

^{27}Al NMR of the incommensurate phase in AlPO_4

T. Apih, U. Mikac, A. V. Kityk,* and R. Blinc
J. Stefan Institute, SI-1000, Ljubljana, Slovenia
 (Received 23 September 1996)

The temperature dependence of the quadrupole perturbed ^{27}Al NMR spectra has been measured in α , β , and incommensurate phases of AlPO_4 . The observed ^{27}Al NMR line shapes show that the incommensurate phase is not a superposition of differently oriented single- k domains but rather corresponds to a planar triply- k modulated structure. The three modulation waves are correlated and the relative phase shifts are $\Psi_1 + \Psi_2 + \Psi_3 = 0$. The amplitude of the AlO_4 twist angle in the I phase is estimated as $1.5^\circ - 2^\circ$.
 [S0163-1829(97)02006-7]

The existence of an incommensurate (I) phase intermediate between the high-temperature hexagonal β and the low-temperature trigonal α phase in berlinite (AlPO_4) is by now well established.¹⁻⁶ It is analogous to the I phase in quartz⁷ (SiO_2), the main difference being the somewhat larger temperature range of the I phase (~ 4 K for AlPO_4 instead of 1.3 K for quartz). The existence of the I phase was predicted by Aslanyan and Levanyuk² and related to the occurrence of a Lifshitz-like invariant built by coupling of the strains and the spatial derivatives of the order parameter. The I phase is triply modulated in the a - b plane with no modulation along the c axis. The three modulation wave vectors \mathbf{k}_i are of equal length and at 120° to each other. At the β - I transition the \mathbf{k}_i modulation vectors point along the directions of the twofold axes of the β phase which are lost in the α phase. On approaching the I - α transition the \mathbf{k}_i vectors move away from these crystallographic directions.

According to x-ray observations⁶ the average structure of the I phase is the same as of the β phase, i.e., it has the $P6_222$ symmetry. The actual symmetry will depend on the displacement mode of the I modulation. The dimensionality of the order parameter is $n=6$ so that we have three complex order-parameter components:

$$Q(\mathbf{k}_1) = \rho_1 \exp[i\Phi_1(\mathbf{r})], \quad (1a)$$

$$Q(\mathbf{k}_2) = \rho_2 \exp[i\Phi_2(\mathbf{r})], \quad (1b)$$

$$Q(\mathbf{k}_3) = \rho_3 \exp[i\Phi_3(\mathbf{r})]. \quad (1c)$$

In the plane-wave modulation limit we have

$$\Phi_i(\mathbf{r}_i) = \mathbf{k}_i \mathbf{r} + \Psi_i, \quad i = 1, 2, 3. \quad (2)$$

According to theoretical expectations,⁵ two different structures of the I phase are possible:

$$(i) \quad \rho_1 \neq 0, \quad \rho_2 = \rho_3 = 0 \quad (3a)$$

and

$$(ii) \quad \rho_1 = \rho_2 = \rho_3 \neq 0. \quad (3b)$$

In the first case (i) we have a superposition of single- \mathbf{k} modulated domains with different orientations of the \mathbf{k} vectors. The orientations of the \mathbf{k} vectors in different domains differ by 120° . The bulk sample composed of equal proportions of the single- \mathbf{k} domains will give rise to six incommensurate satellites around a Bragg spot just as in case (ii) where we have a genuine triply-modulated I phase. It is therefore hard to determine from scattering experiments whether (i) or (ii) holds. The electron microscopy, on the other hand, suggests that case (ii) is realized. It is however sensitive to the structure at the surface rather than to the bulk. NMR experiments, on the other hand, are sensitive to the bulk and the local rather than average structure and can easily discriminate between cases (i) and (ii).

The displacement of the atom j in the unit cell due to the n -dimensional plane-wave-type modulation wave⁷⁻⁹ can be expressed as

$$\mathbf{u}_j(\mathbf{r}) = \sum_{i=1}^3 \mathbf{u}_{i0} \sin(\mathbf{k}_i \mathbf{r} + \Psi_i), \quad i = 1, 2, 3, \quad (4)$$

where the \mathbf{u}_{i0} are proportional to the amplitudes ρ_i . If the relation between the quadrupole perturbed NMR frequency shifts of the covalently bonded ^{27}Al nuclei and the nuclear displacements is assumed to be purely local and linear we have

$$\nu(\mathbf{r}) = \nu_0 + \sum_{i=1}^3 \nu_i \sin(\mathbf{k}_i \mathbf{r} + \Psi_i). \quad (5)$$

