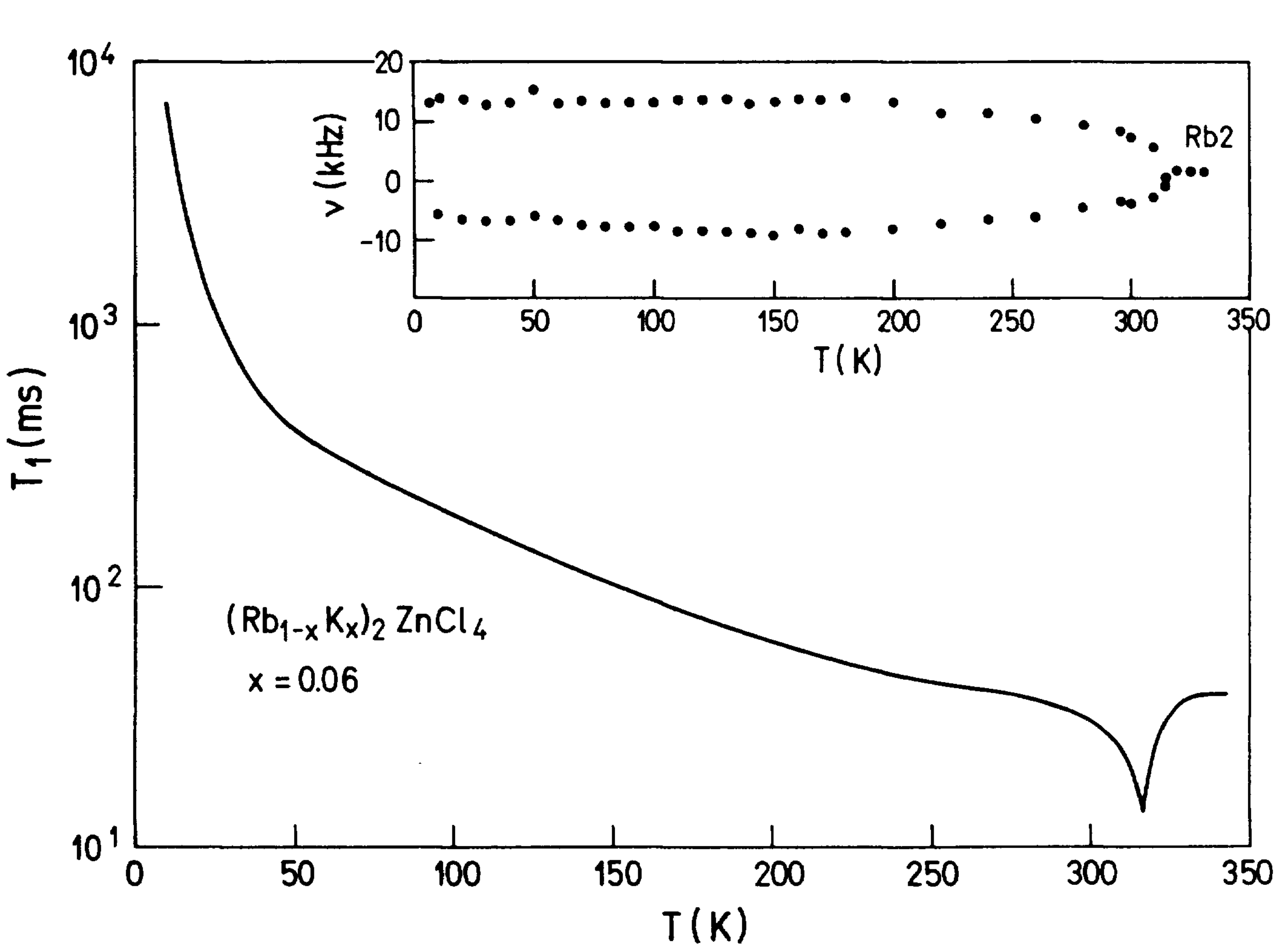

FIG. 7. Temperature dependence of the average value of T_1 for $x=0.06$ between 320 and 6 K. The inset shows the temperature dependence of the Rb 2 line splitting for the same impurity concentration and temperature range.

