with (4.2)–(4.5) and (4.9) shows that at low temperatures the expression for the resonance frequency (4.11) may be used provided that $\lambda(T)$ is substituted for λ, where

$$\lambda(T)=\lambda\left[\frac{\gamma_2 M_1(0)+\gamma_1 M_2(0)}{\gamma_2 M_1(T)+\gamma_1 M_2(T)}\right]^{1/2} \quad . \tag{4.15}$$

5. CONCLUSION

The temperature dependence of the antiferromagnetic and ferrimagnetic resonance frequencies has been evaluated by spin-wave theory in a temperature-dependent Hartree-Fock approximation. Corrections to the macroscopic theory, due to spin correlations at low temperatures, are best represented for the antiferromagnet by a temperature-dependent perpendicular susceptibility, as is already well known. In ferrimagnets, when a static perpendicular susceptibility may not be defined in the absence of anisotropy, the same corrections are represented by an effective temperature dependence of the Weiss field parameter.

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NMR Study of Phase Transitions in Rochelle Salt[*]

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Nuclear-magnetic-resonance techniques have been used to measure the spontaneous polarization of ferroelectric Rochelle salt in the vicinity of the higher-temperature Curie point (T_C). The polarization was found to be proportional to $(T_C - T)^{1/2}$, but the technique did not allow measurements closer than 0.1 °C to T_C. In addition, the Na^{23} nuclear quadrupole coupling constant and field gradient asymmetry parameter in the low-temperature phase were found to be 1363 ±3.4 kHz and 0.737 ± 0.004, respectively. These values are in accord with the model of Blinc, Petkovsek, Zupancic, and with the notion of an antiferroelectric low-temperature phase.

INTRODUCTION

The use of the Na^{23} nuclear magnetic resonance (NMR) to study ferroelectricity in Rochelle salt has been discussed in three earlier papers.[1-3] In the first of these,[1] the measurement of the Na^{23} electric quadrupole coupling constants in the ferroelectric phase and in both nonferroelectric phases of deuterated Rochelle salt is described. With the aid of a model proposed in the same paper, the experimental results are analyzed to determine the atomic displacements responsible for the ferroelectric behavior of the crystal. The second paper[2] makes use of the same model and a similar set of measurements on nondeuterated Rochelle salt to find values for the displacements causing ferroelectricity in that material. However, in the second case, the measurements were made only in the ferroelectric phase and the higher-temperature nonferroelectric phase. The third paper[3] describes methods of determining spontaneous polarization and domain characteristics from NMR measurements and the application of these methods to the study of radiation effects in Rochelle salt.

The present paper is concerned with further

NMR studies of the phase changes in Rochelle salt using the techniques of the first three papers. Specifically, the Na^{23} quadrupole coupling constants have been measured for the lower-temperature nonferroelectric phase of Rochelle salt, and the NMR technique has been employed to investigate the temperature dependence of the spontaneous polarization near the transition temperature. This technique was used since it is a truly static method of measuring spontaneous polarization, and thus it is free from electrocaloric effects. Since some deviations from the predictions of molecular field theory have been reported in the vicinity of the lower-temperature Curie point in Rochelle salt,[4] it was hoped that this study might find similar results, but it did not. The quadrupole coupling constant obtained for the low-temperature phase fits nicely into the pattern established by the earlier measurements on both deuterated[1] and undeuterated[2] Rochelle salt.

EXPERIMENTAL

The Rochelle salt crystals and apparatus used in these experiments are the same as those described previously,[2,3] but with the addition of an improved temperature-control system. This control system operates by circulating the cooling liquid (iso-octane) through a heat exchanger where it is cooled by dry ice or liquid nitrogen. The iso-octane goes from the heat exchanger through an electric heater to the Dewar flask containing the sample and back-to-heat exchanger. By using the signal from a thermocouple next to the Rochelle salt sample, in order to control the current in the heater, it is possible to hold the sample temperature constant to within 0.05 °C in the vicinity of the higher-temperature Curie point. As the temperature is lowered the iso-octane becomes more viscous and the degree of temperature control decreases. For this reason the study of spontaneous polarization versus temperature could not be carried out with precision at the lower-temperature Curie point. However, the control system is adequate for making measurements in the lower-temperature nonferroelectric phase, where the Na^{23} quadrupole coupling constant is less temperature dependent.

When the Na^{23} NMR spectrum is observed with the magnetic field perpendicular to one of the crystal axes of Rochelle salt in either of the nonferroelectric phases, each line of the spectrum is actually a superposition of two lines which coincide because of the orthorhombic symmetry of the crystal.[2] Each pair of lines separates when the crystal becomes ferroelectric because of the lower symmetry of the ferroelectric phase. It has been established that the separation of such a pair of satellite lines is proportional to the spontaneous polarization of the crystal.[3] In the experiments described in this paper, the spontaneous polarization was determined by measuring the splitting of such a satellite pair as a function of temperature.

