Nuclear-Magnetic-Resonance Study of the Ferroelectric Transitions in $NaH_3(SeO_3)_2$ and $NaD_3(SeO_3)_2$

R. Blinc, J. Stepišnik, and I. Zupančič

The University of Ljubljana and Nuclear Institute "J. Stefan," Ljubljana, Yugoslavia

(Received 23 April 1968)

The angular dependences of the proton, deuteron, and Na^{23} magnetic-resonance spectra have been measured as a function of temperature in both normal (STSe) and deuterated (D–STSe) sodium tri-hydrogen selenite, and the electric field gradient tensors at the sodium and deuteron sites have been determined. These data show that the two ferroelectric transitions in STSe $(2/m{\rightarrow}1{\rightarrow}m)$ are accompanied by a doubling of the unit-cell edges in the a and b directions with respect to the paraelectric unit cell, whereas there is just one transition in D–STSe $(2/m{\rightarrow}m)$, which is connected with a doubling in the b direction only. The triclinic ferroelectric phase which exists in STSe between -79 and $-173°C$ thus does not appear in D–STSe. The transitions are accompanied by an ordering of hydrogens (which in the paraelectric phase are rapidly jumping from one equilibrium site in the H bond to another) as well as by a distortion of the SeO_3^- and Na^+ network.

INTRODUCTION

THE interesting dielectric properties of NaH_3-$(SeO_3)_2$—henceforth designated STSe—were first discovered by Pepinsky and Vedam,[1] who observed a transition from a paraelectric $(2/m)$ to a ferroelectric phase (1) at $T_{CI} = -79°C$. Below $-79°C$, spontaneous polarization was observed along both the a and the b axis. Later it was found[2-4] that there is a second transition at $T_{CII} = -173°C$, which is connected with the disappearance of the spontaneous polarization in the b but not in the a direction.

Although the structure of STSe in the paraelectric phase (space group $P2_1/a$ with two formula units per unit cell, $a = 11.76$ Å, $b = 4.84$ Å, $c = 5.80$ Å, $\beta = 118.5°$) has been solved by Unterleitner,[5] there is very little known[5,6] about the structure of triclinic ferroelectric phase I, and practically nothing about the monoclinic ferroelectric phase II. Since interesting ferroelectric and antiferroelectric properties—which seem to be somewhat analogous to the ones found in STSe—were observed as well in $KH_3(SeO_3)_2$, $RbH_3(SeO_3)_2$, and $CsH_3(SeO_3)_2$ by Shuvalov, Ivanov, and others,[6,7] it was felt that a study of the nature of the phase transitions in STSe might be worthwhile and might throw some light on the dielectric anomalies in the whole trihydrogen selenite family.

An additional reason for our decision to study this crystal was the rather drastic changes in the dielectric properties upon deuteration.[4,8] Whereas it is well known that the replacement of hydrogen by deuterium produces significant isotope effects in the dielectric properties of hydrogen-bonded ferroelectrics such as triglycine sulfate, KH_2PO_4, etc., in all these compounds the crystal structures of the undeuterated and the deuterated compounds are isomorphous. In STSe, on the other hand, it seems[4] that deuteration suppresses the occurrence of ferroelectric phase I, and the crystal makes a transition from the paraelectric phase to the ferroelectric phase II directly. In order to elucidate these effects on the atomic level and to determine the nature of the phase transitions, we decided to measure the nuclear-magnetic-resonance spectra of H, D, and Na^{23} as a function of temperature and crystal orientation.

EXPERIMENTAL

The proton and Na^{23} magnetic-resonance spectra have been measured at 9900 G with a wide line NMR spectrometer, using a Pound-Knight-Watkins (PKW) regenerative oscillator, whereas the deuteron data were obtained at a field of 13400 G. In the case of the Na^{23} resonance, both the first-order splitting of the satellites and the second-order shift of the central line were studied. The shifts were measured relative to a $NaNO_3$ water solution placed in a separate coil in the same magnetic field. The Na^{23} signal of this solution was measured by a nonoscillating NMR detector obtaining the high-frequency power from the regenerative oscillator. The values of the quadrupole shifts thus do not critically depend on any magnetic field or oscillator frequency drifts.

RESULTS

A. Proton Magnetic Resonance

The angular dependence of the second moments of the proton resonance absorption lines have been measured about all three axes in the paraelectric phase and in ferroelectric phase I, whereas in ferroelectric phase II the data have been collected only for a rotation around the b axis (Fig. 1). The angular dependences of the second moments in the two ferroelectric phases are very similar and have approximately the same form as

[1] R. Pepinsky and K. Vedam, Phys. Rev. **114**, 1217 (1955).
[2] N. R. Ivanov, L. A. Shuvalov, R. M. Fedosyuk, and K. A. Pluzhnikov, Zh. Eksperim. i Teor. Fiz. Pis'ma v Redaktsiyu **4**, 220 (1966) [English transl.: JETP Letters **4**, 151 (1966)].
[3] Y. Makita, J. Phys. Soc. Japan **19**, 576 (1964).
[4] R. Blinc, A. Levstik, J. Stepišnik, Z. Trontelj, and I. Zupančič, Phys. Letters **26A**, 290 (1968).
[5] F. A. Unterleitner (private communication).
[6] Y. Makita, J. Phys. Soc. Japan **20**, 1567 (1965).
[7] L. A. Shuvalov, N. R. Ivanov, and T. K. Sitnik, Kristallografiya **12**, 366 (1967) [English transl.: Soviet Phys.—Crist. **12**, 315 (1967)].
[8] R. Blinc, A. Jovanovič, A. Levstik, and A. Prelesnik, J. Phys. Chem. Solids **26**, 1359 (1965).

