

^{39}K and ^{77}Se NMR study of the paraelectric-to-incommensurate phase transition of K_2SeO_4

B. Topič,* A. von Kienlin, A. Götzhäuser, and U. Haeblerlen

Arbeitsgruppe Moleküllkristalle, Max-Planck-Institut für Medizinische Forschung, Jahnstrasse 29, D-6900 Heidelberg, Germany

R. Blinc

Institut Jožef Stefan, Univerza E. Kardelja, v Ljubljana, Jamova 39, YU-61111 Ljubljana, Slovenia, Yugoslavia

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The ^{39}K quadrupole-coupling and chemical-shift tensors have been determined from the angular dependences of the ^{39}K line shifts of the $^{39}\text{K} \pm \frac{1}{2} \leftrightarrow \mp \frac{1}{2}$ central NMR transitions in the paraelectric (P) and incommensurate (I) phases of K_2SeO_4 . The main effect of the P - I phase transition on these tensors is the appearance of nonzero off-diagonal elements V_{ab} and V_{bc} which reflects the destruction of mirror planes by frozen-in soft-mode displacements along the b axis. From the angular dependences of the ^{77}Se line shifts the ^{77}Se chemical-shift tensor has been determined in the paraelectric phase of K_2SeO_4 . In contrast to the ^{39}K quadrupole-coupling and chemical-shift tensors it remains unaffected on going through T_I and changes only slightly at T_C .

I. INTRODUCTION

K_2SeO_4 belongs to a large group of A_2BX_4 -type crystals which exhibit incommensurate (I) phases. It undergoes two successive phase transitions at $T_I=128$ K and $T_C=93$ K. The crystal structure of the paraelectric (P) phase, which is isomorphous with $\beta\text{-K}_2\text{SO}_4$, is orthorhombic with space group $Pcmn$ (D_{2h}^{16}) and holds four formula units per unit cell.¹ The intermediate phase is incommensurate and can be viewed as the result of the condensation of a soft mode² with a wave vector $\mathbf{q}=(1-\delta)\mathbf{c}^*/3$. At T_C , δ vanishes discontinuously and the ferroelectric (F) commensurate phase with a tripled unit cell along the c axis is realized. The crystal structure of this phase is orthorhombic with space group $Pc2_1n$ (C_{2v}^9) and the spontaneous polarization along the b axis.² Although K_2SeO_4 is no doubt one of the best studied crystals of the A_2BX_4 family, no NMR studies were reported up to now, most likely because ^{39}K , ^{77}Se , and ^{17}O are poor candidates for NMR studies. The availability of high-field superconducting magnets for solid-state NMR has, however, changed the situation. Therefore, we decided to perform a ^{39}K -quadrupole-perturbed and a ^{77}Se -NMR study on K_2SeO_4 in fields of $|\mathbf{B}_0|=8.36$ T and 6.3 T, respectively, corresponding to ^{39}K and ^{77}Se Larmor frequencies of 16.628 MHz and 51.5 MHz. It turned out that in this field it is quite easy to record ^{39}K spectra in a reasonable amount of time. The results concerning the ^{39}K quadrupole coupling and ^{77}Se chemical-shift tensors should throw additional light on the nature of the structural phase transitions in this compound.

II. EXPERIMENT

Single crystals of K_2SeO_4 , grown by slow evaporation from aqueous solution at 45 °C were used in our experiment. They had a volume of about 1 cm³ and were

oriented under a polarization microscope. Three sample crystals which could be rotated in the NMR goniometer about the crystallographic a , b , and c axes, respectively, were prepared for the ^{39}K NMR measurements. For defining the a , b , and c axes we chose the convention $a > c > b$, where $a=1.044$ nm, $b=0.600$ nm, and $c=0.766$ nm. The c axis is the room-temperature pseudohexagonal axis.

Severe dead-time problems of the 16.628 MHz pulse spectrometer forced us to record ^{39}K spectra by Fourier transforming the second half of spin echoes. Depending on the temperature of the crystal and type of spectrum between 200 and 2000 echoes were accumulated. The repetition time varied, depending on the temperature and, accordingly, on T_I , between 300 ms and 10 s.

A standard nitrogen-gas-flow temperature regulation unit was used. The temperature instability over the measuring period was usually less than 0.5 K. Only at temperatures around $T_C=93$ K was a precooling of the nitrogen gas necessary to maintain the required stability. $^{77}\text{Se}(I=\frac{1}{2})$ -NMR spectra were recorded in a field $|\mathbf{B}_0|=6.3$ T, corresponding to a Larmor frequency of 51.5 MHz. Since the ^{77}Se spin-lattice relaxation time was expected to be inconveniently long we used a heavily γ -irradiated crystal for these measurements. This enabled us to keep the repetition time t_r during accumulations down to 60 s at room temperature. Close to liquid-nitrogen temperature we had to increase t_r to 200 s.

