$$\Delta_{S^z,e,\downarrow} = 2\pi(\rho J)^2$$
$$\times [S^z(\omega_0 - \omega_{S^z})\, b^-(\omega_0 - \omega_{S^z}) - (S^z+1)\,\omega_0 b^-(\omega_0)] \;,$$

$$\Delta^{S^z+1}_{S^z,\uparrow} = \pi(\rho J)^2\,[S(S+1) - S^z(S^z+1)]\,\omega_0 b^+(\omega_0)\,,$$

$$\Delta^{S^z-1}_{S^z,\uparrow} = \pi(\rho J)^2[S(S+1) - S^z(S^z+1)]$$
$$\times(\omega_0 - \omega_{S^z-1} - \omega_{S^z})\, b^+(\omega_0 - \omega_{S^z-1} - \omega_{S^z})\,,$$

$$\Delta^{S^z-1}_{S^z,\downarrow} = -\,\pi(\rho J)^2\,[S(S+1) - S^z(S^z+1)]\,\omega_0 b^-(\omega_0)\,,$$

$$\Delta^{S^z+1}_{S^z,\downarrow} = -\,\pi(\rho J)^2\,[S(S+1) - S^z(S^z+1)]$$
$$\times(\omega_0 - \omega_{S^z+1} - \omega_{S^z})\, b^-(\omega_0 - \omega_{S^z+1} - \omega_{S^z})\,,$$

$$b^\pm(x) = (e^{\pm\beta x} - 1)^{-1} \;,$$

$$\Delta_{e,S^z} = \pi c\rho J^2\{2[(S^z+1)^2 n_{S^z+1} + S^{z^2} n_{S^z}]$$
$$+ [S(S+1) - S^z(S^z+1)]\,[n_{S^z+1} + n_{S^z} + (n_{S^z+1} - n_{S^z})$$
$$\times \tanh(\tfrac{1}{2}\beta(\omega_S - \omega_0))]\} \;,$$

$$\Delta_e^{S^z} = 2\pi c\rho J^2 S^z[S(S+1) - S^{z^2}]\,n_{S^z} \;,$$

$$\Delta_{es} = \sum_{S^z=-S}^{S-1} \Delta_{e,S^z} + \Delta_e^S - \Delta_e^{-S} \;.$$

The quantities Δ_{SL} and Δ_{eL} are the lattice relaxation rates for the localized and conduction-electron spins, respectively.

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Low-Temperature Transitions in Tetramethylammonium Manganese Chloride

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We have measured the proton nuclear magnetic resonance of tetramethylammonium manganese chloride, a linear chain antiferromagnet, in the temperature region 0.4–300 K. In addition, its ac magnetic susceptibility was measured in applied fields of 0 to 22 kG in the temperature range 0.3–4.2 K. When measured along the crystallographic *c* axis, the zero-field susceptibility had an anomaly at 0.84 K. When the external field was applied perpendicularly to the *c* axis below 0.8 K, a critical field of 11.5 kG was observed in *dM/dB*. The proton NMR did not indicate any *cooperative transition* to a magnetically ordered state of the Mn^{2+} spins. It did indicate, however, a gradual diminution of fluctuations in the crystallographic *ab* plane until a nonrandom order had been established between chains below approximately 0.8 K. We find that the tetramethylammonium groups cease all rotations below 39 K. In the region of 40 to 50 K, the tetramethylammonium groups not only undergo some hindered rotations, but their orientation is different from the published room-temperature x-ray diffraction results. Above 50 K only a single narrow NMR line is observed and, consequently, no additional information on the crystal structure could be obtained.