The particular satellite pair used for this experiment is the same pair used in the earlier studies.[3] The crystal was oriented with the magnetic field perpendicular to the crystal *c* axis and making an angle of 60° with the *a* axis. At this orientation, and for a Na^{23} Larmor frequency of 12.300 MHz, the satellite pair under study occurs at 12.760 MHz at 28 °C in the higher-temperature nonferroelectric phase, where the two components of the pair coincide. Under these conditions the satellite pair achieves a maximum splitting of 71 kHz, the largest obtainable in the ferroelectric phase.

Very close to the Curie point, where the satellite splitting is of the order of a linewidth or less, the satellites overlap and become unresolvable. However, the resulting single observable resonance is broader than either of its two components, and the broadening depends upon the satellite separation. This broadening was studied as a function of satellite separation so that the polarization measurements could be carried into the overlap region. Figure 1 shows a plot of the results of that study. Both broadening and satellite separation are given as fractions of the satellite linewidth. Linewidth, as used here, is the frequency separation of the maxima of the derivative of the resonance. The broadening is defined as the increase in linewidth due to satellite separation. Thus when the separation goes to zero, the broadening goes to zero, and, as the separation becomes larger than the natural linewidth, the broadening becomes equal to the separation. The data for this plot were obtained by graphically superposing actual satellite resonances, with their centers a known distance apart, and measuring the resulting broadening. This procedure is valid because it is known that the individual satellite lines do not exhibit any change of linewidth in the vicinity of the Curie temperature.[2]

Figure 1 indicates that a splitting of about 40% of the natural linewidth is needed to cause a 10% increase in the observed linewidth. A linewidth increase of 10% was the minimum which could be reliably detected. Since the natural linewidth of the satellites under study was 7.3 kHz, the minimum measurable splitting was about 3 kHz.

The Na^{23} quadrupole coupling constant in the lower-temperature nonferroelectric phase was measured at − 25 °C by the same method used in the two higher-temperature phases.[2] In this method, measurements of satellite frequencies

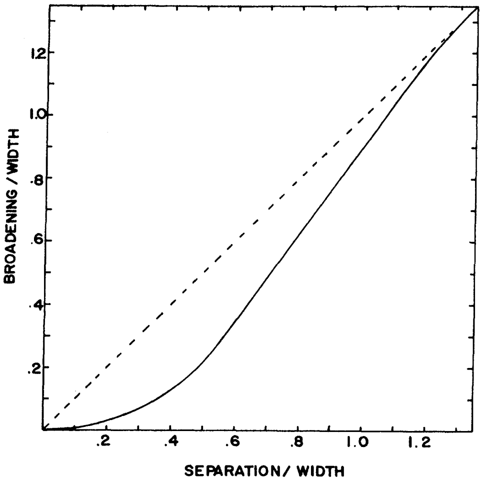

FIG. 1. Fractional satellite broadening versus fractional satellite separation. Dotted line represents a broadening equal to separation, the result expected for fully resolved satellite lines.

are made at only nine orientations for which the magnetic resonance pattern itself can be used to orient the crystal, thus minimizing errors due to slight misorientation. These measurements are analyzed with the aid of the equations of Volkoff *et al.*[5] to yield the components of the electric-field-gradient tensor in the crystal coordinate system multiplied by the nuclear quadrupole moment. The details of this technique have been described in an earlier paper.[2]

RESULTS AND DISCUSSION

Spontaneous Polarization

Figure 2 shows a plot of the measured satellite splitting versus temperature. The vertical scale on the left of the graph shows the satellite splitting in kHz, while that on the right gives the equivalent spontaneous polarization. The calibration in terms of polarization was accomplished by equating the maximum observed splitting, at 3 °C, to the known maximum spontaneous polarization. Because of the 3-kHz minimum detectable satellite splitting, the polarization could only be measured to within 0.1 °C of the transition temperature. Figure 3 is a plot of the square of the satellite splitting versus temperature near the Curie point.