in the paraelectric phase but the magnitude of the second moment increases by about 50% on cooling below T_{CI}. This result agrees with the measurements of the temperature dependence of the second moment of polycrystalline STSe where an increase at T_{CI} by about 50% was also reported.[9,10] Although these data unambiguously demonstrate that the transition from the paraelectric phase to the ferroelectric is associated with a rearrangement of the hydrogens, very little can be concluded on a quantitative basis about the nature of the changes involved.

B. Na²³ Magnetic Resonance

The angular dependences of the first-order quadrupole splittings between the two $\pm\frac{3}{2}\rightarrow\pm\frac{1}{2}$ Na²³ transitions in STSe have been measured for crystal rotations about three mutually orthogonal axes in the paraelectric phase at 20°C, in the triclinic ferroelectric phase I at −162°C, and in the monoclinic ferroelectric phase II at −182°C.

The electric quadrupole splitting can be obtained as a first-order perturbation of the quadrupole Hamiltonian

$$\mathcal{H}_Q = [eQ/6I(2I-1)] \sum_{j,k} V_{jk}(I_jI_k - I_kI_j - \delta_{jk}I^2).$$

First-order perturbation yields the equation

$$2(\Delta\nu)_x = a_x + b_x \cos2\vartheta_x + c_x \sin2\vartheta_x,$$

where $2(\Delta\nu)_x$ is the frequency difference between the two satellites in the spectrum. The angle ϑ_x is the angle of rotation measured between the Y axis of the crystal and the constant magnetic field. The a_x, b_x, and c_x are related to the elements of the electric field gradient (EFG) tensor by

$$a_x = \tfrac{3}{4}(eQ/h)(\psi_{yy} + \psi_{zz}),$$

$$b_x = (eQ/h)(\psi_{yy} - \psi_{zz}),$$

$$c_x = -(eQ/h)\psi_{yz}$$

for a rotation about the X axis of the crystal. The equations for Y and Z rotations are anaogous and can be obtained by cyclic permutation of the subscripts.

After diagonalization of the quadrupole coupling tensor, the quadrupole coupling constant and the directional cosines are obtained. These results are presented in Fig. 2. The orthogonal rotation axes were chosen to be parallel to the b, c and $b \times c$ crystallographic axes. The quadrupole coupling tensors (Table I) were calculated from the Fourier coefficients of the rotation patterns using the method of Volkoff,[11] and agree rather well with the ones obtained from the angular dependences of the second-order shifts of the $\frac{1}{2}\rightarrow-\frac{1}{2}$ transitions. Only the second-order quadrupole
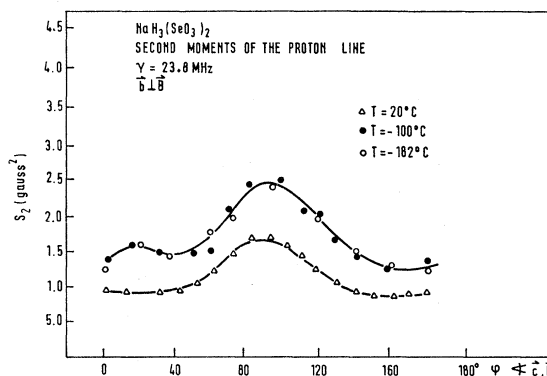
⁹ R. Blinc and M. Pintar, J. Chem. Phys. **35**, 1140 (1961).
¹⁰ G. V. Gavrilova-Podolskaja, *Proceedings of the International Conference on Ferroelectricity* (Prague, 1966), Vol. 2, p. 390.
¹¹ G. M. Volkoff, Can. J. Phys. **31**, 820 (1953).

FIG. 1. Angular dependence of the second moments of the proton magnetic-resonance absorption spectra in all three phases of NaH₃(SeO₃)₂.

shifts of the $\frac{1}{2}\rightarrow-\frac{1}{2}$ transitions have been measured for D-STSe (Fig. 3) for crystal rotations about the a, b and a × b axes. The results are presented in Table II.

In the paraelectric phase of both STSe and D-STSe, there is just one chemically nonequivalent Na²³ site. There are, however, in agreement with the structure proposed by Unterleitner, two physically nonequivalent Na²³ sites which are related by a twofold screw axis parallel to the b direction. The largest principal axis of the field-gradient tensor lies approximately in the (a, b) plane, making an angle of 12°30′ with the b axis. The field-gradient tensor is nearly axially symmetric.

The differences between the normal and the deuterated samples are within the limits of experimental error so that the paraelectric phases of STSe and D-STSe seem to be isomorphous. Paraelectric D-STSe thus as well belongs to point group $2/m$ with two molecules (and Na²³ atoms) per unit cell.