In principle, the satellite transitions $m = \pm \frac{3}{2} \leftrightarrow m' = \pm \frac{1}{2}$ are best suited for studying electric-field-gradient (EFG) tensors of spin- $\frac{3}{2}$ nuclei.³ Therefore we searched intensively for such transitions in the ^{39}K spectra of K_2SeO_4 . They were indeed detectable at special crystal orientations, but even in the commensurate P phase they were very broad; indeed so broad that it was completely hopeless to extract any useful information from such transitions, in particular for the more interesting I phase. In

what follows on ^{39}K NMR, we shall be concerned exclusively with the so-called central transitions $m = \pm\frac{1}{2} \leftrightarrow m = \mp\frac{1}{2}$. The width of the resonance lines corresponding to these transitions was about 400 Hz in the commensurate P and F phases. The dispersion due to the second-order quadrupole and, additionally, chemical shifts was about 30 kHz.

III. STRUCTURAL CONSIDERATIONS

The paraelectric unit cell of K_2SeO_4 holds eight K and four Se atoms. The K and Se sites are pairwise magnetically equivalent due to the presence of inversion centers in the space group. All Se sites are crystallographically equivalent, which implies that it is sufficient to measure and quote one Se shielding tensor only. There are two sets of crystallographically inequivalent K^+ ions, K(1) and K(2). The K(1) ions are surrounded highly symmetrically by 11 oxygen atoms with an average distance of 0.313 nm, while the K(2) ions are surrounded by only 9 oxygens at an average distance of 0.293 nm. Because K(2) is surrounded less symmetrically by fewer and nearer ligands than K(1) we expect that the EFG tensor and consequently the quadrupole coupling constant (QCC) of K(1) is smaller than that of K(2). This conclusion is substantiated by a point-charge calculation of the EFG's at the sites of K(1) and K(2). This calculation also predicts the principal directions of the EFG's of K(1) and K(2) and at least the ratios of the corresponding principal values. The comparison of the results of this calculation with experiment will be the basis of the assignment of the measured quadrupole coupling tensors.

All K and Se atoms lie on mirror planes perpendicular to the crystal b axis. As a consequence one of the principal axes of the ^{39}K EFG and ^{77}Se shielding tensors must be parallel to the b axis. The other two principal directions must lie in the mirror plane. If a crystal of K_2SeO_4 is rotated about its b axis, the rotation axis itself being perpendicular to the applied field \mathbf{B}_0 , the ^{39}K spectrum will consist of four resonance lines, two from K(1) and two from K(2) potassium ions. For the same crystal rotation the ^{77}Se spectrum will consist of two lines. For such a crystal, rotation orientations will be encountered where \mathbf{B}_0 is parallel to the in-plane principal directions. These orientations can be spotted, as we shall see, directly in the rotation patterns of the line positions of the ^{39}K and ^{77}Se spectra and can be used to determine the ^{77}Se shielding and ^{39}K QCC tensors essentially by inspection. When crystals of K_2SeO_4 are rotated about either the a or the c axis, pairs of magnetically inequivalent, but crystallographically equivalent nuclei will give rise to one common line. The ^{39}K spectrum then consists of two resonances lines while the ^{77}Se spectrum consists of a single line only. The orientation with $\mathbf{B}_0 \parallel \mathbf{b}$ gives direct information about the corresponding principal ^{77}Se shielding component.

The appearance of the spectra in the incommensurate phase will be discussed in connection with the corresponding experiments. In the ferroelectric phase the number of ^{39}K and ^{77}Se resonance lines increases sixfold with the respect to the corresponding numbers in the paraelectric phase.

IV. RESULTS AND DISCUSSION

A. ^{39}K NMR

1. Paraelectric phase

Figure 1 shows the angular dependence of the second-order quadrupole shifts of the ^{39}K resonance lines at $T = 17^\circ\text{C}$. In agreement with the predictions based on crystal symmetry there are four ^{39}K central lines for the rotation $\mathbf{b} \perp \mathbf{B}_0$ and only two for the rotations $\mathbf{a} \perp \mathbf{B}_0$ and $\mathbf{c} \perp \mathbf{B}_0$. From these data the ^{39}K EFG tensors were determined by the well-known Volkoff method.⁴ As we have indicated above we can analyse these data essentially by inspection: We know that for $\mathbf{b} \parallel \mathbf{B}_0$ the magnetic field is along one of the principal directions x , y , or z of the QC tensors. Say, it is parallel to the y axis. For this so-called canonical orientation of \mathbf{B}_0 the second-order shift of the central transition is

$$\Delta\nu_y = \frac{1}{48\nu_L} \left[\frac{eQ}{h} (V_{zz} - V_{xx}) \right]^2. \quad (1)$$

The value of $\Delta\nu_y$ can be taken directly from Fig. 1 (left panel). V_{zz} , V_{xx} , and V_{yy} are the principal EFG components. The other two canonical orientations occur in the rotation pattern where \mathbf{B}_0 moves in the a - c plane. We find them by noting that they must be at a 90° distance from each other and that they are characterized by local extrema of the second-order shifts. One gets the second order shifts for these canonical orientations of \mathbf{B}_0 by cyclic permutation of the indices in Eq. (1). Taking the condition $V_{xx} + V_{yy} + V_{zz} = 0$ into account, these equations can readily be solved and there is even redundancy for a consistency check. The results agree with those of the Volkoff method and are listed in Table I(a).