I. INTRODUCTION

There has been considerable interest recently in compounds whose magnetic properties approximate one-dimensional systems. Magnetic susceptibility,[1] electron-magnetic-resonance linewidths,[2] and neutron-scattering measurements[3,4] have shown $N(CH_3)_4MnCl_3$ to be a particularly good example of such behavior below 55 K. The crystal structure[5] of tetramethylammonium manganese chloride (TMMC) is such that there are infinite chains of Mn^{2+} ions bridged by Cl^{-1} ions; the Mn^{2+}-Mn^{2+} separation is 3.25 Å along the chain and 9.15 Å between chains. The Mn^{2+} ions along the chain form the one-dimensional antiferromagnetic system with the Mn^{2+} spins aligned perpendicularly to the axis.[1] The space between chains is occupied by disordered tetramethylammonium (TMA) ions.

Although magnetic-susceptibility measurements[1] above 0.3 K indicated the presence of a magnetic transition at 0.84 K, the neutron-scattering measurements[3] showed no evidence of three-dimensional magnetic correlations at temperatures as low as 1.1 K. Consequently, it was suggested that the magnetic transition might be somewhat below 0.84 K. In order to resolve this uncertainty, we undertook proton-magnetic-resonance experiments as well as ac-magnetic-susceptibility experiments both in zero and in applied fields.

The proton NMR can be, and commonly is, used as a microscopic probe of the local magnetic field in magnetic compounds. Such local fields at the proton sites consist of contributions from three major sources; the static applied field (approximately 4700 G for most of our experiments), that from the neighboring protons (a few gauss), and that from the Mn^{2+} spins (hundreds of gauss), all averaged over a time of the order of the reciprocal of the resonance linewidth. At a cooperative transition, the appearance of either the magnetization of a ferromagnet or of the sublattice magnetization of an antiferromagnet will be reflected in an abrupt change in the local field at the proton sites. NMR is thus a highly sensitive method of detecting whether or not such a transition has occurred.

In addition to the contribution of the local field at a proton site due to the Mn^{2+} spins, that due to the neighboring protons gives a measure of the directions and of the motions of the proton-proton vectors. Since the protons are located on the methyl groups, one can then determine the orientation and the rotations, if any, of the methyl groups, as well as that of the entire tetramethylammonium ions.

II. EXPERIMENTAL DETAILS

The single crystals used in this investigation were grown from a dilute (~10%) HCl solution of reagent-grade $MnCl_2 \cdot 4H_2O$ and $(CH_3)_4NCl$, with a slight excess of the manganese salt. The crystals grew as rose-pink hexagonal rods and were of good optical quality. Spectrochemical analysis of the crystals showed no magnetic impurities to be present except for Cr, whose concentration was less than 0.001 wt%.

The room-temperature structure of TMMC has been determined[5] and its space group is $P6_3/m$, with lattice constants $a_0 = 9.151$ Å and $c_0 = 6.494$ Å. The structure consists of linear chains composed of Mn^{2+} ions, bridged by three Cl^{-1} ions, and of disordered TMA ions. The proton positions were not determined. Recent x-ray[6] and neutron-diffraction measurements[4] showed that TMMC undergoes a first-order phase change to a monoclinic structure at 128 K. The x-ray results show that $\beta = 120.69°$ and the new lattice constants are $a_0 = 9.038$ Å, $b_0 = 18.424$ Å, and $c_0 = 6.459$ Å. This phase change, which is of little significance in our experiment, corresponds to a slight distortion of the hexagonal structure and a doubling of one of the unit-cell dimensions. The neutron-diffraction results are similar but indicate a quadrupling of a unit-cell dimension.

The susceptibility was measured with a Hartshorn bridge operating at 270 Hz. The NMR spectra were obtained using a field-effect-transistor (FET) marginal oscillator with magnetic field modulation and phase-sensitive detection at 80 Hz. The applied dc field was measured with a separate proton magnetometer.

We estimate that the crystal could be oriented in the apparatus with an uncertainty of ± 2°. The alignment in the NMR experiment was checked at low temperatures by rotation of the dc field about the crystallographic c axis, an axis of symmetry for the NMR spectra.

