^{39}K NMR study of the antiferroelectric phase transition in potassium thiocyanate

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The ^{39}K electric field gradient (EFG) and chemical-shift tensors have been determined in KSCN above and below T_c. Whereas all the data below T_c are compatible with the site symmetry of the K$^+$ ions given by the space group D_{2h}^{11} (*Pbcm*) of the low-temperature orthorhombic phase, this is not the case for the EFG data above T_c. The symmetry of the paraelectric phase is broken on the quadrupole-coupling time scale but not on the chemical-shift-tensor time scale, allowing for an interesting insight into the dynamics of the SCN$^-$ head-tail disordering process. The transition is of the order-disorder type for the SCN$^-$ groups and of a displacive type for the K$^+$ ions.

I. INTRODUCTION

According to structural data,[1-3] potassium thiocyanate (KSCN) undergoes at $T_c = 413$ K, a first-order antiferroelectric phase transition from a paraelectric, body-centered tetragonal structure with the space group D_{4h}^{18} and $Z = 2$ to an orthorhombic, antiferroelectric, and ferroelastic form with the space group D_{2h}^{11} and $Z = 4$. The transition is connected with a head-tail ordering[3,4] of the linear SCN$^-$ dipoles which are dynamically disordered between two equivalent equilibrium orientations at $T > T_c$. In the low-temperature phase, the SCN$^-$ dipoles are ordered in an antiparallel arrangement[2,3] forming—alternatively with the K$^+$ ions—layers perpendicular to the crystal c axis. The ordering of the SCN$^-$ groups is linearly coupled with a spontaneous displacement of the K$^+$ ions in the a-b plane. X-ray diffuse scattering[5] points towards the existence of a soft phonon at the Z point of the Brillouin-zone boundary in the tetragonal phase but no neutron-scattering study has been performed as yet to verify this suggestion or the existence of a coupling between the orientational dynamics of the SCN$^-$ dipoles and the phonon modes.

In order to throw some additional light on the microscopic nature of this transition and, in particular, on the coupling between the SCN$^-$ and K$^+$ motion, we decided to perform a ^{39}K nuclear magnetic resonance study of KSCN. We particularly hoped to determine the electric field gradient (EFG) and chemical-shift tensors at the ^{39}K sites to get some clue on the local structural changes occurring at T_c. Since the chemical-shift interactions are weaker than the quadrupole coupling interactions, we deal with two different time scales and have the possibility of performing a "two clock" experiment which could also elucidate the dynamics of the structural fluctuations at T_c.

II. EXPERIMENT

Fourier transform ^{39}K NMR spectra were recorded in two different superconducting magnets with ^{39}K nuclear Larmor frequencies of $\omega_L/2\pi = 16.628$ and 12.8 MHz, respectively. About 400 free-induction decays were accumulated for each spectrum. The single crystal grown at room temperature (i.e., at $T < T_c$) was rotated around three mutually perpendicular crystallographic axes a, b, and c to determine the electric field gradient tensors at the K sites.

III. STRUCTURAL CONSIDERATIONS

According to the crystal structure[1-3] there are two ^{39}K nuclei in the primitive cell above T_c. Both are physically and chemically equivalent and lie on the fourfold rotation axis. The two ^{39}K EFG tensors should therefore be axially symmetric $V_{XX} = V_{YY}$ and the largest principal axis V_{ZZ} should point along the fourfold c axis. Below T_c the primitive cell is doubled and the symmetry reduced from tetragonal to orthorhombic. The K$^+$ ions are displaced from their positions in the tetragonal phase by the ordering of the SCN$^-$ two-position dipoles. They move towards the more spacious direction, i.e., along the a axis. There should be four chemically equivalent K sites in the primitive cell for $T < T_c$. The corresponding EFG tensors should not be axially symmetric anymore. Since the K$^+$ ions lie on a twofold axis parallel to the a direction, one of the principal axes of the EFG tensor should point along the a axis. There should be two pairs of physically nonequivalent ^{39}K EFG tensors in the primitive cell which differ in the orientation of the principal axes. Below T_c one also expects the existence of different antiferroelectric domains. The ^{39}K EFG tensors in these

domains should be related by a 90° rotation around the c axis.