In order to assign the two measured QC tensors to the potassium ions K(1) and K(2) we performed a point-charge model calculation of the EFG tensors at the sites of K(1) and K(2). The most characteristic difference between the calculated K(1) and K(2) EFG tensors was that the K(2) EFG tensor had one very small principal value with associated principal direction near the a axis, while the principal direction corresponding to the smallest principal value of the K(1) EFG tensor was parallel to the b axis. These results were stable with regard to a variation of the charges assigned to the potassium, oxygen and selenium ions within a reasonable range. The QC tensor, assigned in Table I(a) to K(2), does have one very small principal value (0.146 MHz) and the corresponding principal direction is within 17.3° parallel to the a axis. The principal direction associated with the smallest principal value of the other measured QC tensor is along the b axis. Hence we conclude that this tensor is to be associated with K(1). There are two K(1) and two K(2) ions in the unit cell. We get the best agreement between the calculated and experimentally determined principal axes systems, if we assign the QC tensors specified in Table I(a) to those ions K(1) and K(2) whose fractional coordinates are given directly in Ref. 1. The QC tensors of the other K

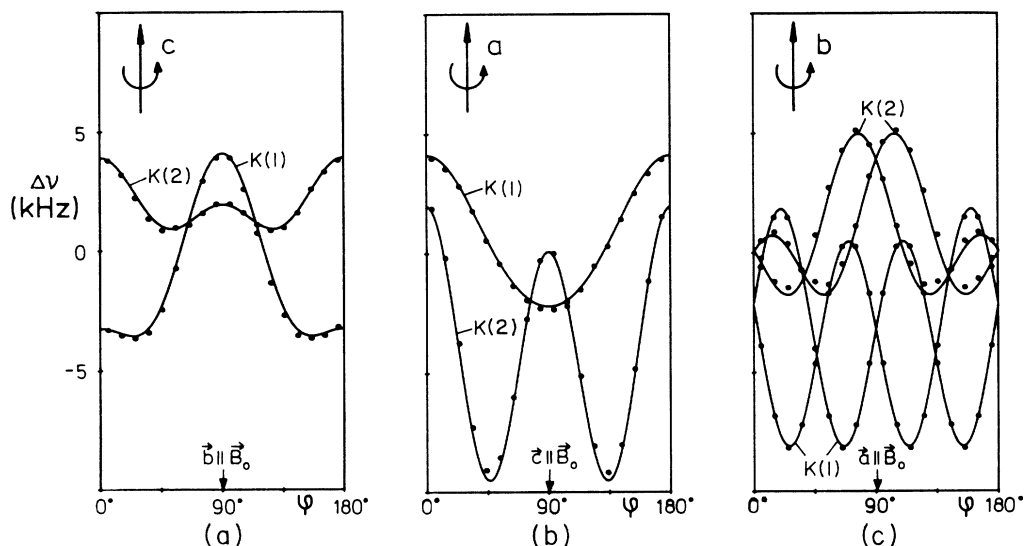


FIG. 1. Angular dependence of the second-order quadrupole shifts of the ^{39}K NMR central transitions in K_2SeO_4 at $T = 290$ K.

TABLE I. Eigenvalues (MHz) and principal directions of the ^{39}K quadrupole coupling tensors of K_2SeO_4 in the (a) P phase at $T = 290$ K and (b) I phase at $T = 126$ K. The polar angles Θ and Φ of the principal directions are specified in the crystal a, b, c frame.

Principal value (MHz)	Principal direction	
	Θ (deg)	Φ (deg)
(a) P phase at $T = 290$ K		
K(1)		
-1.02	109.9	0.0
0.22	90.0	90.0
0.80	19.9	0.0
$e^2qQ/h = 1.02$ MHz	$\eta = 0.56$	
K(2)		
0.15	103.7	0.0
0.91	90.0	90.0
-1.06	13.7	0.0
$e^2qQ/h = 1.06$ MHz	$\eta = 0.73$	
(b) I phase at $T = 126$ K		
K(1)		
-1.13	111.4	3.9
0.18	96.2	96.4
0.95	22.4	21.6
$e^2qQ/h = 1.13$ MHz	$\eta = 0.68$	
K(2)		
0.26	105.9	10.6
1.13	82.9	98.6
-1.39	17.5	345.3
$e^2qQ/h = 1.39$ MHz	$\eta = 0.63$	

ions follow by applying the appropriate symmetry transformations. The signs of the QC tensors given in Table I(a) have been chosen according to the results of the point charge calculations.