On cooling below $T_{CI} = -79°C$, the number of Na²³ lines in STSe increases by a factor of 4. The results are consistent with a symmetry change $2/m\rightarrow1$ and with a doubling of the unit-cell edges in the a and b directions, so that there are eight nonidentical Na²³ sites in the unit cell. To a rather good approximation one can, however, describe the Na²³ spectra by retaining the apparent symmetry relations about the b axis. In this approximation (Table I), one may say that the eight Na²³ sites are physically nonequivalent but that only four of them are chemically nonequivalent. The asymmetry parameters and quadrupole coupling constants are larger than in the paraelectric phase.

The second ferroelectric transition of STSe at −173°C results in another drastic change in the Na²³ spectra (Fig. 2). The number of Na²³ lines is reduced by a factor of two, and there are now only four physically nonequivalent Na²³ sites in the unit cell with two of these positions being also chemically nonequivalent. This result is consistent with a symmetry change from $1\rightarrow m$ and with a disappearance of the doubling of the unit cell in the a direction, whereas the doubling in the b direction still persists.
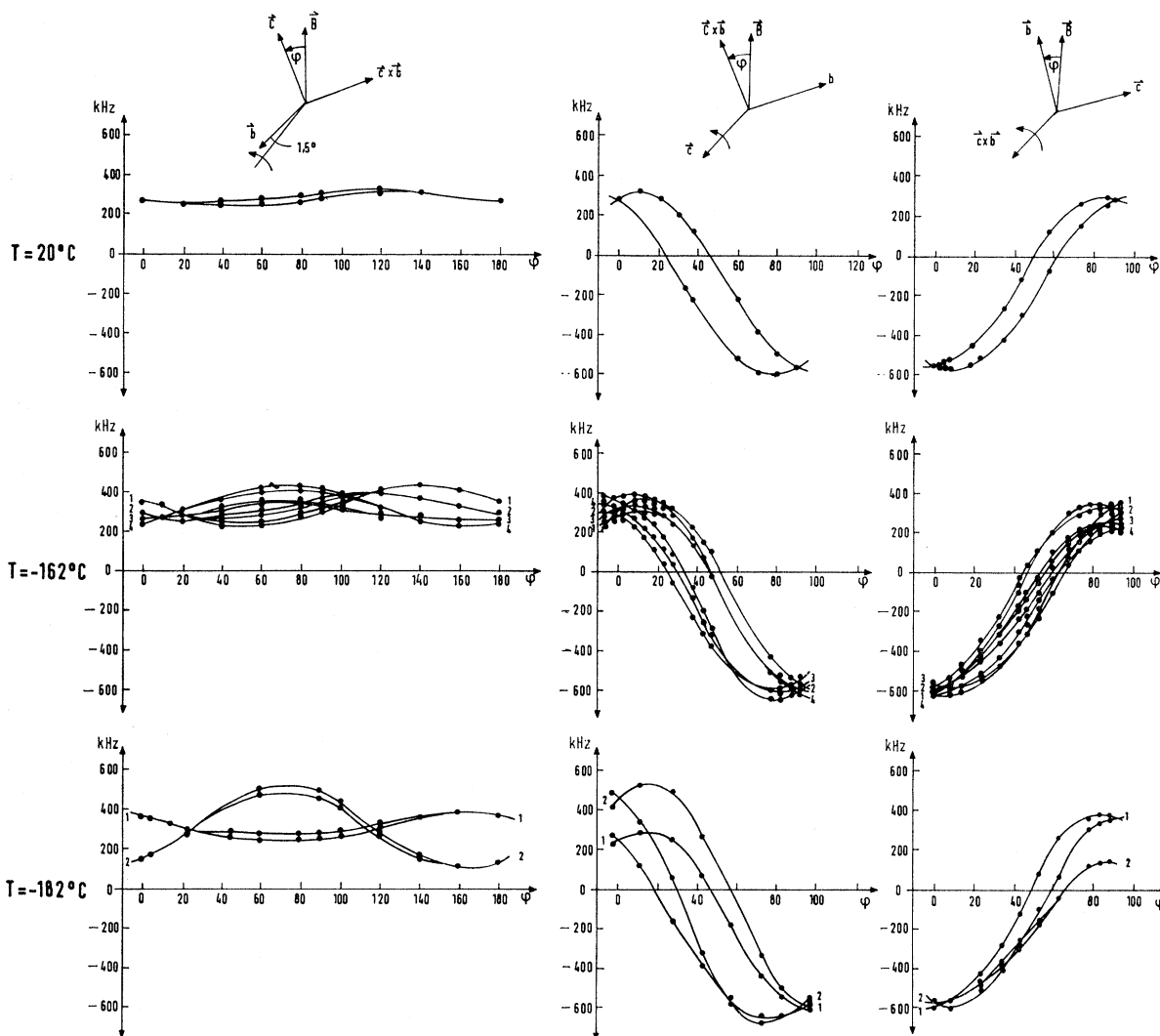
Fig. 2. Angular dependence of the first-order quadrupole splitting of the Na[23] spectra of $NaH_3(SeO_3)_2$ in the paraelectric phase and in the two ferroelectric phases.

