

Electric Field Gradient Modulation in Incommensurate Systems X_2YZ_4 *.**

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Z. Naturforsch. **41a**, 256–260 (1986); received August 1, 1985

The subject of the paper is the plane wave limit of static incommensurate displacement modulation in the crystal structure, which is related to the commensurate ferrophase modulation. Using the point charge model, the corresponding electric field gradient modulation and quadrupole perturbed NMR spectra are calculated. The corrections up to the 4th order owing to the incoherent displacements of the charges in the vicinity of the resonant nucleus are considered. Comparison with the experimental data shows a reasonable agreement.

Introduction

It is known that the members of the X_2YZ_4 family of compounds ($X=Cs, K, NH_4, Rb$; $Y=Be, Cd, Co, Zn, Se$; $Z=Br, Cl, F, O$) exhibit incommensurate displacively modulated structure(s) at intermediate temperatures between the paraphase and ferrophase [1, 2].

The paraphase structure [3] belongs to the symmetry space group Pnam. In the unit cell there are two parallel mirror planes in which all of the eight X atoms are located. The remaining atoms form four YZ_4 tetrahedra which also lie in the mirror planes with one edge ($Z(1) – Z(2)$) and the centre (Y) in the plane and the two apexes with the atoms $Z(3)$ and $Z(4)$ symmetrically to the sides of the plane.

We call this structure the basic structure because the ferrophase and the incommensurate phase can be derived from it by superimposing a displacement modulation with the wave vector parallel to the mirror planes. The modulation wave length is commensurate in the first case and incommensurate in the second with the basic structure.

The incommensurate structure, which we shall be dealing with, is only an approximation, called the plane wave limit (p.w.l.), which is quite acceptable far away from the low temperature phase transition to the ferrophase. Near the phase transition the structure becomes more complicated (solitons [4]).

If a single resonance line depends on the conformation of the basic cell (unit cell in the basic structure) we expect this line to split because of displacement modulation. If the modulation is commensurate the number of new lines is the same as the number of basic cells in the modulation period. If, on the other hand, the modulation is incommensurate the modulation period is infinite and we have an infinite number of lines distributed, however, on a finite frequency region because the displacements are finite as well.

In the following we shall discuss the displacement modulation, especially the incommensurate one, and how it is related to the frequency distribution of the magnetic resonance which senses the conformation of the probe surrounding.

Displacement Modulation

Let us illustrate the X_2YZ_4 family structural changes by observing the behavior of a mirror plane atom. It is not difficult to imagine the generalization for an atom at an asymmetric site.

Figure 1 shows a schematic basic cell of Pnam symmetry with only one atom (characterized by the integer k) and its symmetry equivalents indicated. As mentioned above, we shall assume that this atom

* Presented at the VIIth International Symposium on Nuclear Quadrupole Resonance Spectroscopy, Darmstadt, July 22–26, 1985.

** Work supported in part by the Research Community of Slovenia.

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lies in the mirror plane $z = 1/4$ or $z = 3/4$. Therefore it will have only four symmetry equivalents instead of eight: $k(x_k, y_k, z_k)$, $k'(1-x_k, 1-y_k, \frac{1}{2}+z_k)$, $k''(\frac{1}{2}+x_k, \frac{1}{2}-y_k, z_k)$ and $k'''(\frac{1}{2}-x_k, \frac{1}{2}+y_k, \frac{1}{2}+z_k)$.

We derive the approximate ferrophase structure from the basic structure by superimposing a sinusoidal displacement modulation with the wave length of three basic cell lengths:

$$u_{ik}(m) = A_{ik} \cos \left(m \frac{2\pi}{3} + \Phi_{ik} \right) = A_{ik} \cos (\varphi + \Phi_{ik}). \quad (1)$$

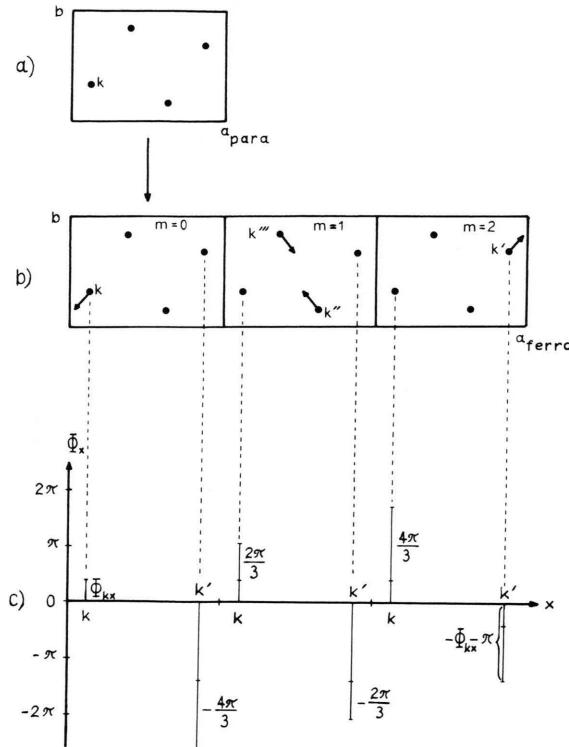


Fig. 1. Relation between the paraphase and ferrophase structures for the X_2YZ_4 family: a) paraphase unit cell; b) ferrophase unit cell with the displacements of atom k and its symmetry equivalents; c) phase shifts of the x -components of the displacements for some symmetric atoms.