On approaching T_f from above the ^{39}K quadrupole coupling constants of both K(1) and K(2) increase approximately linearly with decreasing temperature (Fig. 2). Their values at $T = 132$ K are $e^2qQ/h = 1.121$ MHz for K(1) and $e^2qQ/h = 1.368$ MHz for K(2). The fit between

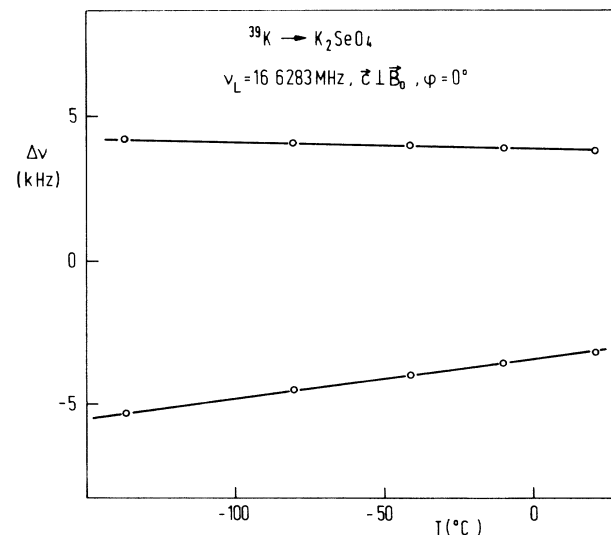


FIG. 2. Temperature dependence of the ^{39}K NMR lines in the paraelectric phase of K_2SeO_4 .

the experimental (dots) and calculated angular dependences (solid lines), which is decently good at $T = 17^\circ\text{C}$ (Fig. 1), becomes increasingly unsatisfactory with decreasing temperature [Fig. 3(a)]. This is due to the chemical-shift anisotropy, which we have disregarded so far. Its contribution to the shift of the ^{39}K NMR lines at room temperature is negligible, but becomes more and more important on approaching T_I . The usual way of separating the chemical-shift anisotropy from the quadrupole contribution to the observed line shifts is based on the different dependences of these two effects on the magnetic field strength \mathbf{B}_0 . Since the ^{39}K gyromagnetic ratio is too small to allow a substantial decrease of \mathbf{B}_0 , we determined both contributions at the largest available value of \mathbf{B}_0 in the following way:

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

$$\Delta\nu_i(\varphi_i) = \frac{1}{\nu_L} [A_i + B_i \cos(2\varphi_i) + C_i \sin(2\varphi_i) + D_i \cos(4\varphi_i) + E_i \sin(4\varphi_i)], \quad (2)$$

where $i = a, b, c$ labels the rotation axes. 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 rotation axes. Note that these two Fourier coefficients are unaffected by the anisotropic chemical shift. The expression for D_i and E_i can be written as⁵

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

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

where $i = a, j = b$, and $k = c$. D_j, \dots, E_k are obtained by

cyclic permutation of the indices. These six equations can be solved for the five unknowns 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 $A_i - A_{qi}, \dots, C_i - C_{qi}$ give the Fourier coefficients A_{ci}, B_{ci} , and C_{ci} of the chemical shift contribution. From them the chemical shift tensors can be determined in the usual way and are listed in Table II for $T = 132\text{ K}$. The assignment of the chemical shift tensors follows automatically from that of the QC tensors. The corresponding angular dependences (lines) are shown in Fig. 3(c). The final fit where both chemical-shift anisotropy and quadrupole contribution are taken into account is shown in Fig. 3(b).

As mentioned above the chemical-shift contribution to the line shifts decreases with increasing temperature. When the procedure described above was applied to the room temperature angular dependences $\Delta\nu_i(\varphi_i)$, σ_{iso} , and $\Delta\sigma$ became as small as -3 ppm and 13 ppm , respectively, and therefore practically negligible in comparison to the quadrupolar contribution.

2. Incommensurate phase

As shown in Fig. 4 the phase transformation from the P to the I phase at $T_I = 128\text{ K}$ results in a broadening of the ^{39}K NMR lines into frequency distributions limited by edge singularities which are typical for incommensurate phases.⁶ Two limiting cases are distinguished in the literature. In the first one, the linear term in the expansion of the resonance frequency in powers of the incom-