Table I. Na[23] quadrupole coupling tensor elements ψ of $NaH_3(SeO_3)_2$ in kHz. Q stands for the quadrupole coupling constant, η for the asymmetry parameter, μ_a, μ_b, and μ_c for the direction cosines of the largest principal axis of the field gradient with respect to the a, b, and c axes, respectively.

| | Paraelectric phase (+20°C) | | Triclinic ferroelectric phase (−162°C) | | | Monoclinic ferroelectric phase (−182°C) | |
	T_1	T_2	T_3	T_4	T_5	T_6	T_7
ψ_{aa}	−564	−576	−656	−648	−768	−488	−904
ψ_{bb}	+1120	+1224	+1196	+1140	+1236	+1204	+1175
ψ_{cc}	−556	−648	−540	−492	−472	−716	−264
ψ_{ab}	±330	±320	±280	±440	±260	±442	±602
ψ_{ac}	−10	−180	−116	+72	+90	−78	−222
ψ_{bc}	±170	±228	±298	±56	±126	±158	±10
Q	1198±8	1299±8	1280±8	1245±8	1280±8	1321±8	1342±8
η	0.082 ±0.010	0.331 ±0.010	0.260 ±0.010	0.225 ±0.010	0.274 ±0.010	0.197 ±0.010	0.679 ±0.010
μ_a	0.183	0.158	0.133	0.228	0.129	0.234	0.262
μ_b	0.979	0.982	0.979	0.973	0.989	0.970	0.965
μ_c	0.093	0.100	0.152	0.041	0.078	0.066	−0.030
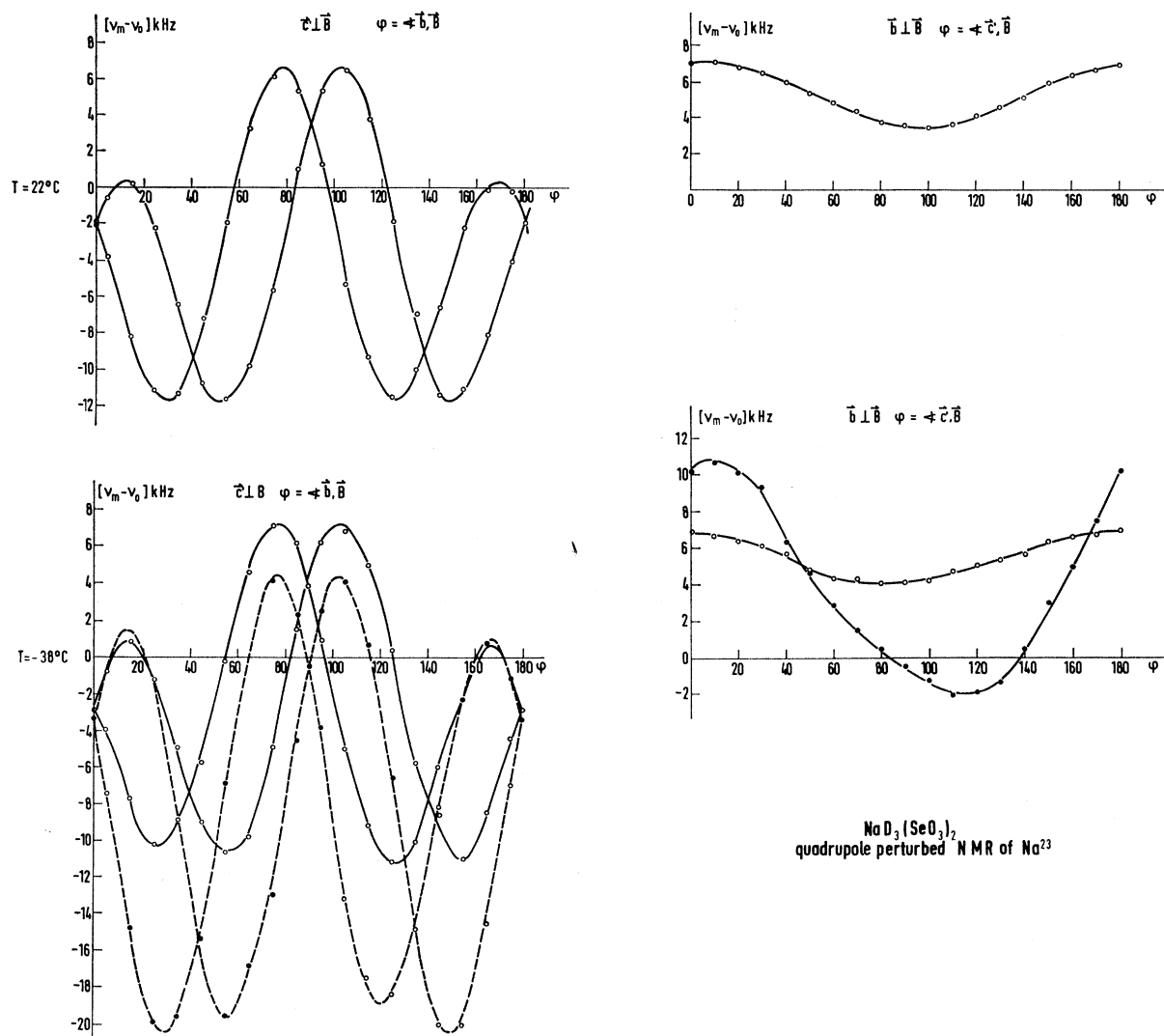
Fig. 3. Angular dependence of the second-order shifts of the $\frac{1}{2} \rightarrow -\frac{1}{2}$ transition in the high- and low-temperature pase of $NaD_3(SeO_3)_2$.

