SOVIET PHYSICS JETP VOLUME 23, NUMBER 4 OCTOBER, 1966

STUDY OF LOCAL MAGNETIC AND ELECTRIC FIELDS IN $NaNiF_3$

M. P. PETROV and G. A. SMOLENSKIĬ

Semiconductor Institute, Academy of Sciences, U.S.S.R.

Submitted to JETP editor November 1, 1965

J. Exptl. Theoret. Phys. (U.S.S.R.) **50**, 871-876 (April, 1966)

Shifts of NMR resonance frequencies in a single crystal of $NaNiF_3$ are studied as functions of the orientation and magnitude of the external magnetic field, and also as functions of the temperature. For the ^{19}F nuclei, these shifts are caused by dipole and hyperfine interaction with the Ni^{2+} ions, which leads to the appearance of local magnetic fields on the ^{19}F nuclei. Values of the spin density on the fluorine nuclei are calculated, and NMR and Néel-temperature data for $NaNiF_3$ and $KNiF_3$ crystals are compared. Qualitative agreement is established between the theory of superexchange and experiment. The shifts of the NMR resonance field in ^{23}Na are connected with second-order quadrupole effects. It is shown that the electric field near the sodium nuclei has a preferred axis, whose direction coincides with [110] or [$\bar{1}$10] for different nuclei in the planes z = 1/4 and z = 3/4. No local magnetic field is observed on the sodium nuclei; this indicates absence of hyperfine interaction between the sodium nuclei and unpaired electrons in the e_g orbitals of the Ni^{2+}.

NUCLEAR magnetic resonance makes it possible to measure with high accuracy the internal magnetic fields in crystals, and at the same time to study the spin-density distribution, the exchange interactions, and the chemical bond. If the nuclei on which the resonance is observed possess a quadrupole moment, then there is also a possibility of studying the quadrupole interactions and of obtaining information about the size and the local symmetry of the electric fields.

In the present work, the magnetic resonance of ^{19}F and ^{23}Na nuclei is studied in a single crystal of $NaNiF_3$. The compound $NaNiF_3$ has a structure of the perovskite type with an orthorhombic distortion. The parameters of the elementary cell are a = 5.361 Å, b = 5.524 Å, and c = 7.688 Å.[1] At 149°K there is observed a transition to an antiferromagnetic state with appearance of weak ferromagnetism. It is noteworthy that despite the similarity of a number of physical properties (the optical, for example) to those of the compound $KNiF_3$, which has a cubic structure of the perovskite type, the Néel temperature in $NaNiF_3$ is lower by nearly a factor two than in $KNiF_3$, where T_N = 275°K. In Anderson's papers[2,3] a connection is established between the NMR parameters and the superexchange energy, which is responsible for the magnetic ordering. It is therefore of interest to investigate to what extent the theory of superexchange agrees with NMR data on $NaNiF_3$ and $KNiF_3$.

The measurements were carried out by means of an oscillator adjustable over the range 6 to 30 Mc/sec. The magnetic field was measured with an IMI-2 magnetic-induction gauge based on the nuclear resonance of protons and lithium. The crystal on which the measurements were made had the form of a plate, of dimensions 14 × 11 × 2.5 mm. A surface of the plate coincided with the (110) plane. The conditions of preparation of the crystal were described earlier.[4]

NUCLEAR MAGNETIC RESONANCE ON ^{19}F

Results of the experiments. Two lines were observed from fluorine nuclei in positions (4c) and (8d). The position of the lines depends on the orientation of the crystal in the external magnetic field. The angular dependence of the magnetic field H_0 at resonance was recorded under the following conditions: 1) $H_0 \perp [010]$, and the angle between H_0 and [001] is varied (Fig. 1); 2) $H_0 \perp [100]$, and

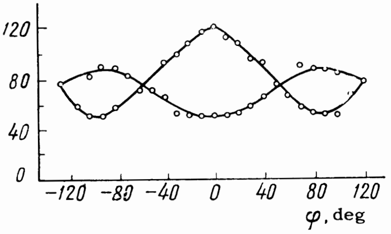

FIG. 1. Angular dependence of the shift of resonance field of ^{19}F nuclei in $NaNiF_3$ at room temperature; resonance frequency $f_0 = (\gamma/2\pi)H_0(1 + \Delta H/H_0) = 29.12$ Mc/sec.