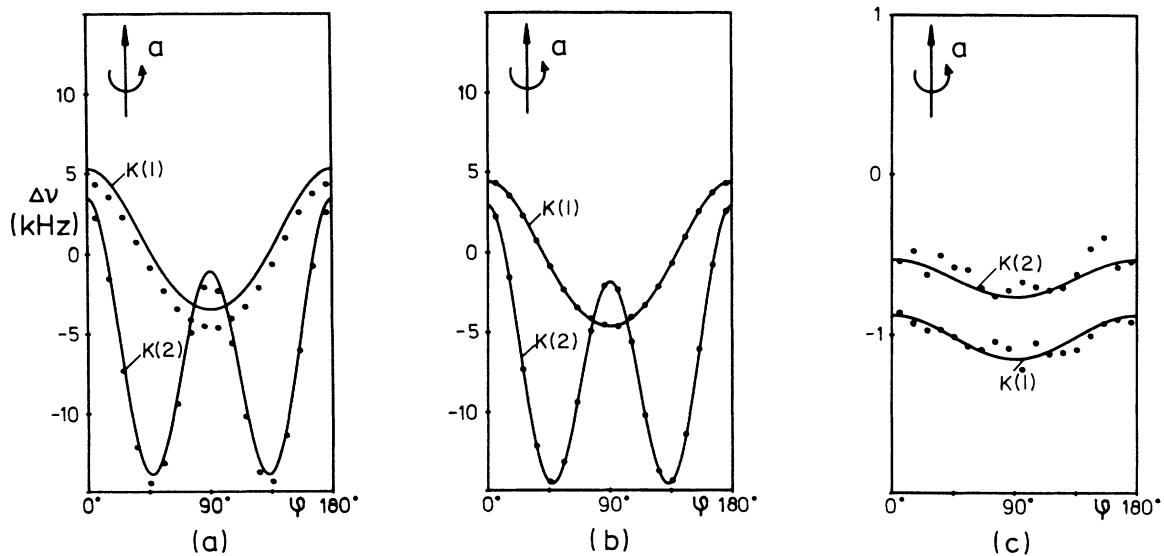


FIG. 3. Angular dependence of the shifts of ^{39}K NMR lines in K_2SeO_4 at $T = 132\text{ K}$. Calculated angular dependences (lines) were determined by taking into account (a) only quadrupole contribution, (b) both chemical shift anisotropy and quadrupole contribution, and (c) only chemical shift anisotropy contribution.

TABLE II. Eigenvalues (ppm) and principal directions of the ³⁹K chemical shift tensors of K₂SeO₄ in the *P* phase at *T* = 132 K. For the definition of Θ and Φ see Table I. The shifts are referenced to the ³⁹K resonance in a saturated aqueous solution of KCl.

Principal value (ppm)	Principal direction	
	Θ (deg)	Φ (deg)
<i>P</i> phase at 132 K		
K(1)		
-47.8	90.6	0.0
-52.9	90.0	90.0
-69.3	0.0	0.0
$\Delta\sigma = -18.9$ ppm	$\eta = 0.07$	
K(2)		
-32.5	103.8	0.0
-31.9	90.0	90.0
-46.9	13.0	0.0
$\Delta\sigma = -14.7$ ppm	$\eta = 0.01$	

incommensurate displacements is dominant. It is often assumed that the temperature dependence of the splitting between the edge singularities, $\Delta\nu$, can be described in this case by the power law $\Delta\nu \propto (T_I - T)^\beta$. In the second case crystal symmetry forces the linear term in the expansion of $\Delta\nu$ to vanish, leaving the quadratic term as the dominant one. The temperature dependence of $\Delta\nu$ is then proportional to $(T_I - T)^{2\beta}$.

We have measured the temperature dependence of the splitting between the edge singularities for several crystal orientations encompassing linear and quadratic cases. The average result for β is $\beta_{av} = 0.49 \pm 0.05$ and thus equal within the experimental error to the mean-field

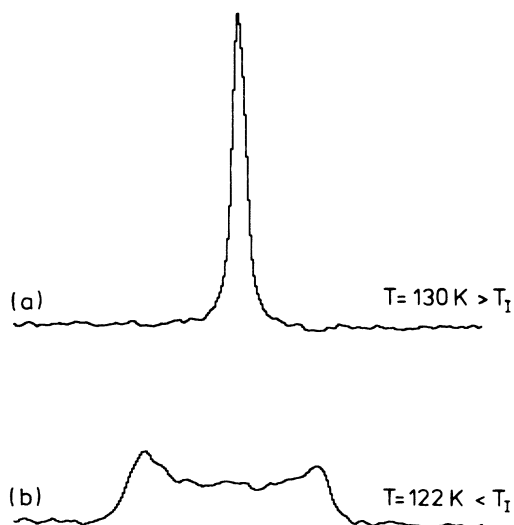


FIG. 4. ³⁹K NMR spectra in K₂SeO₄ in the (a) paraelectric and (b) incommensurate phases.

value 0.5. This value of the critical exponent β is valid in the temperature range $T_I > T > T_I - 20$ K.

In Fig. 5 the angular dependences of the ³⁹K NMR shifts at $T = T_I - 2$ K are shown. As can be seen, the rotation pattern for $\mathbf{b} \perp \mathbf{B}_0$ is practically identical with the one just above T_I . The reason for this is that the quadratic case is realized for these crystal orientations because \mathbf{B}_0 is moving in a plane which in the *P* phase is the mirror plane on which the K ions are located. By contrast there is a clear doubling of all paraelectric lines for $\mathbf{a} \perp \mathbf{B}_0$ and $\mathbf{c} \perp \mathbf{B}_0$, corresponding to the appearance of edge singularities. For these crystal orientations the linear case is realized. These qualitative changes of the ³⁹K spectra may be quantified by considering the ³⁹K EFG tensor \vec{V} expressed in the *a, b, c* axes system.