The Na^{23} spectra in D-STSe demonstrate (Fig. 3) that $NaD_3(SeO_3)_2$ does not have a triclinic phase and at $-3°C$ makes a transition from $2/m \rightarrow m$ which is accompanied by a doubling of the unit cell in the b direction. Within the limits of experimental error the Na^{23} quadrupole coupling tensors in the low-temperature phase of the deuterated crystal and in the second ferroelectric phase of the normal crystal are identical (Table II). In both cases at two of the four nonidentical Na^{23} sites the quadrupole coupling tensors suffer only a small change, whereas at the remaining two Na^{23} sites the changes are very pronounced and the asymmetry parameter, in particular, is quite large.

C. Deuteron Magnetic Resonance

The angular and temperature dependence of the deuteron resonance spectra have been measured (Fig.

4) for crystal rotations around the b, c and b × c axes, and the field gradients at the deuteron sites were again determined, using the method of Volkoff[11] (Table III).

In agreement with the results of Chiba[12] we find that there are six nonidentical deuteron sites in the paraelectric unit cell of D-STSe. Four of these belong to one chemically nonequivalent set—the so-called β deuterons—and two to another chemically nonequivalent set, the α one. This agrees rather well with the structure of Unterleitner,[5] according to which the various SeO_3 tetrahedra are connected by two types of hydrogen bonds: by a relatively short one,

$$R(O2—D_\beta\text{---}O3) = 2.56 \text{ Å},$$

[12] T. Chiba and G. Soda, in *Magnetic Resonance and Relaxation*, edited by R. Blinc (North Holland-Publishing Co., Amsterdam, 1967), p. 722.
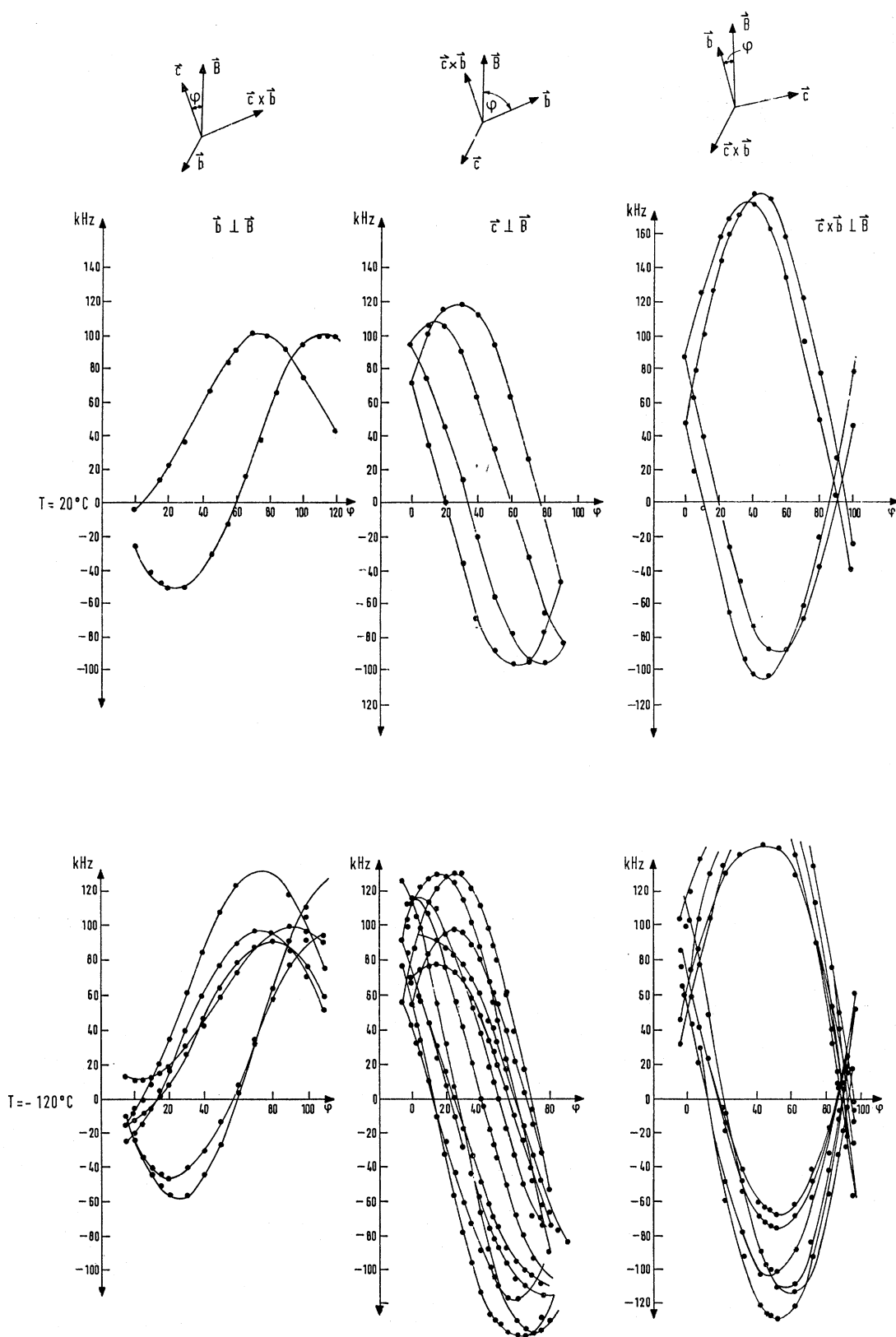
FIG. 4. Angular dependence of the quadrupole splitting of the deuteron magnetic-resonance spectra of $NaD_3(SeO_3)_2$. $\gamma = 8.7$ Mc/sec.