Integer i ($i = 1, 2, 3$ or x, y, z) denotes the direction, integer k counts the atoms in the basic cell, and integer m counts the basic cells along the modulation wave. The conformation of the zero-th modulated basic cell is determined only by the modulation amplitudes A_{ik} and the corresponding phase shifts Φ_{ik} .

The relations between the phase shifts of the modulation waves corresponding to the symmetric atoms are determined by the symmetry $Pna2_1$ of the ferrophase.

Let us set the observation window to the width $3a$ (a – basic cell length), i.e. the length of the ferrophase unit cell. The modulation phase relations within the window are determined by the phase shifts. The translation of the window by $n \cdot a$ is performed by increasing the modulation phase angle $\varphi = m \frac{2\pi}{3}$ by $n \frac{2\pi}{3}$ to all the atoms inside the window. Table 1 and Fig. 1 show the phase shift relations for the four symmetric atoms in $Pna2_1$: $k, k', k'',$ and k''' .

In the plane wave approximation of the incommensurate structure we assume that besides the decrease of the modulation amplitude the only deviation from the ferrophase structure is the following: The modulation phase angle jumps between the basic cells become irrational fractions of 2π $\left(\varphi = m \left(\frac{2\pi}{3} - \delta \right) \right)$, whereas the phase shifts in the chosen window remain the same as in the ferrophase. However, the window width must not be too large, it must be comparable to a . This can be justified if we remember the structure of the soliton limit of incommensurate states. From one commensurate domain to another the phase delays must be the same for all the atoms since in the commensurate domains the modulation phase relations must be the same as in the ferrophase. In the p.w.l. the soliton width is much greater than the intersoliton distance, and because of continuity we except the

Table 1. The phase shift relations between the symmetric atoms.

	$k(x, y, z)$	$k'(1-x, 1-y, \frac{1}{2}+z)$	$k''(\frac{1}{2}+x, \frac{1}{2}-y, z)$	$k'''(\frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}+z)$
u_x	Φ_x	$-\Phi_x - \pi$	Φ_x	$-\Phi_x - \pi$
u_y	Φ_y	$-\Phi_y - \pi$	$\Phi_y - \pi$	$-\Phi_y$
u_z	Φ_z	$-\Phi_z$	Φ_z	$-\Phi_z$

phase shifts in the p.w.l. to remain the same. Let us mention that also in the p.w.l. we can find basic cells where the conformation is similar to the ferrophase one, namely where

$$m \left(\frac{2\pi}{3} - \delta \right) \cong m' \frac{2\pi}{3}. \quad (2)$$

m and m' are integers. This condition is periodically approached but never exactly fulfilled.

EFG Modulation

A component of the EFG tensor in the modulated structure where the displacements of the atoms, important for the NMR or NQR, are given by

$$u_i = A_i \cos(\varphi(m) + \Phi_i) \quad (3a)$$

for the probe; and by

$$u_{ik} = A_{ik} \cos(\varphi(m) + \Phi_{ik}) \quad (3b)$$

for the surrounding atoms, can be expanded in powers of atomic displacements:

$$V = V_0 + \sum_{n=1}^{\infty} \frac{1}{n!} \left(\sum_{k,i} u_{ik} \frac{\partial}{\partial x_{ik}} + \sum_i u_i \frac{\partial}{\partial x_i} \right)^n V. \quad (4)$$

If the displacements are described by simple modulation waves, the observed quantity V is a periodic function of the coordinates for which it is calculated. The nonlinear dependence of V on the coordinates brings into the expansion also higher harmonic terms:

$$V(\varphi) = V^{(0)} + \operatorname{Re} [V^{(1)} e^{i\varphi} + V^{(2)} e^{2i\varphi} + V^{(3)} e^{3i\varphi} + \dots]. \quad (5)$$