Here ν_i is proportional to the amplitude of the i th component of the modulation wave ρ_i . The phases $\Phi_i = \mathbf{k}_i \mathbf{r} + \Psi_i$ take on any value in the interval $[-\infty, +\infty]$ with equal probability. Instead of a single sharp NMR line we find for each physically nonequivalent site in the high-temperature unit cell a characteristic frequency distribution^{8,9} in the I phase:

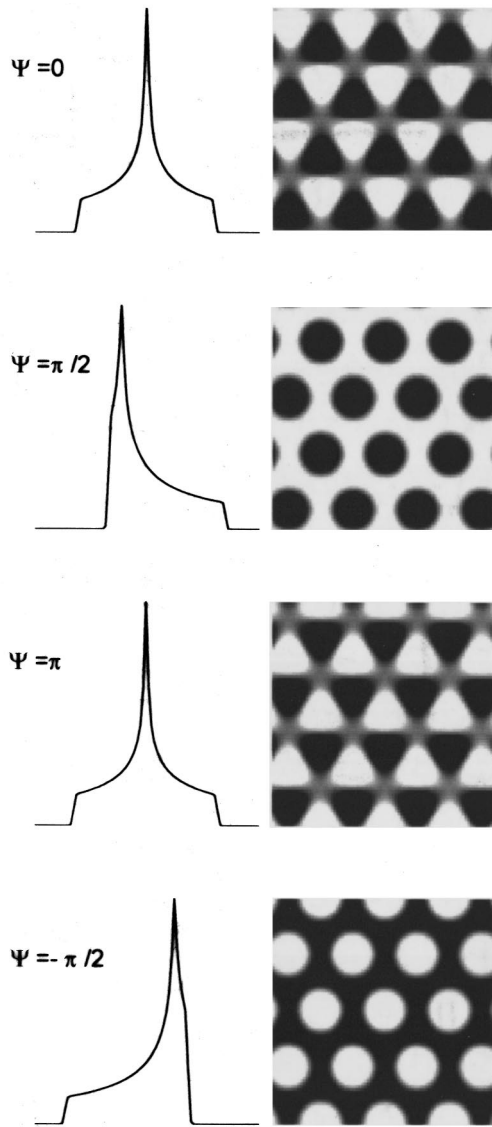


FIG. 1. The NMR frequency distributions expected for the planar triply \mathbf{k} modulated incommensurate phase of AlPO_4 for $\rho_1 = \rho_2 = \rho_3 \neq 0$, $\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 = 0$, and $|\mathbf{k}_1| = |\mathbf{k}_2| = |\mathbf{k}_3|$. These three modulation waves are correlated and the line shapes are calculated for three possible values of the relative phase shifts $\Psi = \Psi_1 + \Psi_2 + \Psi_3 = 0, \pm\pi/2$, and π . The corresponding electron microscopy patterns, where the black region corresponds to a given sense of displacements and the white one to opposite sense (Ref. 4), are also shown.

$$f(\nu) = \int d\Phi_1 d\Phi_2 d\Phi_3 \delta[\nu - \nu(\Phi_1, \Phi_2, \Phi_3)], \quad (6a)$$

$$\Phi_i = \mathbf{k}_i \mathbf{r} + \Psi_i. \quad (6b)$$

Here the integration over the phase space must take care of possible correlations⁸ between the different modulation waves. The modulation waves are independent if the \mathbf{k} vectors are independent and if the corresponding phases Ψ_i are not correlated. If, however, the number of modulation waves

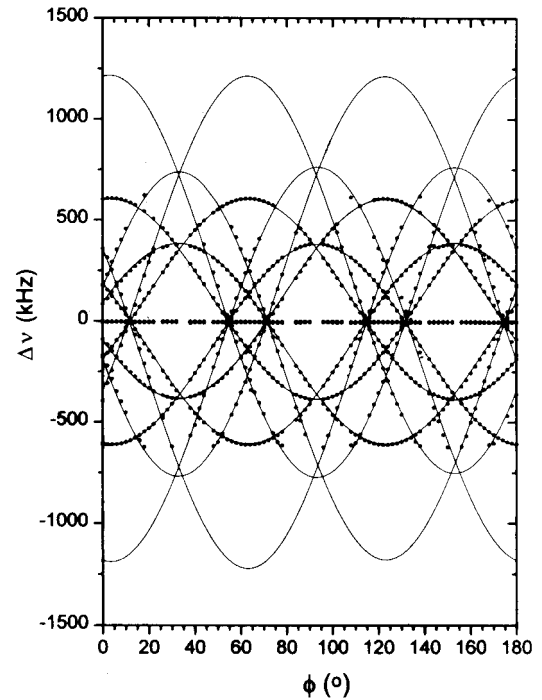


FIG. 2. Angular dependences of the $1/2 \rightarrow -1/2$, $\pm 1/2 \rightarrow \pm 3/2$ and $\pm 3/2 \rightarrow \pm 5/2$ ^{27}Al NMR transition frequencies in AlPO_4 in a 9 T magnetic field for a rotation around the threefold c axis at $T = 300$ K. Φ denotes the angle between the direction of the external magnetic field and the twofold b axis.

is larger than the dimension of the space spanned by the corresponding wave vectors, the modulation waves will be correlated and the NMR spectrum will strongly depend on the relative phases of these modulation waves.