The plot shows that the polarization obeys the law

$$P_s \propto (T_C - T)^{\beta}$$

near the Curie point with $\beta = \frac{1}{2}$. In this expression P_s is spontaneous polarization, T_C is the Curie temperature, and T is temperature. In order to confirm that β is really $\frac{1}{2}$, a log-log plot of satellite separation versus $T_C - T$ was made. From that plot it was found that β could be varied slightly if T_C was changed also. This procedure

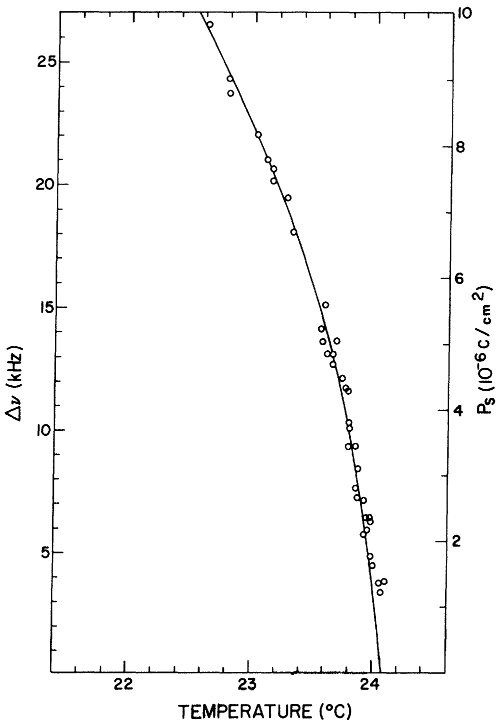

FIG. 2. Satellite separation versus temperature near the higher-temperature Curie point. Scale on the right side indicates spontaneous polarization calibrated by setting the maximum separation of 71 kHz at 3 °C equal to the peak spontaneous polarization of 26×10^{-8} C/cm^2.

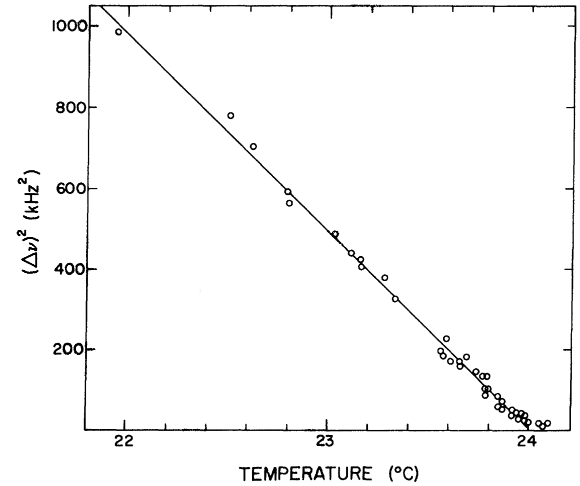

FIG. 3. Square of the satellite separation versus temperature near the higher-temperature Curie point.

was used to established limits of error for β and for T_C. The β was thus found to be 0.50 ± 0.04 and T_C was established as 24.0 ± 0.05 °C. If either of these quantities was chosen outside of the stated limits, the log-log plot of the data could not be fitted satisfactorily by a straight line.

The behavior observed in this experiment is exactly that predicted by the molecular field theory.[6] This result was something of a disappointment, but it is undoubtedly a result of the limitation placed on the experiment by the 3-kHz minimum detectable satellite separation. This limitation makes it impossible to measure the spontaneous polarization in the interesting temperature range within 0.1 °C of the Curie temperature. However, the experiment had to be performed to determine this fact.

Although the molecular field theory is expected to be invalid very close to the transition temperature, deviations from the theory are not expected farther than 0.1 °C from the Curie temperature. Ginzburg[7] has estimated that for barium-titanate-type ferroelectrics the molecular field theory should be valid to within about 0.4 °C of the transition temperature. Dielectric measurements on triglycine sulphate by Gonzalo[8] to within 0.05 °C of the Curie temperature agreed with the molecular field theory. The only observation of a different behavior was made by Craig[9] near the lower-temperature transition in Rochelle salt. At temperatures closer than 0.1 °C to the phase transition he measured β to be $\frac{1}{3}$, in agreement with measurements of the magnetic polarization in several ferromagnetic[10–12] and antiferromagnetic[13,14] materials. Thus it appears that the effects being sought occur in the temperature range made inaccessible by the overlap of the resonances.

Quadrupole Coupling Constant

Table I lists the magnitudes of the components of the electric field gradient at the sodium site, multiplied by the Na^{23} nuclear quadrupole moment, as determined by the method described earlier in this paper. There are four Na^{23} sites per unit cell, and the magnitudes of the electric field gradient components are the same for all four sites. However, the signs of the off-diagonal components differ from site to site. Table II gives the signs of these components for each site. The sites are identified by the notation used in Refs. 1 and 2.

TABLE I. Electric field gradient components (kHz) at Na^{23} sites in Rochelle salt: low-temperature phase.