TABLE II. Na²³ quadrupole coupling constant Q (in kHz) asymmetry parameter and direction cosines of the largest principal axis in $NaD_3(SeO_3)_2$.

		Q	η	μ_a	μ_b	μ_c
Paraelectric phase +20°C	T_1	1215±15	0.14±0.05	0.191	0.975	0.091
Ferroelectric phase −30°C	T_2	1248±15	0.06±0.05	0.215	0.972	0.088
	T_3	1285±15	0.63±0.05	0.245	0.970	0.020

and by another one of medium length

$$R(\text{O1}\!-\!D_\alpha\text{---O1}) = 2.61 \text{ Å},$$

in the midst of which there is a center of symmetry (see Fig. 6). The values of the two quadrupole coupling constants, $(e^2qQ/h)_B = 127$ kHz and $(e^2qQ/h)_\alpha = 148$ kHz agree moderately well with the relations[13,14] proposed for the dependence of the quadrupole coupling constants on the O—O bond distance. The direction cosines of the largest principal axis of the field-gradient tensor of the β deuterons agree within one degree with the direction of the O2—O3 hydrogen bond, thus confirming the x-ray structure of Unterleitner and supporting the statement derived from the Na²³ data that the paraelectric structures of STSe and D-STSe are isomorphous. For the α deuterons this agreement is not quite so good—within 5°—but it can still be taken as evidence for the isomorphism of the two paraelectric structures and the essential correctness of Unterleitner's model. The observed deviation of the q_{zz} direction from the direction of the O1—D_α---O1 bond might be due to the influence of the nearby sodium ions.

The direction cosines of the second largest principal axis of the deuteron EFG tensors agree rather well with the bisector of the angle between the normals to the Se—O---O' and O---O'—Se' planes, indictaing that above the Curie point the deuteron sees an EFG tensor

FIG. 5. Temperature dependence of the β-deuteron spin-lattice relaxation time in $NaD_3(SeO_3)_2$ as obtained by a "signal decay" method.

averaged over the two equilibrium sites in the O---O' bonds. The lifetime of the deuteron near a given SeO₃ group should be thus much smaller than the inverse of the quadrupole splitting frequency. This result is consistent with the preliminary deuteron and Na²³ spin-lattice relaxation time measurements, which both show a nearly identical temperature dependence and a T_1 maximum in the paraelectric phase (similar to the one observed in KD_2PO_4,[15] indicating that the relatively slow deuteron interbond motion dominates the Na²³ and the D relaxation times at higher temperatures and the fast deuteron intrabond motion at lower temperatures close to the Curie point (Fig. 5).

Below the Curie point one finds twelve nonidentical deuteron sites, six of which are chemically nonequivalent. This is consistent with the Na²³ data and confirms the doubling of the unit cell along the b axis. The α sites split into two (α_1 and α_2) and the β sites into four (β_1, β_2, β_3, β_4) chemically nonequivalent ones. The directions of the second largest principal axis change on going through the Curie point, and below T_C they coincide, within a few degrees, with the normals to the various Se—O---O' planes. This indicates that below T_C the deuterons see the instantaneous electric field gradient; hence it suggests deutron ordering in one of the two possible equilibrium sites. The data suggest that two β deuterons (β_1 and β_2) are localized at O2 and two (β_3 and β_4) at O3. If one combines this statement with the rule that one may have only HSeO₃ and H₂SeO₃ groups in the structure, a complete assignment of the deuteron arrangement can be made (Fig. 6).

The fact that the largest principal axis of the EFG tensors still approximately agree with the O—O bond directions disagrees with the suggestion which has sometimes been made in analogy[16] with $LiH_3(SeO_3)_2$, namely, that below T_C the α deuterons form a free O—D group, and are no longer hydrogen-bonded. The slight changes in the quadrupole coupling constants and q_{zz} directions, on the other hand, demonstrate a distortion of the SeO₃ groups resulting in six H bonds of different length as compared to two nonequivalent ones in the paraelectric phase.