IV. DETERMINATION OF THE EFG TENSORS

The angular dependence of the second-order quadrupolar shift $\Delta v_i(\varphi_i)$ of the central NMR line is[6]

$$\Delta v_i(\varphi_i) = \frac{1}{v_L}[\, A_i + B_i \cos(2\varphi_i) + C_i \sin(2\varphi_i)$$

$$+ D_i \cos(4\varphi_i) + E_i \sin(4\varphi_i)] \,, \qquad (1)$$

where $i = a,b,c$ labels the rotation axes. The coefficients A, B, C, D, and E are known functions[6] of the EFG tensor components V_{ij}. It is possible to determine all five independent EFG tensor components from the Fourier coefficients D_i and E_i alone if they are known for three mutually orthogonal rotational axes. Note that these two Fourier coefficients are unaffected by the anisotropic chemical shift, which contributes to the $\cos(2\varphi_i)$ and $\sin(2\varphi_i)$ terms as well as to the isotropic part of the shift. The expressions for D_i and E_i can be written as[6]

$$D_i = \tfrac{3}{32}(eQ/h)^2[\tfrac{1}{4}(v_{jj} - V_{kk})^2 - V_{jk}^2]\,, \qquad (2a)$$

$$E_i = \tfrac{3}{32}(eQ/h)^2(V_{jj} - V_{kk})V_{jk}\,, \qquad (2b)$$

where $i = a$, $j = b$, and $k = c$. $D_j, \ldots, E_k$ are obtained by cyclic permutation of the indices. These six equations can be solved for the five unknown V_{ij}. An overall sign ambiguity remains as usual. Once the EFG tensor components V_{ij} are known, the contributions A_{qi}, B_{qi}, and C_{qi} to the experimental Fourier coefficients A_i, B_i, and C_i can be calculated. The differences between the experimental and the calculated coefficients

$A_i - A_{qi}, \ldots, C_i - C_{qi}$ give the Fourier coefficients A_{ci}, B_{ci}, and C_{ci} of the chemical-shift contribution. From them the chemical-shift tensors, $\overset{\leftrightarrow}{\sigma}$ can be determined in the usual way:

$$\overset{\leftrightarrow}{\sigma} = \begin{bmatrix} A_{c1} & C_{c3} & C_{c2} \\ C_{c3} & A_{c2} & C_{c1} \\ C_{c2} & C_{c1} & A_{c3} \end{bmatrix}\,. \qquad (2c)$$

The assignment of the chemical-shift tensors follows automatically from that of the EFG tensors. The final fit where both chemical-shift anisotropy and quadrupole contributions are taken into account is shown in Figs. 1 and 2 as a solid line. The corresponding tensors are listed in Table I. The chemical-shift tensors are separated into an isotropic part $\delta = \tfrac{1}{3}\mathrm{Tr}\overset{\leftrightarrow}{\sigma}$ and an anisotropic part $\Delta\overset{\leftrightarrow}{\sigma} = \overset{\leftrightarrow}{\sigma} - \delta\mathbf{1}$.

V. RESULTS AND DISCUSSION

Figure 1 shows the angular dependence of the shift of the central $\tfrac{1}{2} \to -\tfrac{1}{2}$ ^{39}K resonance lines at $T = 380$ K $< T_c$. In agreement with the prediction based on crystal symmetry, there are two ^{39}K central lines for $a\bot H_0$ and only one such line for $b\bot H_0$ and $c\bot H_0$ in a virgin crystal. The presence of two lines in the c rotation (i.e., $c\bot H$) shown in the inset to Fig. 1 is due to the existence of two 90° antiferroelectric domains which formed after the crystal was heated to the paraelectric phase and cooled back to the antiferroelectric phase.