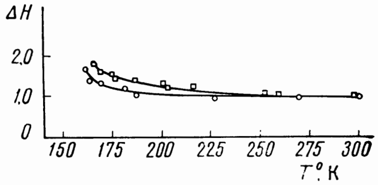

FIG. 2. Temperature dependence of the shifts of resonance fields (in relative units): □ – NMR of ^{19}F; ○ – NMR of ^{23}Na.

the angle between H_0 and [001] is varied. The results in the two cases agreed within the limits of experimental error. The line width between extrema of the derivative was $\delta H = 12 \pm 3$ Oe. The temperature dependence was studied for $\varphi \approx 54°$, where only one line is observed. The results of the temperature measurements are shown in Fig. 2. The temperature variation of the line shift agrees, within the limits of experimental error, with the variation of the magnetic susceptibility. With lowering of the temperature to 175°K, the intensity of the signal increases; but near that temperature there occurs an abrupt change of form of the signal, and the intensity begins to decrease. Below 161°K no NMR signal is observed.

Discussion of the results. To describe the shifts of resonance field on the fluorine nuclei, we use a Hamiltonian of the form[5]

$$\mathcal{H} = -g_N\beta_N \mathbf{I}(\mathbf{H}_0 + \mathbf{H}^D) + 2SA\mathbf{I}. \qquad (1)$$

Here g_N is the nuclear g-factor, β_N is the nuclear magneton, **I** is the nuclear spin operator, **S** is the spin operator of the Ni^{2+} ion, A is the hyperfine-interaction constant, and $\mathbf{H}^D$ is the dipole field:

$$\mathbf{H}^D = \sum_i \frac{3(\mathbf{r}_i\chi_m\mathbf{H})\mathbf{r}_i}{Nr_i^5} - \frac{\chi_m\mathbf{H}}{Nr_i^3},$$

where χ_m is the molar susceptibility, $\mathbf{r}_i$ is the radius vector drawn from the nucleus under consideration to the i-th Ni^{2+} ion, and N is Avogadro's number. The sum extends over all the paramagnetic ions of the specimen.

To calculate the dipole fields, we use the dipole sum obtained in[6] for $KNiF_3$, but with allowance for the difference in size of the molar susceptibilities of $NaNiF_3$ and $KNiF_3$. Then

$$H_{\parallel}^D / H_0 = -2H_{\perp}^D / H_0 = 1.94 \cdot 10^{-3}$$

at T = 298°K. The symbols ⊥ and ∥ refer to the orientations in which H_0 is perpendicular and parallel to the Ni-F bond; $\chi_m = 2.39 \times 10^{-3}$.[1] The sum of the Lorentz field and the demagnetizing field under these conditions varies with orientation of the crystal between about +1 and −4 Oe; it is taken into account only in the estimate of the experimental error.

In the calculation of the hyperfine-interaction constant from the experimental data, we will basically follow reference[6]; and we neglect possible deviations of the Ni-F-Ni bond from a 180° bond. On this assumption

$$A = A_s + A_p(3\cos^2\varphi - 1), \qquad (2)$$

where A_s and A_p are determined by the equations

$$Ng\beta g_N\beta_N \frac{(\Delta H_{\perp} - H_{\perp}^D)}{H_{0\perp}} = \left(\chi_m - \frac{8N\beta^2}{10Dq}\right)(2A_s - 2A_p),$$
$$Ng\beta g_N\beta_N \frac{(\Delta H_{\parallel} - H_{\parallel}^D)}{H_{0\parallel}} = \left(\chi_m - \frac{8N\beta^2}{10Dq}\right)(2A_s + 4A_p). \qquad (3)$$

Here φ is the angle between the direction of $\mathbf{H}_0$ and the direction of the Ni-F bond, $10Dq = 7620\ \mathrm{cm}^{-1}$,[7] g is the electronic g-factor ($g = 2.28$[6]), and β is the Bohr magneton.