The temperature dependence of an EFG tensor \vec{V} in the *I* phase can be described by expanding it into powers of the *I* modulation amplitude *A*.⁷ Limiting ourselves to the local approximation⁸ and to terms not higher than quadratic and assuming, that the incommensurate displacements are essentially in the *b* direction,² the EFG tensor at a ³⁹K site in K₂SeO₄ can be written as

$$\vec{V}^I = \vec{V}^P + \begin{vmatrix} 0 & V_{ab}^{(1)} & 0 \\ V_{ab}^{(1)} & 0 & V_{bc}^{(1)} \\ 0 & V_{bc}^{(1)} & 0 \end{vmatrix} A \cos\vartheta + \begin{vmatrix} V_{aa}^{(2)} & 0 & V_{ac}^{(2)} \\ 0 & V_{bb}^{(2)} & 0 \\ V_{ac}^{(2)} & 0 & V_{cc}^{(2)} \end{vmatrix} A^2 \cos^2\vartheta \quad (4)$$

with $\vartheta = \mathbf{q}_I \cdot \mathbf{x} + \vartheta_0$, where \mathbf{q}_I is the incommensurate wave vector and ϑ_0 the initial phase. \vec{V}^P is the ³⁹K EFG tensor in the *P* phase, its elements V_{ab} and V_{bc} are zero. We expect that the primary effect of the *P-I* phase transition on the ³⁹K EFG tensors is the appearance of nonzero V_{ab} and V_{bc} elements which reflects the destruction of the paraelectric mirror plane by the frozen-in soft mode displacements along *b* below T_I .

Indeed we find immediately below T_I , where the incommensurate displacements are still small, that only the linear term in the above expansion is important. This confirms the direction of the displacements found in the diffraction study.² The ³⁹K quadrupole coupling tensors at $T = 126$ K, i.e., in the linear regime of Eq. (4), are listed in Table I(b). We stress that these data are valid for those ³⁹K nuclei which lie on extreme displacements of the modulation wave, i.e., for $|\cos\vartheta| = 1$. There is a quasicontinuous distribution of ³⁹K QC tensors between these two extremes.

A comparison between the ³⁹K QC tensors in the *P* and *I* phases, cf. Tables I(a) and I(b), reveals that the major effect of the incommensurate phase transition on these tensors is a rotation of the principal axes systems, accompanied by only a slight change of the quadrupole coupling constants QCC and asymmetry parameters η . At $T = 126$ K two of the K(1) QC tensors are rotated by $\pm 9^\circ$ around an axis which bisects the *a* and *c* axes. The rotation of the other two K(1) QC tensors follows from the

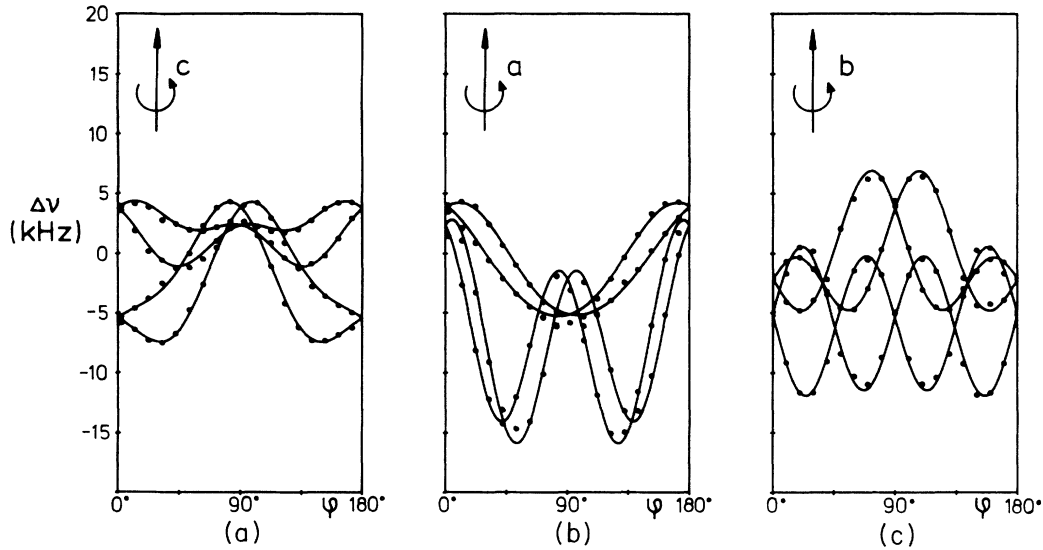


FIG. 5. Angular dependence of the shifts of ^{39}K NMR lines in K_2SeO_4 at $T = 126$ K.

crystal symmetry. For the K(2) QC tensors the rotation axes lie as well in the a - c plane but subtend an angle of $\pm 40^\circ$ with the a axis. The rotation angle of these tensors is $\pm 11^\circ$. The rotation angles of both K(1) and K(2) QC tensors increase on further cooling of the crystal. Nonlocal effects³ seem to be too small to be observed.