The coincidence of the paraelectric and ferroelectric lines at the Curie point further seems to show that the transition is of first order.
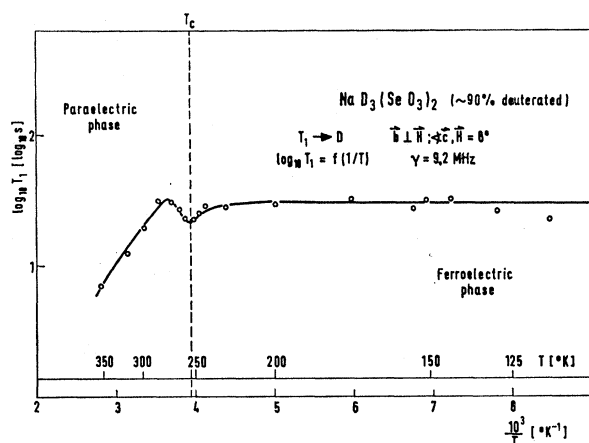
[13] T. Chiba, J. Chem. Phys. **41**, 1352 (1964).
[14] R. Blinc and D. Hadži, Nature **212**, 1307 (1966).

[15] J. L. Bjorkstam, Phys. Rev. **153**, 599 (1967).
[16] Jan H. Van den Hende, Acta Cryst. Suppl. **16**, A184 (1963).

TABLE III. Quadrupole coupling constants Q (in kHz), asymmetry parameters and direction cosines μ_a, μ_b, and μ_c of the largest (q_{zz}) and the second largest (q_{yy}) principal axis of the field gradient at the deuteron sites in $NaD_3(SeO_3)_2$ as compared with the $R(O\text{---}O)$ direction and the normals to the Se—O---O' planes ($n_{Se\text{-}O\text{---}O'}$).

		q_{zz}	$R(O\text{---}O)$ direction	q_{yy}	Normal to the plane Se—O---O'
		Paraelectric phase $T=20°C$			
T_β	$Q=127\pm2$	$\mu_a=0.172$	0.198	-0.882	-0.743[a]
	$\eta=0.098$	$\mu_b=0.779$	0.788	0.384	0.436[a]
		$\mu_c=0.576$	0.589	-0.270	-0.325[a]
T_α	$Q=147\pm2$	$\mu_a=0.339$	-0.437	-0.682	-0.702[a]
	$\eta=0.172$	$\mu_b=0.704$	-0.703	0.640	0.658[a]
		$\mu_c=0.642$	0.560	0.351	0.273[a]
		Ferroelectric phase $T=-100°C$			
$T_{\beta1}$	$Q=167\pm5$	$\mu_a=-0.231$	-0.198	0.938	$+0.957$
	$\eta=0.184$	$\mu_b=-0.788$	-0.788	-0.336	-0.284
		$\mu_c=-0.570$	-0.589	0.083	-0.038
$T_{\beta2}$	$Q=138\pm5$	$\mu_a=-0.040$	-0.198	0.531	$+0.957$
	$\eta=0.134$	$\mu_b=-0.840$	-0.788	-0.476	-0.284
		$\mu_c=-0.541$	-0.589	0.701	-0.038
$T_{\beta3}$	$Q=148\pm5$	$\mu_a=-0.222$	-0.198	0.431	0.530
	$\eta=0.302$	$\mu_b=-0.765$	-0.788	-0.631	-0.588
		$\mu_c=-0.608$	-0.589	0.644	0.611
$T_{\beta4}$	$Q=111\pm5$	$\mu_a=0.229$	-0.198	0.972	0.530
	$\eta=0.209$	$\mu_b=0.762$	-0.788	-0.210	-0.588
		$\mu_c=0.605$	-0.589	-0.104	0.611
$T_{\alpha1}$	$Q=147\pm5$	$\mu_a=-0.390$	-0.437	-0.902	-0.702
	$\eta=0.377$	$\mu_b=-0.724$	-0.703	0.423	0.658
		$\mu_c=0.570$	0.560	-0.080	0.273
$T_{\alpha2}$	$Q=138\pm5$	$\mu_a=-0.312$	-0.437	0.744	-0.702
	$\eta=0.188$	$\mu_b=-0.717$	-0.703	-0.592	0.658
		$\mu_c=0.623$	0.560	-0.308	0.273

[a] Average.

DISCUSSION

The above results elucidate the structural rearrangements and the changes in the deuteron motion connected with the phase transition in D-STSe at $-3°C$. The transition is of the mixed type: It is an order-disorder transition of deuterons combined with a distortion of the Na^+ and SeO_3^- network in which the deuterons move.

The situation is much less clear in the undeuterated compound. From the Na^{23} data, one may conclude that the ferroelectric phase I of STSe (stable between $-79°C$ and $-173°C$) does not occur in D-STSe, whereas the paraelectric phase and the ferroelectric phase II of STSe are isomorphous with the disordered and ordered phases respectively of D-STSe. The low-temperature values of the proton second moments (S_2) of a powdered sample (2.30 G^2) as well as the observed angular dependence of S_2 measured on a single crystal in the ferroelectric phase II (at $-182°C$) agree within the—relatively large—limits of experimental error with the theoretical values calculated on the basis of the "rigid lattice" deuteron positions. The values of the proton second moments in the paraelectric phase, however, are smaller than what one would expect if the only proton motion
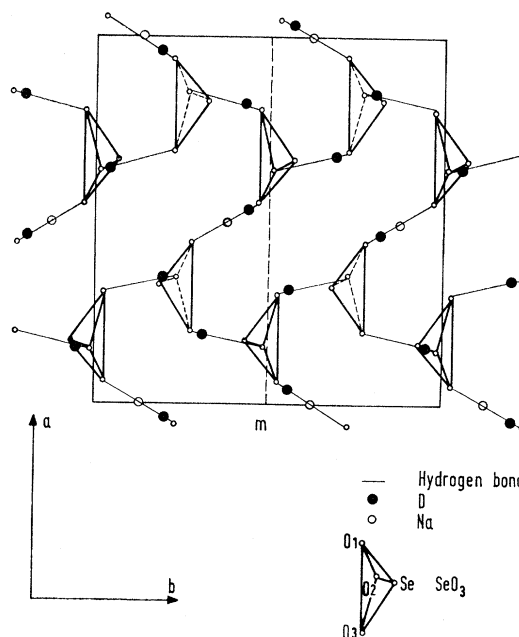