On using the experimental values of $\Delta H_{\parallel}$ and $\Delta H_{\perp}$ (cf. Fig. 1), we find

$$A_s = (41 \pm 4) \cdot 10^{-4}\mathrm{cm}^{-1}, \quad A_p = (9.0 \pm 1.2) \cdot 10^{-4}\mathrm{cm}^{-1}.$$

From a knowledge of A_s and A_p, it is possible to calculate the spin densities f_s and f_p, corresponding to the unpairedness of spins in the 2s and 2p shells of the fluorine:[8]

$$f_s = 2SA_s / A_{2s} = (0.55 \pm 0.05)\,\%,$$
$$f_p = 2SA_p / A_{2p} = (4.2 \pm 0.6)\,\%. \qquad (4)$$

Here S = 1 is the spin of the nickel ion; $A_{2s} = 1.503\ \mathrm{cm}^{-1}$ and $A_{2p} = 0.0429\ \mathrm{cm}^{-1}$[6] are the hyperfine-interaction constants for electrons in the 2s and 2p shells of an isolated ion of fluorine. We note that the calculated spin densities do not include corrections for an excited state and for interactions of the 1s and 2s shells of fluorine.[9]

If one uses the method of molecular orbitals,[6] the spin densities are expressed in terms of parameters that describe covalence between the Ni^{2+} and F^- ions and overlapping of the corresponding atomic orbitals. Then

$$f_s = \lambda_s^2 / N', \quad f_p = \lambda_p^2 / N'. \qquad (5)$$

Here N′ is a normalizing factor, close to unity; $\lambda_s = \gamma_s + S_s$, $\lambda_p = \gamma_p + S_p$; S_s and S_p are atomic overlap integrals between the 2s and 2p orbitals of fluorine and the 3d orbital of Ni^{2+}, which belongs to the e_g representation;[1)] and γ_s and γ_p are parameters that describe the covalence between those same orbitals. It is possible to calculate the overlap integrals from the known atomic wave functions

---

[1)] In the method of molecular orbitals, the notation usually used is that of Mulliken's representation,[10] in which small letters are used to describe single-electron states.

and then, by use of the f_s and f_p obtained from experiment, to estimate the covalence.

As was shown in the papers of Anderson,[2,3] the energy of superexchange interaction, which is responsible for the magnetic ordering in insulators, is directly connected with these same parameters of overlap and covalence, obtained from NMR experiments. It is therefore possible to compare the ratio of the Néel temperatures of $NaNiF_3$ and $KNiF_3$ as obtained from magnetic measurements with that calculated by theory.[2,3] From[2] it follows that

$$\xi = \frac{(T_N)_{\mathrm{NaNiF_3}}}{(T_N)_{\mathrm{KNiF_3}}} \approx \frac{[7.6(\lambda_p{}^2 - S_p{}^2) - 30.5(\lambda_s{}^2 - S_s{}^2)]_{\mathrm{NaNiF_3}}}{[7.6(\lambda_p{}^2 - S_p{}^2) - 30.5(\lambda_s{}^2 - S_s{}^2)]^2_{\mathrm{KNiF_3}}}. \tag{6}$$

On substituting in formula (6) the values of λ_s and λ_p obtained from (5), we find $\xi = 0.73$, whereas according to magnetic measurements $\xi = 0.54$. In this calculation, all the overlap integrals have been taken equal for the two crystals, in view of the small difference in interatomic Ni-F distances in $NaNiF_3$ and in $KNiF_3$.[1] The values of λ_p and λ_s for $KNiF_3$ were taken from[11], again without taking into account the above-mentioned corrections for excited states and for 1s-2s interactions.

No great significance should be attached to numerical agreement between the calculated and observed Néel-temperature ratios, in view of the assumptions made above. Nevertheless, the fact that formula (6) correctly describes the trend in a change of the Néel temperature is reassuring.