Taking into account the relations

$$\begin{aligned} \frac{\partial}{\partial x_i} &= - \sum_k \frac{\partial}{\partial x_{ik}}, \quad \frac{\partial^2}{\partial x_i^2} = \sum_k \frac{\partial^2}{\partial x_{ik}^2}, \\ \frac{\partial^2}{\partial x_i \partial x_j} &= \sum_k \frac{\partial^2}{\partial x_{ik} \partial x_{jk}}, \quad \frac{\partial^2}{\partial x_i \partial x_j} = - \frac{\partial^2}{\partial x_{ik} \partial x_{jk}}, \end{aligned} \quad (6)$$

we obtain, up to the second order:

$$\begin{aligned} V^{(0)} &= V_0 + \frac{1}{4} \sum_{i,k} (A_{ik}^2 + A_i^2) \frac{\partial V}{\partial x_{ik}^2} + \frac{1}{2} \sum_{i,j > i,k} [A_{ik} A_{jk} \cos(\Phi_{ik} - \Phi_{jk}) + A_i A_j \cos(\Phi_i - \Phi_j) \\ &\quad - A_i A_{jk} \cos(\Phi_i - \Phi_{jk}) - A_j A_{ik} \cos(\Phi_j - \Phi_{ik})] \frac{\partial^2 V}{\partial x_{ik} \partial x_{jk}} + \dots, \\ V^{(1)} &= \sum_{i,k} (A_{ik} e^{i\Phi_{ik}} - A_i e^{i\Phi_i}) \frac{\partial V}{\partial x_{ik}} + \dots, \\ V^{(2)} &= \frac{1}{4} \sum_{i,k} (A_{ik}^2 e^{2i\Phi_{ik}} + A_i^2 e^{2i\Phi_i}) \frac{\partial^2 V}{\partial x_{ik}^2} + \frac{1}{2} \sum_{i,j > i,k} [A_{ik} A_{jk} e^{i(\Phi_{ik} + \Phi_{jk})} \\ &\quad + A_i A_j e^{i(\Phi_i + \Phi_j)} - A_i A_{jk} e^{i(\Phi_i + \Phi_{jk})} - A_j A_{ik} e^{i(\Phi_j + \Phi_{ik})}] \frac{\partial^2 V}{\partial x_{ik} \partial x_{jk}} + \dots. \end{aligned} \quad (7)$$

Table 2. The EFG modulation coefficients calculated for the environment of 9 atoms in Rb_2ZnCl_4 (with structure data [3]).

Rb(1)	XX	YY	ZZ	XY	YZ	XZ
ind.						
00	2.36	2.02	-4.38	2.43	0	0
02	0.43	0.22	-0.55	-0.07	0	0
11	0	0	0	0	$0.33 + 0.08i$	$0.27 - 1.11i$
22	$-0.20 - 0.01i$	$-0.05 - 0.25i$	$0.32 + 0.17i$	$0.22 - 0.13i$	0	0
Rb(2)						
00	-2.43	-1.02	3.45	-0.46	0	0
02	0.34	0.31	-0.62	0.12	0	0
11	0	0	0	0	$0.83 + 1.43i$	$0.27 + 1.23i$
22	$-0.09 - 0.13i$	$-0.27 + 0.08i$	$0.21 + 0.15i$	$0.02 + 0.02i$	0	0

An example for the expansion of V_{xx} : $V_{xx}(\varphi) \propto XX_{00} + XX_{02} S^2 + \operatorname{Re} [XX_{11} S e^{i\varphi} + XX_{22} S^2 e^{2i\varphi}]$.

Here we introduced the absolute value of the order parameter

$$S = \frac{A_{lk}}{A_{lk} \text{ (ferrophase)}}$$

which is proportional to all the displacements.

Two further expansion coefficients have also been calculated, but only for the case of nonmodulated probe positions. This study will be published elsewhere.

Table 2 shows the EFG modulation coefficients for Rb sites in Rb_2ZnCl_4 , calculated by the use of (7) from the displacement modulation amplitudes obtained from the structure data for the ferrophase [3].

Calculation of Spectra and Experimental Verification

The EFG tensor has five independent components, and each of them can be differently modulated. If one measures a quantity which depends on the EFG, one must have enough data in order to be able to calculate the modulation parameters of all the EFG components. Pure NQR usually cannot provide all necessary data from the splitting of transition frequency(ies) which depends only on the combination of the EFG eigenvalues and not on the tensor orientation which is modulated, too. The dependence of NQR on the EFG eigenvalues makes

it difficult also to express the resonance frequency modulation by the modulations of the EFG components in the laboratory system. With strict assumptions and some success this calculation was performed for the halogene resonance in Rb_2ZnBr_4 and in Rb_2ZnCl_4 . The halogen NQR frequency modulation was expressed by the modulation of the larger EFG eigenvalue only and it was shown when this assumption is justified. The calculations were used for semiquantitative explanation of pure NQR spectra in the incommensurate phase of these compounds. The results will be described in more detail in a further publication.