Let us first discuss the triply modulated case (ii). In AlPO_4 the three modulation waves are coplanar and therefore correlated:

$$\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 = 0, \quad (7a)$$

$$|\mathbf{k}_1| = |\mathbf{k}_2| = |\mathbf{k}_3|. \quad (7b)$$

It has been proposed that $\mathbf{k}_1 = \mathbf{q}_1$, $\mathbf{k}_2 = \mathbf{q}_2 - \mathbf{q}_1$, and $\mathbf{k}_3 = -\mathbf{q}_2$ with $\mathbf{q}_1 = \alpha \mathbf{a}^* + \beta \mathbf{b}^*$ and $\mathbf{q}_2 = -\beta \mathbf{a}^* + (\alpha + \beta) \mathbf{b}^*$. The relative phases of the three modulation waves are fixed by the condition

$$\Psi_1 + \Psi_2 + \Psi_3 = \Psi, \quad (7c)$$

where Ψ can be $0, \pm\pi/2$, or π . The resulting incommensurate NMR frequency distributions are very specific and could be used to discriminate between different possible structures of the I phase of AlPO_4 corresponding to the different values of Ψ (Fig. 1). Because of the correlation between the modulation waves the $3-k$ case is in fact reduced to the $2-k$ case

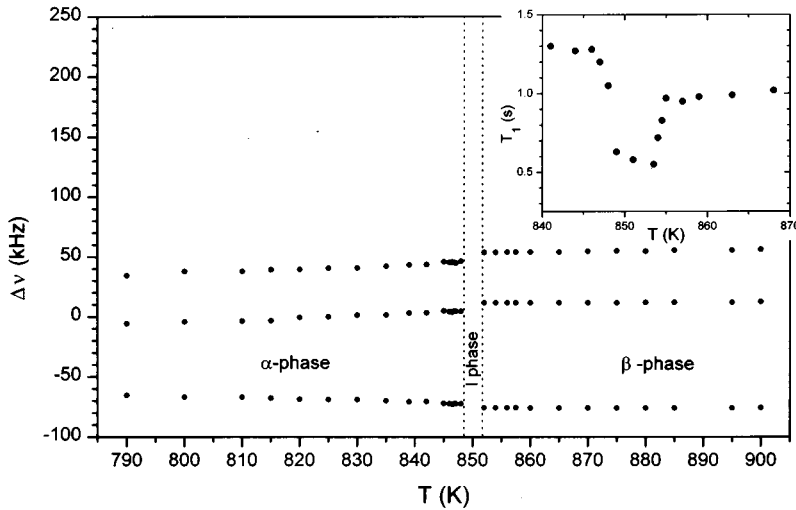


FIG. 3. Temperature dependence of the three ^{27}Al $3/2 \rightarrow 5/2$ NMR transition frequencies between 820 and 930 K in the region of the $\alpha \rightarrow I \rightarrow \beta$ transitions. The data were taken on a virgin single crystal on heating. The inset shows the temperature dependence of the effective ^{27}Al spin-lattice relaxation time T_1 exhibiting a dip on going into I phase.

where the relation between the frequency shift and two independent modulation waves is no longer linear.

In the $1-k$ modulated “stripe” phase (i) where we have domains $\rho_1=K, \rho_2=\rho_3=0; \rho_2=K, \rho_1=\rho_3=0;$ and $\rho_3=K, \rho_1=\rho_2=0$, the NMR line shape is simply given by

$$f_1(\nu) = \int_{-\infty}^{+\infty} \delta[\nu - \nu(\Phi_i)] d\Phi_i = \frac{\text{const}}{d\nu/d\Phi_i}$$

$$= \frac{\text{const}}{\sqrt{1 - [(\nu - \nu_0)/\nu_1]^2}}. \quad (8)$$

This is due to the fact that the NMR line shape does not depend on the direction of the modulation wave vector \mathbf{k} as long as the associated displacements and frequency changes are the same. In contrast to case (ii) the frequency distribution $f(\nu)$ is limited here by two edge singularities at $\nu - \nu_0 = \pm \nu_1$.