NUCLEAR MAGNETIC RESONANCE IN ^{23}Na

Experimental results. In the general case, there are observed two lines, of width $\delta H = 9 \pm 2$ Oe, whose position depends on the orientation of the crystal in the external magnetic field. The shift of these lines was measured in relation to the position of the NMR of ^{23}Na in NaCl and the NMR of ^{61}Cu in the copper wire from which the coil used with the specimen was made. Figure 3 shows the angular dependence of the position of the NMR line of sodium in $NaNiF_3$, when $H_0 \perp [110]$ and the angle between H_0 and $[\bar{1}10]$ is varied; the magnetic field remains always in the plane of the plate. The resonance frequency is $f_0 = 9.01$ Mc/sec. As is evident from the figure, with such an orientation the position of one line is independent of angle, whereas the position of the other has an angular dependence. For $\theta = \pm 90°$, the two lines coincide, and the shift is $\Delta H = 9.1 \pm 2.5$ Oe.

A similar behavior of the lines was observed also upon rotation of the crystal about $[\bar{1}10]$, when $H_0 \perp [\bar{1}10]$ and the angle between H_0 and [110] was varied.

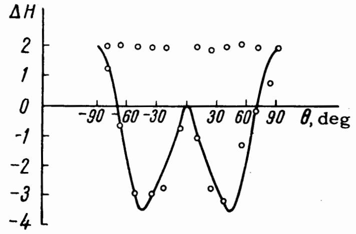

FIG. 3. Angular dependence of the shift of the NMR line of ^{23}Na (in relative units); T = 298°K.

Also observed was the behavior of the line shift upon change of temperature (Fig. 2) and of the external magnetic field. It was found that the shift changes in inverse proportion to the value of f_0. A similar rule is observed for the line width in a poly-crystalline specimen as a function of f_0. Thus, for example, at $f_0 = 9$ Mc/sec the width is $\delta H = 32 \pm 3$ Oe, and at $f_0 = 6.29$ Mc/sec it is $\delta H = 47 \pm 4$ Oe.

Discussion of results. For interpretation of the ^{23}Na NMR data it is necessary to take into account, besides the interaction of the sodium nucleus with the magnetic moments of the paramagnetic ions, also the interaction of the quadrupole moment of the nucleus with the electric field in the crystal. If the electric field has a symmetry lower than cubic, then there occurs a splitting of the NMR line into three, since the spin of ^{23}Na is $I = 3/2$. The central line remains, in a first approximation, unshifted; the position of the two others depends on the orientation of the crystal with respect to the external field and is independent of the value of the latter. In the experiments, however, only two lines were observed, and there was an inverse proportionality of the shift to the value of f_0. Such a behavior of the line can be explained by taking account of the effects of quadrupole interaction in the second approximation.

As is known, in the second approximation the central line is shifted; the amount of the shift, for the case in which the electric field has axial symmetry, is described by the expression (cf.[12])

$$\frac{\gamma \Delta H}{2\pi} = \frac{-\nu_Q{}^2}{16 f_0}\left[I(I+1) - \frac{3}{4}\right](1 - \cos^2\theta)(9\cos^2\theta - 1),$$
$$\nu_Q = 3e^2qQ / 2hI(2I-1). \tag{7}$$

Here θ is the angle between the direction of the axis of the electric field and H_0; Q is the quadrupole moment; eq is a component of the gradient tensor of the electric field; e is the charge of the electron; h is Planck's constant; and γ is the gyromagnetic ratio of the ^{23}Na nucleus.

The continuous line in Fig. 3 is the function

$-2(\cos^2\theta - 1)(1 - 9\cos^2\theta)$. As is evident from this figure, there is observed a satisfactory agreement between the experimental and theoretical angular dependences of the line shift. From formula (7) it follows that the amount of the shift is inversely proportional to f_0 (or H_0); this also agrees with experiment. Therefore the results obtained can be interpreted as a second-order shift for the central line. In conformity with (7), the calculated value of ν_Q is $(6.3 \pm 0.8) \times 10^{-1}$ Mc/sec.