The ^{39}K EFG and chemical-shift tensors for $T < T_c$ determined from the rotation patterns according to the procedure described in Sec. IV are collected in Table I.
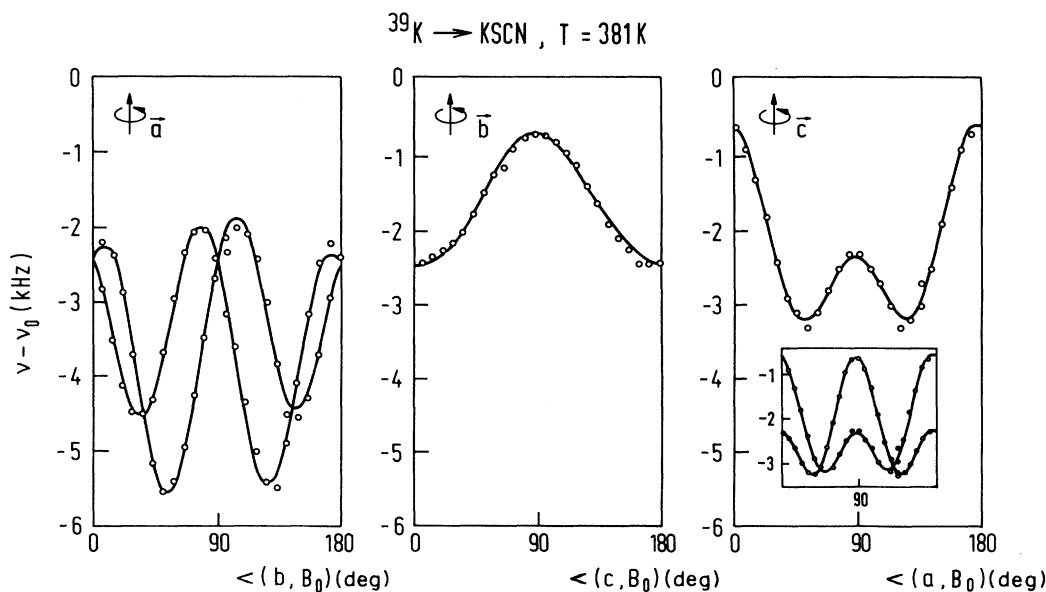

FIG. 1. Angular dependence of the shifts of the ^{39}K NMR central transitions in the antiferroelectric phase of KSCN at $T = 381$ K. The inset for the c rotation shows the two 90° domain lines formed after the crystal was heated through T_c and cooled back into the antiferroelectric phase.

TABLE I. Components of the ^{39}K electric field gradient and chemical-shift tensors $\vec{\sigma} = \delta 1 + \Delta\vec{\sigma}$ in the crystal-fixed a-b-c frame in KSCN.

Orthorhombic antiferroelectric phase at $T = 381$ K

$$\vec{V} = \begin{bmatrix} -81 & 0 & 0 \\ 0 & 249 & \pm 66 \\ 0 & \pm 66 & -168 \end{bmatrix} \text{kHz}$$

$e^2qQ/h = 259$ kHz, $\eta = 0.37$

$$\Delta\vec{\sigma} = \begin{bmatrix} -15.5 & 0 & 0 \\ 0 & -7.5 & -22.2 \\ 0 & -22.2 & 23 \end{bmatrix} \text{ppm}$$

$\delta = -71.4$ ppm

Tetragonal paraelectric phase at $T = 415$ K

$$\vec{V} = \begin{bmatrix} -165 & 0 & 0 \\ 0 & +165 & 0 \\ 0 & 0 & 0 \end{bmatrix} \text{kHz}$$

$e^2qQ/h = 165$ kHz, $\eta = 1$

$$\Delta\vec{\sigma} = \begin{bmatrix} -15.1 & 0 & 0 \\ 0 & -15.1 & 0 \\ 0 & 0 & 30.2 \end{bmatrix} \text{ppm}$$

$\delta = -128.5$ ppm

In agreement with the predictions based on crystal symmetry, all ^{39}K EFG tensors are chemically equivalent and there are two physically nonequivalent ^{39}K sites in the unit cell. The corresponding electric quadrupole coupling constant is $e^2qQ/h = 259$ kHz and the asymmetry parameter

$$\eta = \frac{V_{XX} - V_{YY}}{V_{ZZ}} = 0.37 \ .$$

The ^{39}K chemical shift tensors have the same symmetry as the corresponding EFG tensors. The isotropic chemical shift with respect to a KCl solution is $\delta = -71.4$ ppm.

The data below T_c are compatible with the site symmetry of the K$^+$ ions given by the space group D_{2h}^{11} ($Pbcm$) of the low-temperature orthorhombic phase. One of the principal axes of the EFG tensor corresponding the eigenvalue $V_{XX} = -81$ kHz points along the a direction, whereas the other two principal axes, $V_{ZZ} = 259$ kHz and $V_{YY} = -178$ kHz, lie in the b-c plane and make an angle $\pm 8°$ with the crystal b and c axes, respectively.

The temperature dependence of the splitting between

the ^{39}K $\frac{1}{2} \rightarrow -\frac{1}{2}$ NMR lines, belonging to the two ^{39}K sites which are physically nonequivalent below T_c, is presented in Fig. 3.