On approaching T_C characteristic changes in the ^{39}K NMR spectra of K_2SeO_4 are observed. Extra peaks appear which may be ascribed to the commensurate regions between solitons within the incommensurate phase. The measurement of the temperature dependence of the intensity of these peaks allows a determination of the density of the solitons. We shall report on these measurements separately.

B. ^{77}Se NMR

1. Paraelectric phase

The angular dependence of the ^{77}Se line positions has been measured in the γ -irradiated crystal of K_2SeO_4 for \mathbf{B}_0 rotating in the b - c and a - c planes. The results are shown in Fig. 6. As explained in Sec. III these data can be analyzed by inspection in terms of the ^{77}Se chemical shift tensors $\vec{\sigma}_{1,2}$ of the two magnetically inequivalent ^{77}Se atoms Se(1) and Se(2) in K_2SeO_4 : The b direction is a principal direction of both $\vec{\sigma}_1$ and $\vec{\sigma}_2$, hence the measured shift for $\mathbf{B}_0 \parallel \mathbf{b}$, see Fig. 6(a), gives directly one principal value of both $\vec{\sigma}_1$ and $\vec{\sigma}_2$. The other principal shift

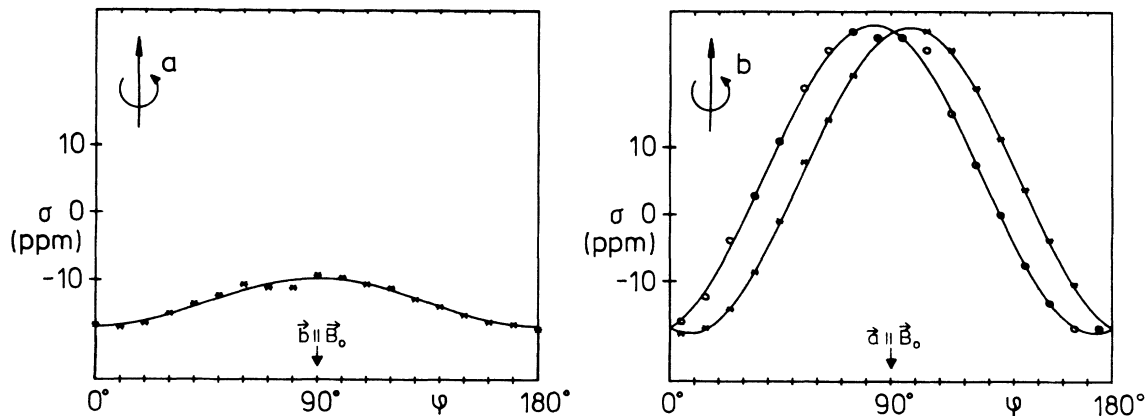


FIG. 6. Angular dependence of the ^{77}Se chemical shifts in K_2SeO_4 at $T = 300$ K. The origin of the vertical scale is σ_{iso} . Orientations where \mathbf{B}_0 is parallel to the crystal axes a and b are marked.

TABLE III. The ^{77}Se chemical shift tensor in K_2SeO_4 at $T=300$ K. The polar angles Θ and Φ are specified in the a, b, c frame. The values in parentheses are imposed by crystal symmetry. Differences to the measured values express experimental errors.

Principal value ^a (ppm)	Principal direction	
	Θ (deg)	Φ (deg)
-18 ± 0.3	7.5	0.5 (0)
-10 ± 0.3	90.5 (90)	90.5 (90)
$+28 \pm 0.3$	97.5	0.0 (0)

$\sigma_{\text{iso}}(\text{K}_2\text{SeO}_4) - \sigma_{\text{iso}}((\text{CH}_3)_2\text{Se}) = (-61.5 \pm 0.5)$ ppm
 $\Delta\sigma = \sigma_{zz} - \frac{1}{2}(\sigma_{xx} + \sigma_{yy}) = (42 \pm 0.5)$ ppm
 $\eta = (\sigma_{xx} - \sigma_{yy}) / \sigma_{zz} = 0.288$

^a Numbers are for the traceless constituent of $\vec{\sigma}(\text{Se})$.

values correspond to the extrema in the rotation pattern for \mathbf{B}_0 moving in the a - c plane, see Fig. 6 (right panel). The orientations of \mathbf{B}_0 for the extrema give directly the corresponding principal directions. The results are summarized in Table III. Principle directions for only one of the two ^{77}Se sites are given in Table III, those for the other site follow from the crystal symmetry. The following considerations suggest that the direction given in Table III should be assigned to the ^{77}Se atom whose coordinates are given directly in Ref. 1.