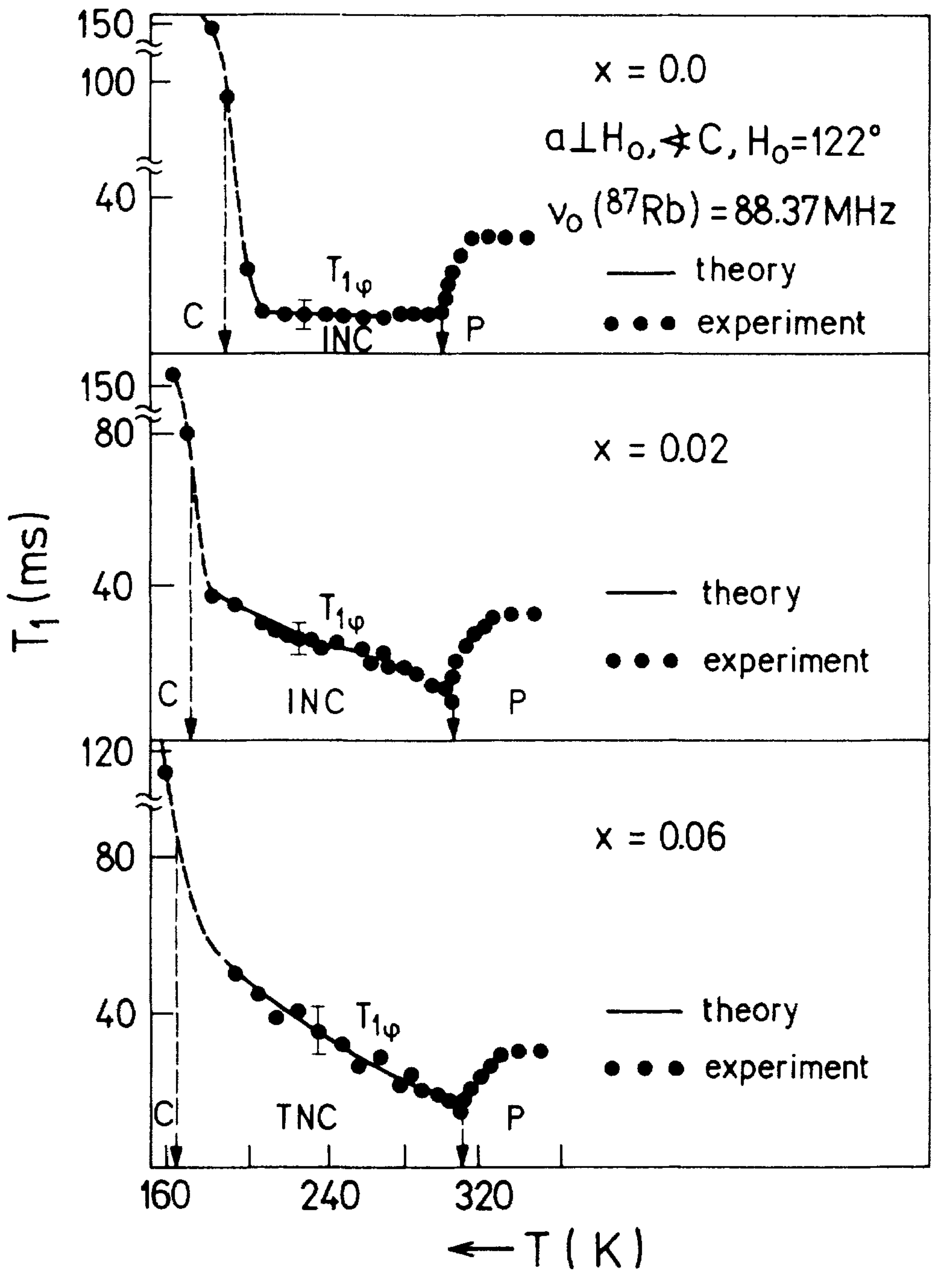

FIG. 8. Temperature dependence of the phason-induced ^{87}Rb $\frac{1}{2} \rightarrow -\frac{1}{2}$ spin-lattice relaxation rate for $x = 0.00$, 0.02, and 0.06. The solid line represents the fit to the theoretical expressions (19) and (15).

agreement with the theoretical model developed in Sec. II. The solid lines in Fig. 8 which represent fits to the theoretical expressions (19) and (15) reproduce both the temperature and K$^+$-ion concentration dependence of the observed $T_{1\Phi}$ with $n = 6$ and $\beta = \frac{1}{3}$.

IV. CONCLUSIONS

The agreement between theory and experiment in the NMR line shape as well as in the phason-induced contribution to T_1^{-1} confirms the random-interaction-type coupling of the substitutional K$^+$-ion impurities with the incommensurate modulation wave in $(\mathrm{Rb}_{1-x}\mathrm{K}_x)_2\mathrm{ZnCl}_4$ crystals.

The results show that the critical exponent β describing the temperature dependence of the order parameter at the paraelectric-incommensurate transition is indeed not affected by the presence of random-interaction-type impurities though the incommensurate-commensurate transition is destroyed by random-phase pinning if the concentration of these defects is high enough. The random pinning of the phase of the modulation wave by randomly distributed substitutional impurities is also demonstrated by the anomalous increase in the Gaussian width of the NMR lines (σ_{ph}^2) in the I phase, as predicted by Eq. (23b). It should be noted that an alternate three-dimensional model of static weak pinning to defects in which the elastic term is treated quite differently[12] yields a much stronger dependence of the phason gap Δ_Φ on n_i and T, which was not observed in the present case.

The question about the nature of the residual temperature-independent phason gap in nominally pure $\mathrm{Rb}_2\mathrm{ZnCl}_4$ is still not definitely settled.[13] We believe that it can be explained by strong random-field-like pinning to symmetry-breaking defects [see Eq. (18)]. In view of the fact that chemical purification does not affect the value of $T_{1\Phi}$ in nominally pure $\mathrm{Rb}_2\mathrm{ZnCl}_4$, it is possible that local strains inducing spontaneous polarization might be responsible for the residual K$^+$-ion independent part of Δ_Φ in a $\mathrm{Rb}_2\mathrm{ZnCl}_4$-type system.

ACKNOWLEDGMENTS

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