The splitting vanishes discontinuously at $T_c = 413$ K demonstrating the disappearance of long-range order for $T > T_c$. The splitting of the ^{39}K NMR lines due to the existence of 90° antiferroelectric domains similarly vanishes at T_c (Fig. 4). This demonstrates that, on the NMR time scale, neither long-range order nor antiferroelectric domain structure persist above T_c.

The ^{39}K EFG data above T_c (Table I) are, however, not compatible with the K$^+$-ion site symmetry given by the space group D_{4h}^{18} ($I4/mcm$) of the high-temperature tetragonal phase. Though the 90° domain splitting disappears and the number of physically nonequivalent K$^+$ sites changes form 2 to 1 as expected and, in addition, the rotation patterns for the a and b rotation are identical as required by the overall tetragonal symmetry, the strong angular dependence of the rotation pattern for the c rotation (Fig. 2) does not agree with the crystal structure proposed by the x-ray studies.[1−5] The asymmetry parameter

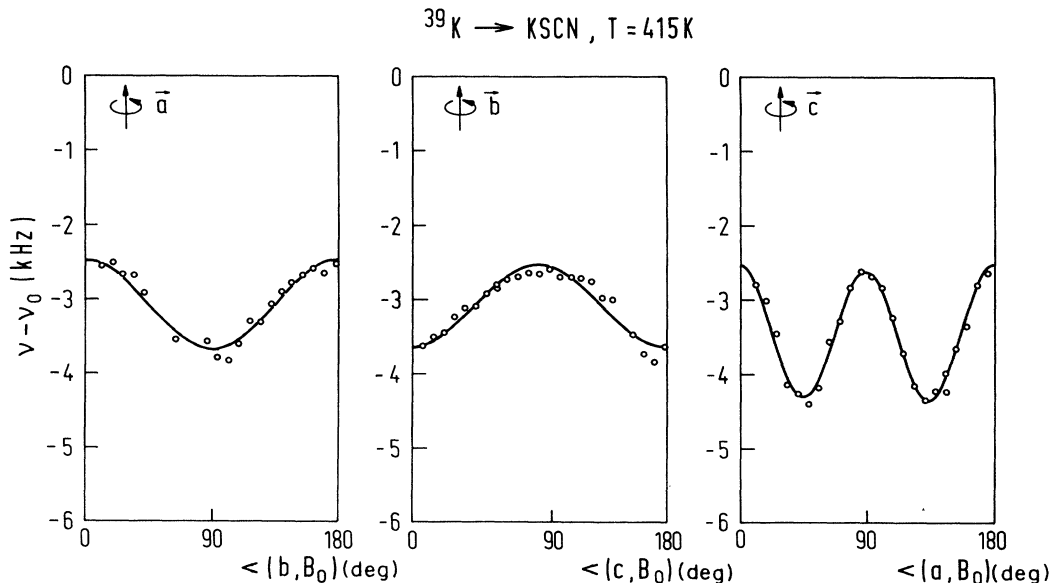^{39}K $\longrightarrow$ KSCN, T = 415K

FIG. 2. Angular dependence of the shifts of the ^{39}K NMR central transitions in the paraelectric phase of KSCN at $T = 415$ K.
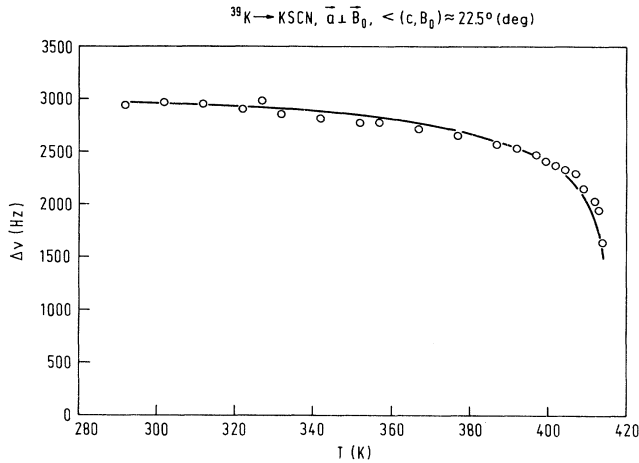
FIG. 3. Temperature dependence of the splitting between the ^{39}K $\frac{1}{2} \rightarrow -\frac{1}{2}$ quadrupole perturbed NMR lines belonging to physically nonequivalent K sites in KSCN. The solid line represents the fit to expression (12a). Here S_1 is determined from the expression (Ref. 4)

$$S_1 = \tanh\left[\frac{T_0}{T}S_1 + A\frac{T_0}{T}S_1^3\right]$$

with $T_0 = 415$ K and $A = 0.35$.