It is more convenient to study the incommensurate modulation by measuring the quadrupole shift of NMR lines. An appropriate nucleus for such measurement is ^{87}Rb with a high magnetic moment and a moderately low quadrupole moment. Several measurements on the subject were published [5–9].

The angular dependence of the second order quadrupole shift for the central NMR line ($v_{1/2} \leftrightarrow -1/2$) and of the first order quadrupole shift for the satellites is described by Volkoff's equations [10]:

$$\begin{aligned} \text{central line: } \Delta v &= X + Y \cos 2\theta + Z \sin 2\theta \\ &\quad + U \cos 4\theta + W \sin 4\theta, \\ \text{satellites: } \Delta v &= A + B \cos 2\theta + C \sin 2\theta. \end{aligned} \quad (8)$$

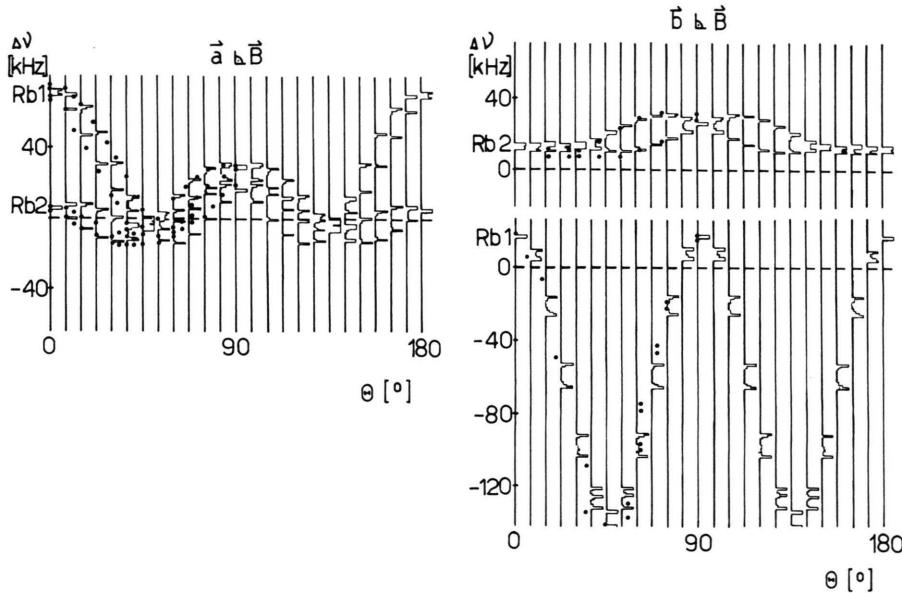


Fig. 2. Angular dependences of the quadrupole shifts of the ^{87}Rb NMR line ($v_{1/2} \leftrightarrow -1/2$), calculated for Rb_2ZnCl_4 and compared with the experimental points (●) from [5].

Here θ is the rotation angle around a chosen axis. The coefficients A, B, C are linear functions of the EFG components and X, Y, Z, U, W are quadratic functions of them. They depend on the choice of rotation axis.

In the case of the central line as well as in the case of the satellites it is seen that for a certain orientation in a magnetic field, the NMR frequency shift modulation in a modulated structure is proportional to a linear combination of modulated Volkoff coefficients and further to a linear combination of the EFG expansion coefficients. Their number is of course infinite. Up to the second order in the parameter S it may be written:

$$\Delta v(\varphi) = \Delta v_{00} + \Delta v_{02} S^2 + \operatorname{Re} [(\Delta v_{1\operatorname{Re}} + i \Delta v_{1\operatorname{Im}}) S e^{i\varphi} + (\Delta v_{2\operatorname{Re}} + i \Delta v_{2\operatorname{Im}}) S^2 e^{2i\varphi}]. \quad (9)$$

The coefficients $\Delta v_{00}, \Delta v_{02}, \Delta v_{1\operatorname{Re}}, \Delta v_{1\operatorname{Im}}, \Delta v_{2\operatorname{Re}}, \Delta v_{2\operatorname{Im}}$ may be calculated taking into account Volk-

koff's equations. The line shape is then proportional to the inverse derivation of the expression above:

$$f(v) \propto \left| \frac{\partial \Delta v}{\partial \varphi} \right|_v^{-1}. \quad (10)$$

We have performed such calculations for Rb_2ZnCl_4 using the EFG modulation coefficients, as presented in Table 2. The results for the central line are shown on Figure 2. They are compared with the experimental angular dependences of the quadrupole shift reported in [5].

The calculations reported here show the importance of the phase shifts joined with the expansion coefficients of the modulated EFG tensor and their relation to the atomic displacement modulation. It is another case where the use of the point charge model for the calculation of the EFG shifts, was fruitful.

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