The temperatures at which the experiments were performed were obtained either by pumping various refrigerants over their respective temperature ranges or, for the intermediate regions not covered by the refrigerants, the cryostat was isolated from the refrigerant and maintained at the required temperatures by electrical heating.

III. RESULTS AND DISCUSSION

Andrew and Bersohn[7] have calculated the NMR spectra for solids containing nuclei of spin $\frac{1}{2}$ arranged in relatively isolated triangular groups, both for single crystals and for powders. The calculations were made not only for stationary groups but also for groups rotating about any fixed axis. They solved the Hamiltonian for the dipolar interaction of three identical nuclei in an external magnetic field and found for the stationary case that the spectrum of a single crystal consists of an unshifted line and three pairs of lines at $\pm y/\mu$, $\pm(3x+y)/2\mu$, and $\pm(3x-y)/2\mu$. In these expressions

$$x = \mu\alpha\left(\tfrac{1}{2} - \tfrac{3}{2}\cos^2\psi\right) \quad , \tag{1}$$

$$y = \mu\alpha\left(\tfrac{27}{4}\sin^4\psi - 3\sin^2\psi + 1\right)^{1/2} \quad , \tag{2}$$

where $\alpha = \frac{3}{2}\mu R^{-3}$, μ is the nuclear magnetic moment, R is the side of the equilateral triangle of protons, and ψ is the angle between the applied

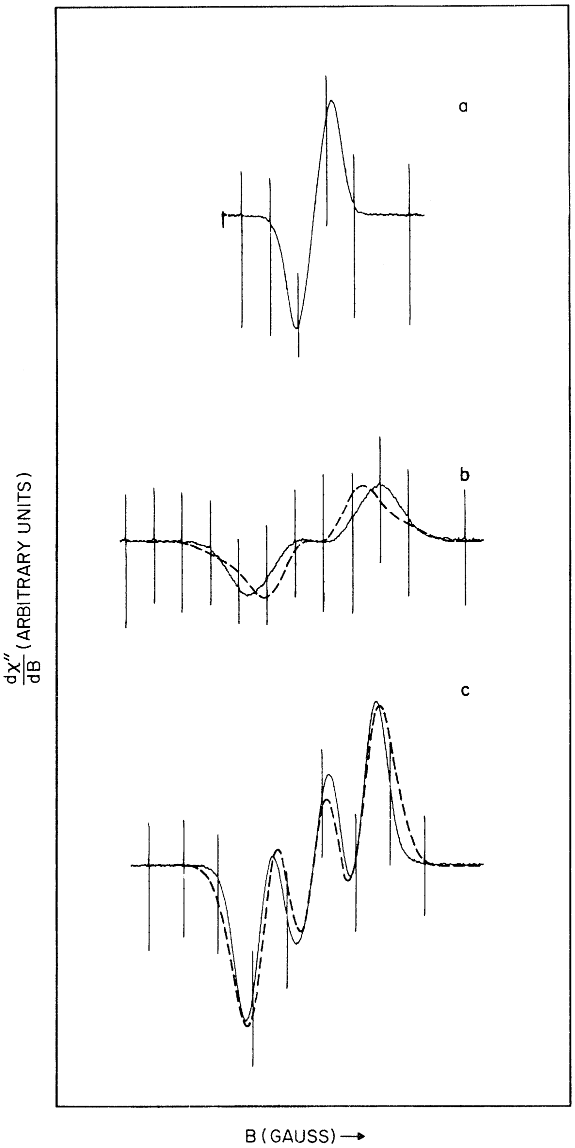

FIG. 1. Typical proton NMR spectra in TMMC with the external field applied along the crystallographic c axis. The ordinate is the derivative of the absorption signal and the abscissa is the magnetic field strength. (a) $T > 60$ K. Markers at 2-G intervals. (b) $50 > T > 39$ K. Markers at 2-G intervals. (c) $39 > T > 6$ K. Markers at 5-G intervals.

magnetic field and the normal to the plane of the proton triangle. It is seen that the spectrum is independent of the positions of the individual protons and depends only on the relative orientation of the normal to the plane of the triangle and the applied field. The line intensities are functions of the ratio x/y.