η equals 1 instead of being zero which excludes the existence of a fourfold axis passing through the K$^+$ sites at $(0,0,\frac{1}{4})$ as given by the x-ray data.[1-5]

There are two different possible explanations of the above data.

(i) The crystal structure of the high-temperature phase of KSCN is not the one given by the x-ray data[1-3] and the phase transition at T_c is not connected with the head-tail disordering of the SCN$^-$ dipoles. The SCN groups are thus for $T > T_c$ not dynamically disordered
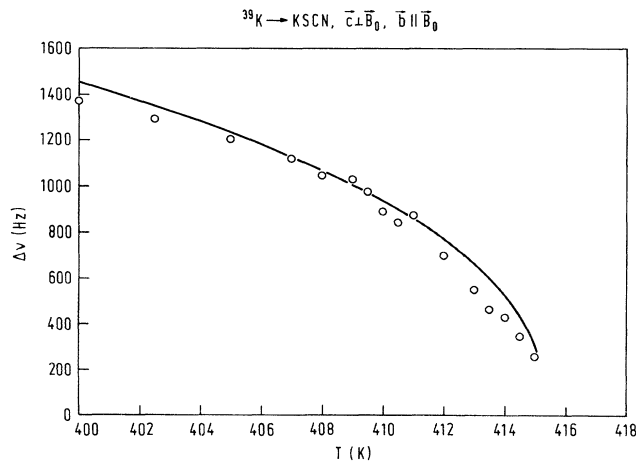

FIG. 4. Temperature dependence of the splitting between the ^{39}K $\frac{1}{2} \rightarrow -\frac{1}{2}$ NMR lines due to the existence of 90° antiferroelectric domains. The solid line represents the fit to expression (12b).

between two equivalent orientations. The argument which could speak for this explanation is that there is hardly enough space available in the structure for single-particle 180° flips of individual SCN$^-$ groups.

(ii) The crystal structure of the high-temperature phase of KSCN as given by x-ray data[1-3] is correct on the time average but not on the ^{39}K quadrupole perturbed NMR time scale $\tau_{NMR} \approx 10^{-5}$ s where the instantaneous, and not the average, structure is seen.

The fact that, for $T > T_c$ in contrast to the EFG tensor, the ^{39}K chemical-shift tensor *is* axially symmetric, $\eta = 0$ (Table I), strongly supports the second of these two possibilities. If this interpretation is correct, all characteristic times for structural fluctuations in KCN above T_c are short compared to the chemical shift tensor time scale $\sim 10^{-2}$ s whereas they are long as compared to the ^{39}K quadrupole coupling time scale ($\sim 10^{-5}$ s).

Let us now see if the above ^{39}K NMR results can be related to the phase transition mechanism and described quantitatively. In the orthorhombic phase there are four 90° antiferroelectric domains which are related by 0°, 90°, 180°, and 270° rotations around the c axis. In these domains the K$^+$ inns are displaced from the tetragonal fourfold axis (i.e., the $0,0,\frac{1}{4}$ position) in the $\pm a$ and $\pm b$ directions, respectively. One may ascribe four separate ^{39}K EFG tensors $\overleftrightarrow{V}(+a)$, $\overleftrightarrow{V}(-a)$, $\overleftrightarrow{V}(+b)$, and $\overleftrightarrow{V}(-b)$ to the four displaced K$^+$ sites in the a-b plane. One of the principal axes of the K$^+$ EFG (or chemical-shift) tensor will, due to symmetry reasons, point in the direction of the displacement, i.e., along $\pm a$ or $\pm b$. In the crystal-fixed a,b,c frame these tensors will thus have the following forms:

$$\overleftrightarrow{V}(\pm a) = \begin{bmatrix} \alpha & 0 & 0 \\ 0 & \beta & \pm w \\ 0 & \pm w & \gamma \end{bmatrix}, \tag{3a}$$

$$\overleftrightarrow{V}(\pm b) = \begin{bmatrix} \beta & 0 & \pm w \\ 0 & \alpha & 0 \\ \pm w & 0 & \gamma \end{bmatrix}, \tag{3b}$$

where $\alpha + \beta + \gamma = 0$.