Crystalline AlPO_4 has the structure of silica where pairs of Si sites are substituted by P and Al atoms thus forming a network of $[\text{AlO}_4]_2^-$ and $[\text{PO}_4]_4^+$ units. There are three physically nonequivalent but chemically equivalent Al sites in the unit cell. The angular dependence of the ^{27}Al ($I=5/2$) quadrupole perturbed NMR spectra of an AlPO_4 single crystal is shown in Fig. 2 for a rotation around the threefold c axis at room temperature in a 9 T magnet. The periodicity of the ^{27}Al NMR pattern is 60° as expected from the crystal structure. For a given Al site $2I=5$ lines are expected. The quadrupole shifts of the $1/2 \rightarrow -1/2$ transitions are too small to be detectable in this experiment. The $\pm 1/2 \rightarrow \pm 3/2$ and $\pm 3/2 \rightarrow \pm 5/2$ satellite transitions which vary with orientation by 600 kHz and 1.2 MHz, respectively, have to be used to monitor the quadrupole shifts and broadening of the ^{27}Al spectra.

The temperature dependence of the three $3/2 \rightarrow 5/2$ transition frequencies at $\Phi=35^\circ$ on heating is shown in Fig. 3. The onset of the I phase shows up as a sudden broadening of these transitions over an interval of 4 K between the α and β phase. The appearance of the I phase is also accompanied by a decrease in the spin-lattice relaxation time T_1 (inset to Fig. 3) due to the presence of low-lying acousticlike phason ex-

citations which are characteristic for the I phase and which modulate the electric-field-gradient (EFG) tensor at the Al sites at a nonzero wave vector. The T dependence of the line shapes for the $3/2 \rightarrow 5/2$ transitions is shown in Fig. 4.

Two characteristic features have to be mentioned.

(i) No edge singularities characteristic for the $1-k$ modulated “stripe” domains are seen. Thus we indeed have a planar triply-modulated $\rho_1=\rho_2=\rho_3 \neq 0$ I structure and not a superposition of differently oriented $1-k$ domains.

(ii) After the initial broadening below T_1 the lines remain symmetric thus ruling out the case that $\Psi_1+\Psi_2+\Psi_3=\Psi=\pm\pi/2$ (Fig. 1). The symmetric line shapes are of

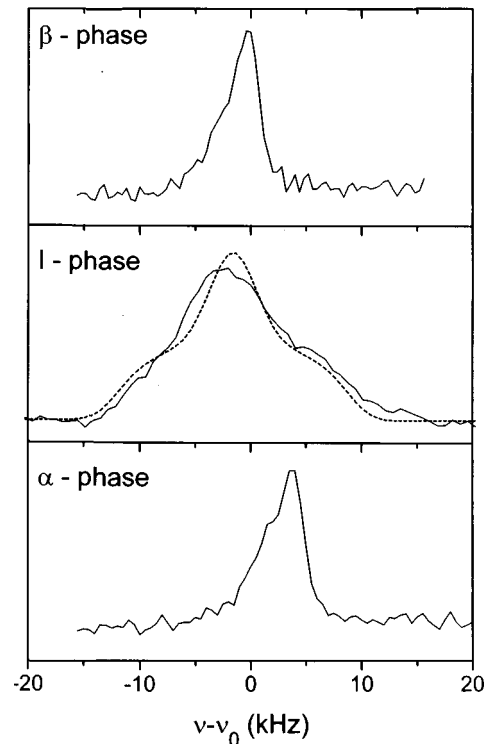


FIG. 4. Observed and theoretical ^{27}Al NMR line shapes in the I phase of AlPO_4 . The theoretical line shape in the I phase (dotted line) is calculated for $\Psi_1+\Psi_2+\Psi_3=0$. The observed spectra in the α and β phases are shown for comparison.

the type compatible with $\Psi=0$. This agrees with the triangular dark-light contrast pattern in the electron microscopy pictures observed in the *I* phase by Snoeck *et al.*⁴

Still another conclusion is related to the magnitude of the order parameter. It is quite plausible⁷ that the *I* phase is

produced by a modulated wave of small-angle AlO_4 and PO_4 rotations. If one compares the $3/2 \rightarrow 5/2$ NMR rotation data at room temperature with the width of the incommensurate frequency distribution in the *I* phase one can estimate the amplitude of the AlO_4 twist angle in the *I* phase as 1.5° – 2° .

*On leave from Institute of Physical Optics, 290005, Lviv, Ukraine.

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