For the case of the equilateral triangle rotating about an axis which makes an angle ϵ with the normal to the triangle and an angle η with the magnetic field, the new values of x and y become

$$x' = \mu\alpha\left(\tfrac{1}{2} - \tfrac{3}{2}\cos^2\eta\right)\left(\tfrac{1}{2} - \tfrac{3}{2}\cos^2\epsilon\right) , \qquad (3)$$

$$y' = \mu\alpha\left(\tfrac{1}{2} - \tfrac{3}{2}\cos^2\eta\right)\left(\tfrac{27}{4}\sin^4\epsilon - 3\sin^2\epsilon + 1\right)^{1/2} . \qquad (4)$$

Powles and Gutowsky[8] have generalized the above equations to account for independent simultaneous rotations about any number of axes. They showed that for each additional rotation the expressions for x' and y' must be multiplied by a factor $(\frac{1}{2} - \frac{3}{2}\cos^2\theta_n)$, where θ_n is the angle between the nth and the $(n-1)$th rotation axes.

For purposes of discussion our experimental results can conveniently be divided into two temperature regions, one where the proton-proton interactions determine the spectra (above 6 K) and the other (below 6 K) where the Mn^{2+} spins play the dominant role. The spectra show that there is a further natural subdivision of the high-temperature region due to the onset of motions of the TMA group.

A. High Temperatures (above 6 K)

In Fig. 1 we show examples of the three distinct kinds of spectra observed in this temperature region. We shall discuss each of these in turn.

(a) $6 < T < 39$ K. A typical example of the spectra in this region with the field along the crystallographic c axis is shown in Fig. 1(c). Throughout this whole region the spectrum is independent of temperature and magnetic field over the range of our experiments, which was 3.9–5.7 kG. The dashed curve, which is the best calculated fit to the data, was obtained under the conditions that both the methyl and the TMA groups were stationary and by using the published room-temperature x-ray-diffraction results[5] for the locations of the carbon and nitrogen atoms. The x-ray-diffraction results showed that a threefold axis of the TMA group lies along the crystallographic c axis. The carbon-nitrogen lines were taken to define the planes of the methyl-group proton triangles, the sides of which were taken to be 1.79 Å, which is the accepted value for tetrahedrally distributed bonds. Following Andrew and Bersohn,[7] we calculated the spectrum using Eqs. (1) and (2) for the positions of the lines and assumed a Gaussian line shape of width 5.5 G (full width at half-height) for the individual lines. The only adjustable parameter in the entire calculation is the width of the Gaussian, which determines primarily the resolution of structure within a spectrum. It is clear from inspection of Eqs. (1)–(4) that when the magnetic field is along the crystallographic c axis the spectrum is unaffected by the onset of hindered rotation of the TMA group about this axis. The spectrum obtained with the field applied perpendicularly to the c axis, however, discriminates between these conditions and shows unequivocally that the TMA group is stationary.

We have also calculated the spectra for different orientations of the TMA group within the crystal lattice. It was found that the observed spectrum was not compatible with TMA groups having a twofold axis along the crystallographic *c* axis or with them having a threefold axis perpendicular to the crystallographic *c* axis. We would not, however, be able to detect a small tilt of the TMA threefold axis away from the *c* axis.

There was no need to invoke any interactions between the protons and the Mn^{2+} spins in order to fit the data, thus indicating that the magnetic field at the protons due to the Mn^{2+} spins was averaging to zero as a result of their fluctuations. The observed linewidth can be accounted for by interactions with the surrounding nuclei.