If the phase transition in KSCN is now of the order-disorder type for the K$^+$ ions similarly as it is for the SCN$^-$ ions, the structure of the paraelectric phase (i.e., phase I) is a dynamic average of these four structures. If the K$^+$ ions would quickly move between the four sites in response to the SCN$^-$ reorientations, as compared to the characteristic NMR time scale, all four structures would appear with the same weighting factor so that

$$\langle \overleftrightarrow{V} \rangle_I = \frac{1}{4}[\overleftrightarrow{V}(+a) + \overleftrightarrow{V}(-a) + \overleftrightarrow{V}(+b) + \overleftrightarrow{V}(-b)]$$

$$= \begin{bmatrix} -\gamma/2 & 0 & 0 \\ 0 & -\gamma/2 & 0 \\ 0 & 0 & \gamma \end{bmatrix}. \tag{4}$$

The tensor $\langle \overleftrightarrow{V} \rangle_I$ will be, in this case, thus axially symmetric around the c axis, the asymmetry parameter η will be zero, and the quadrupole coupling constant $eQ\gamma/h$ will be temperature independent.

In the orthorhombic phase (i.e., designated here as

phase II) the four off-center sites would not be equivalent anymore. In view of the orthorhombic symmetry, we can introduce the order parameter S of the I-II transition as

$$S = P(+a) + P(-a) - P(+b) - P(-b) , \qquad (5)$$

where the $P(i)$ describe the probabilities of occupation of the four off-center sites. In view of the existence of the twofold axis along the a direction we have

$$P(+b) = P(-b) = (1-S)/4 , \qquad (6a)$$

whereas $P(+a) \neq P(-a)$ so that

$$P(+a) = (1+S)(1+S_1)/4 , \qquad (6b)$$

$$P(-a) = (1+S)(1-S_1)/4 , \qquad (6c)$$

where

$$S_1 = \frac{P(+a) - P(-a)}{P(+a) + P(-a)} . \qquad (6d)$$

If the biased motion among the four K sites would be fast on the NMR time scale, the time-averaged EFG tensors at the two physically nonequivalent K sites 1 and 2 would be

$$\langle \vec{V} \rangle_{\mathrm{II},K_1} = \frac{1+S}{2} \left[\frac{1+S_1}{2} \vec{V}(+a) + \frac{1-S_1}{2} \vec{V}(-a) \right]$$
$$+ \frac{1-S}{4} [\vec{V}(+b) + \vec{V}(-b)] , \qquad (7a)$$

$$\langle \vec{V} \rangle_{\mathrm{II},K_2} = \frac{1+S}{2} \left[\frac{1-S_1}{2} \vec{V}(+a) + \frac{1+S_1}{2} \vec{V}(-a) \right]$$
$$+ \frac{1-S}{4} [\vec{V}(+b) + \vec{V}(-b)] . \qquad (7b)$$

If, for $T > T_c$, $S = S_1 = 0$, $\langle \vec{V} \rangle_{K_1} = \langle \vec{V} \rangle_{K_2}$, and both tensors would become identical and axially symmetric in the paraelectric phase as predicted by expression (4).

In view of the nonaxial form of the paraelectric EFG tensor for $T > T_c$ (Table I), we must drop some of the above assumptions. Let us therefore first assume that the motion of the K^+ ions between the "a" and "b" sites, i.e., the "S motion," is slow on the quadrupole coupling time scale so that the tetragonal symmetry is broken for $T > T_c$, whereas the motion between the "$+a$" and "$-a$" sites, i.e., the "S_1 motion," is fast. If the I-II transition is of the order-disorder type for the K^+ ions [i.e., the potential for the motion of the K^+ ions and the EFG tensor elements (3a) and (3b) have the same form above and below T_c], we may put $S = 1$ in expressions (7a) and (7b) whereas $0 < S_1 < 1$. The elements of the EFG tensors α, β, γ, and w will be identical above and below T_c, whereas $S_1 = 0$ for $T > T_c$ and $S_1 \neq 0$ for $T < T_c$.

If, on the other hand, the I-II transition is of the displacive type for the K^+ ions, we may still put $S = 1$ in expressions (7a) and (7b) but the elements of the EFG tensors will change at T_c, i.e., they will depend on S_1.