$2CV_{YZ}$	$2CV_{XZ}$	$2CV_{XY}$	CV_{XX}	CV_{YY}	CV_{ZZ}
237.7 ±1	58.5 ±1	1197.2 ±1	223.7 ±0.5	−133.4 ±0.5	−90.4 ±0.5

TABLE II. Relative signs of off-diagonal electric field gradient components.

	Na^{23}			Site No.
	1	2	3	4
CV_{XY}	+	+	−	−
CV_{XZ}	+	−	−	+
CV_{YZ}	+	−	+	−

These results were analyzed by the method of Volkoff *et al.*[5] to give a nuclear quadrupole coupling constant (e^2Qq/h) and field gradient asymmetry parameter (η) of

$$e^2Qq/h = 1363 \pm 3.4 \text{ kHz},$$

$$\eta = 0.737 \pm 0.004 .$$

Table III lists the direction cosines of the principal axes obtained by the same method. Finally, Table IV gives the values of the nuclear quadrupole coupling constants for the three phases of ordinary and deuterated Rochelle salt.

It is interesting that the Na^{23} quadrupole coupling constants for undeuterated and deuterated Rochelle salt are different in the low-temperature phase, while they are identical in the high-temperature phase. Although the limits of error in the high-temperature phase appear sufficiently large to cast some doubt on whether the two coupling constants are truly equal, this is misleading. Blinc *et al.* in a preliminary measurement[1] examined the spectra of both the deuterated and undeuterated crystals in the high-temperature phase, and found them to be identical. The spectra can be measured with great precision and therefore a direct comparison of spectra is quite accurate. On the other hand, the quadrupole coupling constants involve the analysis and combination of spectral data taken at many orientations with a resultant large decrease in the accuracy of the final result. Thus while the stated limits of error apply to either of the quadrupole coupling constants in the high-temperature phase, Blinc's experiments indicate that the limit of error in the difference is considerably

TABLE III. Direction cosines of the principal axes (error = ±0.02).

x	y	z
0.191	0.581	0.791
0.052	0.799	0.599
0.980	0.156	0.122

TABLE IV. Quadrupole coupling constants.

Phase	Undeuterated[a]		Deuterated (Ref. 1)	
	(kHz)	Temp. (°C)	(kHz)	Temp. (°C)
Upper	1313 ± 14	+30	1313 ± 15	+40
ferroelectric	1285 ± 19	0	1323 ± 15	0
	1407 ± 20	0	1419 ± 15	0
Lower	1363 ± 4	− 25	1395 ± 15	− 40

[a] The data on the two higher-temperature phases are taken from N. C. Miller and P. A. Casabella, Phys. Rev. 152, 228 (1966).

lower.

To be certain that the difference between the coupling constants of the deuterated and undeuterated crystals in the low-temperature phase is not due to the different temperatures at which the crystals were studied, the spectra of the undeuterated crystal were studied at several temperatures. Although not enough data were taken to determine the coupling constant at any temperature other than − 25 °C, it was possible to ascertain that the temperature dependence of the spectra is too weak to account for the difference between the two crystals.

Thus it seems safe to state that the Na^{23} quadrupole coupling constants are the same in both crystals in the high-temperature phase, but different in both the ferroelectric phase and in the low-temperature phase. The difference in the ferroelectric phase has already been explained[2] on the basis of the difference in spontaneous polarization of the two crystals. If the low-temperature phase is antiferroelectric, then the observed difference between the two crystals can also be due to a difference in the antiferroelectric polarization of the two crystals. A low-temperature antiferroelectric phase is predicted by the model[1] used to analyze all of the Na^{23} quadrupole coupling data in Rochelle salt, and thus the results reported here are consistent with the model.

CONCLUSION

The use of the Na^{23} NMR to measure the spontaneous polarization in Rochelle salt has shown that the polarization obeys the law $P_s \propto (T_C - T)^{1/2}$ in the temperature range just below the upper Curie point. Unfortunately, this method could not be used in the interesting temperature range within 0.1 °C of the Curie point, where deviations from the above law are expected.

In addition the Na^{23} nuclear quadrupole coupling constant was measured in the lower-temperature nonferroelectric phase of Rochelle salt. The value obtained agrees well with the model of Blinc.

Furthermore, the coupling constant in the low-temperature phase was found to be significantly different from that in deuterated Rochelle salt. This last result is to be expected if the low-temperature phase is antiferroelectric, as suggested by the model.

Notes added in proof. Since submission of this paper, new data have been obtained on the temperature dependence of the Na^{23} quadrupole coupling constant in both nonferroelectric phase of Rochelle salt. These new data make the conclusions of this paper about the agreement with Blinc's model and the antiferroelectric nature of the low-temperature phase seem doubtful. This new work will be submitted for publication as an addendum to the present paper.

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