FIG. 6. Proposed deuteron arrangement in the low-temperature phase of $NaD_3(SeO_3)_2$.

would be random jumping of protons between the two equilibrium sites in the H bonds. A hindered rotation of the H_2SeO_3 and $HSeO_3$ groups (or what amounts to practically the same, a proton interbond motion) could explain the observed second moment data in the para-electric phase. The relatively large change in the proton second moment on going from the paraelectric phase to ferroelectric phase I indicates a freezing in of both hindered rotation and intrabond proton jumping. The changes in EFG tensors (ψ) at the Na^{23} sites, however, cannot be understood on the basis of proton rearrangements alone. The proton ordering—like the deuteron ordering in D–STSe—is accompanied by a distortion of the Na^+ and SeO_3^- lattice. Unfortunately, there are too many unknown parameters, so that a unique model of ferroelectric phase I cannot be extracted from our data. It should be pointed out, however, that the existence of free O—H groups is excluded on the basis of the infrared spectra. On going from ferroelectric phase I to ferro-electric phase II, the angular dependence of the proton second moments is only slightly changed, but the Na^{23} EFG data indicate a rearrangement of both the hydro-gens and the SeO_3^- and Na^+ ions.

Finally, one may add that from the room-tempera-ture EFG tensors at the Na^{23} sites one obtains—using the point-charge model—the following effective charges for the various ions:

$$e_{Na} = e, \qquad e_{Se} = 1.1e, \qquad e_O = -1.0e, \quad \text{and} \quad e_H = 0.9e,$$

where e stands for the elementary charge, and an antishielding factor $(1 - \gamma_\infty) = 6$ was used.

ACKNOWLEDGMENTS

High-Temperature Critical Indices for the Classical Anisotropic Heisenberg Model

David Jasnow and Michael Wortis*

Department of Physics, University of Illinois, Urbana, Illinois 61801

(Received 15 July 1968)

High-temperature series expansions for the spin-spin correlation function of the classical anisotropic Heinsenberg model are calculated for various lattices and anisotropies through order T^{-8} (close-packed lattices) and T^{-9} (loose-packed lattices). These series are combined and then extrapolated to give the high-temperature critical indices γ (susceptibility), ν (correlation range), and α (specific heat) as functions of anisotropy. Our results are consistent with the hypothesis that the critical indices change only when there is a change in the symmetry of the system, e.g., in interpolating between the Ising and isotropic Heisenberg models, indices remain Ising-like until the system becomes isotropic, at which point they appear to change discontinuously. Previous results for the limiting cases are confirmed and extended.

1. INTRODUCTION

MUCH of the recent study of critical phenomena, both experimental[1] and theoretical,[2] has centered on the determination of and interrelations between the values of the critical indices (exponents), which measure the type and strength of the singular behavior of various physical quantities at the thermodynamic critical point. The most striking fact about the critical indices is their remarkable insensitivity (for fixed dimensionality) to the details of both dynamics and kinematics.[3] It is now appreciated, however, that, within this context of broad similarity, there are small but nonetheless important differences in critical indices between systems with differing dynamics and/or kinematics. Note, as an example, the variation of the high-temperature susceptibility index γ in three dimensions between the spin-$\frac{1}{2}$ Ising model[4,5] ($\gamma \cong 1.250$), the

---

* Alfred P. Sloan Foundation Fellow.

[1] A review of this work, containing extensive references, has recently been given by L. P. Kadanoff, W. Gotze, D. Hamblen, R. Hecht, E. A. Lewis, V. Palciauskas, M. Rayl, J. Swift, D. Aspnes, and J. Kane, Rev. Mod. Phys. **39**, 395 (1967). See also P. Heller, Rept. Progr. Phys. **30**, 731 (1967).

[2] M. E. Fisher, Rept. Progr. Phys. **30**, 615 (1967), which gives extensive references.

[3] More precisely, some of these differences are actually not so small, for example, a change in sign of the interaction (dynamics) of the two-dimensional spin-$\frac{1}{2}$ Ising model on the triangular lattice converts a ferromagnet to a paramagnet having no phase transition [G. Wannier, Phys. Rev. **79**, 357 (1950)]. However, we are emphasizing here the strong parallels between the critical behavior of, for example, the liquid-gas system and the ferro-magnet (experimental) or the somewhat weaker similarity (theoretical) of the three-dimensional Ising and Heisenberg models.

[4] C. Domb and M. F. Sykes, Proc. Roy. Soc. (London) **A240**, 214 (1957).

[5] G. A. Baker, Jr., Phys. Rev. **124**, 768 (1961).