We shall first treat the order-disorder case. Here we have, with the above assumptions,

$$\langle \vec{V} \rangle_{\mathrm{II},K_1,K_2} = \begin{bmatrix} \alpha & 0 & 0 \\ 0 & \beta & \pm S_1 w \\ 0 & \pm S_1 w & \gamma \end{bmatrix} . \qquad (7c)$$

Let us now see if we can explain with this model the temperature dependence of the quadrupole perturbed $\frac{1}{2} \rightarrow -\frac{1}{2}$ ^{39}K NMR frequencies and, in particular, the temperature dependence of the splitting between the two physically nonequivalent K sites and the domain splitting.

The second-order quadrupole shift $\nu - \nu_L$ of the $\frac{1}{2} \rightarrow -\frac{1}{2}$ NMR transition will be for the case that the external magnetic field B_0 is in the b-c plane, given by

$$\nu - \nu_L = \frac{1}{48\nu_L} [(eQV_{xx} - eQV_{yy})^2 - 2(eQV_{zy})^2] , \qquad (8)$$

where $\mathbf{x} \| \mathbf{a}$, $\mathbf{z} \| \mathbf{B_0}$, $\mathbf{y} \perp (x,z)$, and ϕ is the angle between the b axis and B_0. The transformation of the tensor (7c) from the a,b,c into the x,y,z frame yields

$$V_{xx} = \alpha ,$$
$$V_{yy} = -\gamma/2 + (\gamma - \beta)\cos(2\phi)/2 \mp wS_1\sin(2\phi) ,$$
$$V_{zy} = (\gamma - \beta)\sin(2\phi)/2 \pm wS_1\cos(2\phi) ,$$

where the $+$ sign refers to K_1 and the $-$ sign to K_2. For the special case of $\phi = 45°$ we thus find the T dependence of the K_1 and K_2 lines as

$$\nu_{K_1,K_2} - \nu_L = \frac{1}{48\nu_L} [\tfrac{9}{4}\alpha^2 - \tfrac{1}{2}(\beta - \gamma)^2$$
$$\mp 3\alpha wS_1 + w^2 S_1^2] . \qquad (9a)$$

The splitting $\nu_{K_1} - \nu_{K_2}$ is proportional to S_1:

$$\nu_{K_1} - \nu_{K_2} = \frac{\alpha w}{8\nu_L} S_1 , \qquad (9b)$$

whereas the average frequency depends on S_1^2:

$$\frac{\nu_{K_1} + \nu_{K_2}}{2} - \nu_L = \frac{1}{48\nu_L} [\tfrac{9}{4}\alpha^2 - \tfrac{1}{2}(\beta - \gamma)^2 + w^2 S_1^2] . \qquad (9c)$$

Within the same approach we find the T dependence of the lines ν_a and ν_b due to the existence of 90° antiferroelectric domains as

$$\nu_a - \nu_L = \frac{1}{48\nu_L} [\tfrac{9}{4}\gamma^2 - \tfrac{1}{8}(\beta - \alpha)^2 - \tfrac{3}{2}\gamma(\beta - \alpha)\cos2\psi$$
$$+ \tfrac{3}{8}(\beta - \alpha)^2\cos4\psi] , \qquad (10a)$$

$$\nu_b - \nu_L = \frac{1}{48\nu_L} [\tfrac{9}{4}\gamma^2 - \tfrac{1}{8}(\beta - \alpha)^2 + \tfrac{3}{2}\gamma(\beta - \alpha)\cos2\psi$$
$$+ \tfrac{3}{8}(\beta - \alpha)^2\cos4\psi] , \qquad (10b)$$

where $\psi = \angle (a, B_0$ for $B_0 \perp c$. It should be noted that this splitting is independent of S_1 but would depend on S if the "S motion" was not too slow. This splitting vanishes for (i) $\alpha = \beta = -\gamma/2$, i.e., tetragonal symmetry or for (ii) $\gamma = 0$, $\alpha = -\beta$.

In view of the fact that the domain splitting is indeed zero above T_c whereas the tetragonal symmetry is still broken on the time scale of the ^{39}K quadrupole coupling experiment, only the second of these two possibilities agrees with the experimental data. In this case we find

$$\nu_{a,b} - \nu_L = \frac{\alpha^2}{96\nu_L}(3\cos4\psi - 1), \quad B_0 \perp c, \quad T > T_c \qquad (10c)$$

as indeed observed.