The presence of two lines is easily explained by two different directions of the electric-field gradients for different sodium nuclei. According to the data of[1], the sodium and fluorine atoms in position (4c) are not shifted along the z axis; it therefore follows from the experimental results that in the planes $z = 1/4$ and $z = 3/4$, the electric-field gradients lie along $[\bar{1}10]$ and along $[110]$. In the experiments there were observed no satellites of the central line—of which there should, of course, be four. This is connected with the large value of the quadrupole-interaction constant ($\sim \nu Q$).

It is interesting to estimate the contribution to the observed shift from dipolar and hyperfine interaction of the ^{23}Na nucleus with the paramagnetic ions. When H_0 lies in the plane of the plate, then for all dimensions of any crystal under study, the sum of the Lorentz and demagnetizing fields was less than the experimental error ($\sim$2.5 Oe). The contribution to $\mathbf{H}^D$ from nearest-neighbor Ni^{2+} ions is equal to zero for a cubic environment and is small (< 1 Oe) even if the distortion is $\Delta r_i/r_i \approx 0.1$. Consequently, the contribution of the dipole fields to the observed shift ΔH can be neglected. An analysis of the angular dependence of Fig. 3, by the method of least squares, showed that from the hyperfine interaction, also, there is no contribution exceeding the experimental error. This means that the spin density on the sodium nucleus is less than 0.025% at most.

We remark that in the crystals $TlMnF_3$[13] and $RbMnF_3$[14,15], which have a similar perovskite-type structure, there have been observed spin densities of (0.03 ± 0.003)% on the thallium nucleus and (0.052 ± 0.005)% on the rubidium nucleus. These facts agree with the suggestion advanced in[13], that according to symmetry considerations in compounds ABF_3 with perovskite structure, hyperfine interaction of nucleus A with ions B occurs through those orbitals of the paramagnetic ions that belong to representation t_{2g} in the octahedral group. Since in Ni^{2+} (configuration d^8) the unpaired electrons occupy e_g orbitals, whereas the t_{2g} orbitals are fully occupied, the spin density on the sodium nuclei is in first approximation absent. In compounds with Mn^{2+}, there are uncompensated electrons in t_{2g} orbitals; because of their influence, a spin density is observed.

The authors thank P. P. Syrnikov for growing the single crystal of $NaNiF_3$ and A. G. Tutov for orienting it, and also V. M. Yudin for the magnetic measurements.

---

[1] W. V. Rüdorf, J. Kändler, and D. Babel, Z. Anorg. Allgem. Chem. **317**, 261 (1962).

[2] P. W. Anderson, Solid State Physics, Vol. 14 (Academic Press, New York, 1963), p. 99.

[3] P. W. Anderson, Magnetism, Vol. 1 (Academic Press, New York, 1963), p. 25.

[4] M. P. Petrov, FTT **7**, 1663 (1965), Soviet Phys. Solid State **7**, 1348 (1965).

[5] R. G. Shulman, Phys. Rev. **121**, 125 (1961).

[6] R. G. Shulman and S. Sugano, Phys. Rev. **130**, 506 (1963).

[7] R. V. Pisarev, FTT **7**, 1382 (1965), Soviet Phys. Solid State **7**, 1114 (1965).

[8] F. Keffer, T. Oguchi, W. O'Sullivan, and J. Yamashita, Phys. Rev. **115**, 1553 (1959).

[9] A. J. Freeman and R. E. Watson, Phys. Rev. Letters **6**, 343 (1961).

[10] R. S. Mulliken, Phys. Rev. **43**, 279 (1933).

[11] S. Sugano and R. G. Shulman, Phys. Rev. **130**, 517 (1963).

[12] A. Abragam, Principles of Nuclear Magnetism (Oxford, Clarendon Press, 1961).

[13] M. P. Petrov and G. A. Smolenskiĭ, FTT **7**, 2156 (1965), Soviet Phys. Solid State **7**, 1735 (1966).

[14] R. E. Payne, R. A. Forman, and A. H. Kahn, J. Chem. Phys. **42**, 3806 (1965).

[15] M. P. Petrov and G. A. Smolenskiĭ, FTT **7**, 3698 (1965), Soviet Phys. Solid State **7**, 2995 (1966).

Translated by W. F. Brown, Jr.
110