The ^{77}Se atoms in K_2SeO_4 are surrounded by four oxygens in an almost perfect tetrahedral coordination.² This explains why the ^{77}Se chemical-shift anisotropy $\Delta\sigma$ in K_2SeO_4 is only 42 ppm. In NH_4HSeO_4 , e.g., $\Delta\sigma$ is larger than 200 ppm.⁹ The orientation of the principal axes system and the deviations of the principal shift values from their mean therefore result from subtle effects, among which might be small deviations ($\sim 1^\circ$) of the O—Se—O angles from the exact tetrahedral angles.² To check whether the influence of this small distortion of the SeO_4 tetrahedron on the ^{77}Se shift tensor is strong enough to determine the orientation of $\vec{\sigma}$, we performed a point-dipole calculation of the Se $\vec{\sigma}$ tensor following the procedure of Avaramudhan *et al.*¹⁰ Only the four oxygens surrounding the Se atom were taken into account and identical oxygen susceptibilities and Se—O bond distances were assumed. The orientations of $\vec{\sigma}_{\text{calc}}$ for Se(1) and Se(2) are indeed reassuringly close to the experimental results, if we choose the assignment as given in Table III.

2. Incommensurate and ferroelectric phases

According to the low-temperature structural investigations of K_2SeO_4 the SeO_4 tetrahedra become substantially distorted¹¹ in the I and F phases. In the F phase the O—Se—O bond angles range from 105.9° to 114.5° . This leads us to expect the ^{77}Se shift anisotropy $\Delta\sigma$ to be substantially larger in the I and F phases than it is in the P phase. However, when lowering the sample temperature below T_I we could not detect any change in either posi-

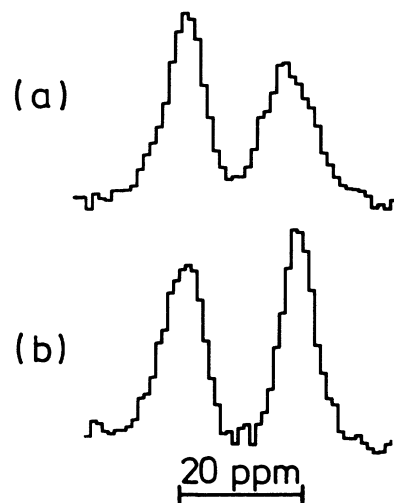


FIG. 7. ^{77}Se NMR spectra in K_2SeO_4 at $T=85$ K with \mathbf{B}_0 in the a - c plane: (a) $\angle(\mathbf{B}_0, \mathbf{a}) = 30^\circ$, (b) $\angle(\mathbf{B}_0, \mathbf{a}) = 60^\circ$.

tion, splitting or appearance of the ^{77}Se spectra. Judging from the intensity of the ^{77}Se NMR signal we are sure that the signal from all ^{77}Se nuclei in the I phase was detected. As these spectra were recorded from the strongly γ -irradiated crystal we wondered whether this crystal underwent the P - I phase transition at all. Therefore it is important to note that in the F phase slight but systematic changes in the spectra could be observed. Two spectra recorded at $T=80$ K with \mathbf{B}_0 in the a - c plane and $\varphi = \angle(\mathbf{B}_0, \mathbf{a}) = 30^\circ$ and $\varphi = 60^\circ$ are shown in Fig. 7. For $\varphi = 30^\circ$ the left or upfield line is noticeably smaller and broader than the right or downfield line, for $\varphi = 60^\circ$ the reverse is true. These observations are consistent with the tripling of the unit cell in the F phase: What was one line in the P phase becomes, in principle, a triplet in the F phase for \mathbf{B}_0 lying in the a - c plane. If the splitting of the component lines is smaller than the line width, the tripling of the unit cell will just lead to a broadening of the NMR line. The splitting of the component lines,

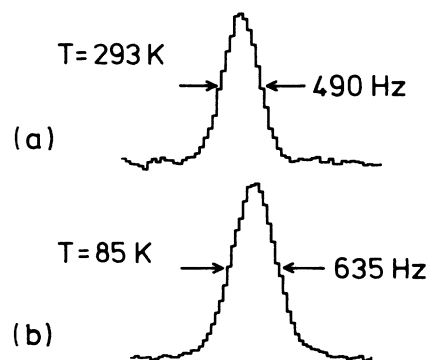


FIG. 8. ^{77}Se NMR spectra in K_2SeO_4 for $\mathbf{B}_0 \parallel \mathbf{a}$ at (a) $T=293$ K and (b) $T=85$ K.

and hence the broadening of the resulting lines, will depend upon the crystal orientation and in general will not be the same for the two observed lines. This is what the two spectra in Fig. 7 display. The tripling of the unit cell in the *F* phase implies that for $\mathbf{B}_0 \parallel \mathbf{a}$ the ^{77}Se resonance spectrum should consist of three lines. In Fig. 8 the low-temperature ^{77}Se spectrum for this crystal orientation is shown. It does not consist of a triplet of resolved lines. It is, however, significantly broader than the high-temperature spectrum and thus suggests an unresolved splitting. We conclude that the crystal indeed underwent the phase transition into the *F* phase in spite of having

been subjected to strong γ -irradiation. What remains puzzling is that the ^{77}Se chemical shift tensor is so little affected by the distortions of the SeO_4 tetrahedra in the *P* and *F* phase.

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*On leave from Institut Jožef Stefan, Jamova 39, YU-61111 Ljubljana, Slovenia, Yugoslavia.

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