The above order-disorder model is, however, unable to explain the temperature dependence of the domain splitting in the orthorhombic phase II as well as the fact that γ is different from zero below T_c. We therefore have to drop the order-disorder model for the K^+ ions and have to assume that for these ions—but not for the SCN^- groups—the transition is of a displacive nature. We still keep the "two-time-scale" model where the "S motion" of the SCN^- ions is slow and the "S_1 motion" of the SCN^- ions is fast compared to the ^{39}K quadrupole coupling time scale. Here the two order parameters S and S_1 are still given by expressions (5) and (6d) in which $P(+a)$ is the probability of finding the SCN^- ions in an arrangement in which the force on the K^+ ion acts along the $+a$ direction, etc. The EFG tensor will again be of the form

$$\vec{V} = \begin{bmatrix} \alpha & 0 & 0 \\ 0 & \beta & w \\ 0 & w & \gamma \end{bmatrix}, \qquad (11a)$$

where, however, the EFG tensor elements will depend on S_1. the elements will not depend on S since on the quadrupole coupling time scale $S = 1$. In this case γ will be zero above T_c where $S_1 = 0$ and the K^+ ions sit in the central position. If, however, S_1 is different from zero, the K^+ ions move away from the central positions along the $\pm a$ or $\pm b$ directions.

The diagonal elements of the EFG tensor have to be invariant at the transformation "$+a$"→"$-a$", i.e., $S_1 \rightarrow -S_1$. Therefore, only quadratic terms can appear in the expansion of α, β, γ in powers of S_1. We find

$$\alpha = \alpha_0 + \alpha_1 S_1^2 + \cdots , \qquad (11b)$$

$$\beta = \beta_0 + \beta_1 S_1^2 + \cdots , \qquad (11c)$$

with $\alpha_0 = -165$ kHz and $\beta_0 = 165$ kHz and

$$\gamma = -(\alpha + \beta) = -(\alpha_1 + \beta_1)S_1^2 + \cdots . \qquad (11d)$$

The off-diagonal element w changes its sign if "$+a$"→"$-a$" or $S_1 \rightarrow -S_1$ and thus has the following form:

$$w = w_1 S_1 . \qquad (11e)$$

The splitting $\nu_{K_1} - \nu_{K_2}$ [expression (9b)] will thus vary in the orthorhombic phase as

$$\nu_{K_1} - \nu_{K_2} = \frac{1}{8\nu_L}\alpha w = \frac{1}{8\nu_L}(\alpha_0 + \alpha_1 S_2^2)w_1 S_1 \approx S_1 , \qquad (12a)$$

whereas the 90° domain splitting for $B_0 \| b$ will go as

$$\nu_a - \nu_b = \frac{\gamma}{16\nu_L}(\beta - \alpha) \approx S_1^2, \quad T < T_c . \qquad (12b)$$

The difference *in* the T dependence of $\nu_{K_1}\nu_{K_2}$ and $\nu_a - \nu_b$ is indeed clearly seen in the experimental data (Figs. 3 and 4). This model explains the fact that $\nu_{K_1} = \nu_{K_2}$ and $\nu_a = \nu_b$ for $T > T_c$, where $S_1 = 0$, whereas the tetragonal symmetry is broken and $\nu_{a,b}$ will depend on ψ for the c rotation as predicted by expression (10c).

The above data thus show that the symmetry of the paraelectric phase is broken on the quadrupole coupling time scale but not on the chemical-shift-tensor time scale. This accounts for the difference in the crystal symmetry of the high-temperature phase as determined by ^{39}K quadrupole perturbed NMR which "sees" the instantaneous structure on a scale 10^{-5} s, and x-ray scattering data which "see" the spatially and time-averaged structure.

Additional support for the above "two-time-scale" displacive model for the K^+ ions is provided by the anomalous temperature and Larmor frequency dependence of the spin-lattice relaxation time in the laboratory and rotating frames[7] as well as by the large change in the isotropic part of the ^{39}K chemical shift tensor $\vec{\sigma}$ at T_c (Table I). Such a change cannot be explained within an order-disorder model for the K^+ ions. the phase transition in KSCN is thus triggered by the "head-tail" ordering of the SCN groups which results in a displacement of the K^+ ions.

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