(b) $39 < T < 50$ K. In the region of 39 K, the spectrum changes character from that shown in Fig. 1(c) to that shown in Fig. 1(b) and then remains essentially unchanged up to 50 K. It should be noted that the width of the spectrum in this region is very nearly one-half of that observed at lower temperatures, and it is also independent of magnetic field. The dominant feature of the spectrum in this region is the central portion of the derivative curve corresponding to an absorption spectrum with a flat top. Such a narrowing of a spectrum is an indication of the onset of some kind of internal motion in the crystal. Apart from complete tumbling, the symmetry of the TMA permits only three kinds of rotation. These are rotations of the methyl groups about the normals to the proton planes (along the N-C lines), rotations of the TMA groups about any of its four threefold axes, and rotations of the TMA group about any of its three twofold axes. If a TMA threefold axis lies along the crystallographic *c* axis, then none of the above rotations or combinations of them gives rise to the observed spectrum since in all cases there is an intense central line which is incompatible with an absorption spectrum having a flat top. On the other hand, if a TMA twofold axis lies along the crystallographic *c* axis, the calculated spectrum corresponds closely to that observed if the TMA group is permitted to rotate about the three twofold axes. Such a calculated spectrum is shown as the dashed curve in Fig. 1(b). The individual lines were assumed to have a Gaussian line shape with a full width at half-height of 3.5 G. It is reasonable that the linewidth decreases to this value from 5.5 G, since the onset of hindered rotations will cause a reduction in the contributions from sources external to the methyl group. We are thus led to the conclusion that there has been a reorientation of the TMA group from that measured at room temperature by x-ray diffraction. We are further led to conclude that upon cooling the crystal through 39.5 K there is not only a transition involving another reorientation of the TMA group such that one of its threefold axes lies along the crystallographic *c* axis, but also the entire TMA group becomes stationary. Recent measurements by Peercy[9] on TMMC show that some changes occur in the Raman spectra in this temperature region.

(c) $T > 50$ K. At approximately 50 K the NMR spectrum becomes a single unstructured broad line which then narrows progressively with increasing temperature. From about 60 K to room temperature the spectrum consists of a single line whose width is 2.4 G, as shown in Fig. 1(a). It can be seen from Eqs. (3) and (4) that for rotations about axes which make an angle $\arccos 1/\sqrt{3}$ with the applied field, the spectrum collapses to a single line. The same result is obtained if there are two simultaneous independent rotations about axes which make an angle $\arccos 1/\sqrt{3}$ with each other. Since the twofold and threefold axes of a regular tetrahedron make precisely that angle, we are unable to distinguish between such motions and free rotation of the TMA groups, which are nearly tetrahedral.

B. Low Temperature (below 6 K)

The zero-field ac magnetic susceptibility has been measured for a single crystal of TMMC, both parallel and perpendicular to the crystallographic *c* axis. The susceptibility, which increased slowly with decreasing temperature down to 0.3 K, is very small and somewhat anisotropic. The perpendicular susceptibility has a somewhat greater change than that of the parallel susceptibility only below 0.6 K. Superimposed on this slowly varying background was a sharp peak in the parallel susceptibility centered at 0.84 K with a full width of about 40 mK. A much smaller but equally narrow peak was observed in the perpendicular susceptibility, but its magnitude can be accounted for by assuming a misalignment of the crystal by about 1°. The peak, which also exhibited a large loss component, occurs at the temperature at which Dingle *et al.*[1] suggested a magnetic transition may take place. To our knowledge, such a peak has not been predicted by theory.

The variation with temperature of the local fields at the proton sites is shown in Fig. 2 for temperatures above 0.45 K, our lowest temperature. The magnetic field was applied along the crystallographic *c* axis. At the lowest temperatures, resonances were also observed which correspond to local fields of −650 and +850 G but, for clarity of presentation, these fields are not included in Fig. 2. The spectrum was independent of the value of the magnetic field for the frequency range of our ex-

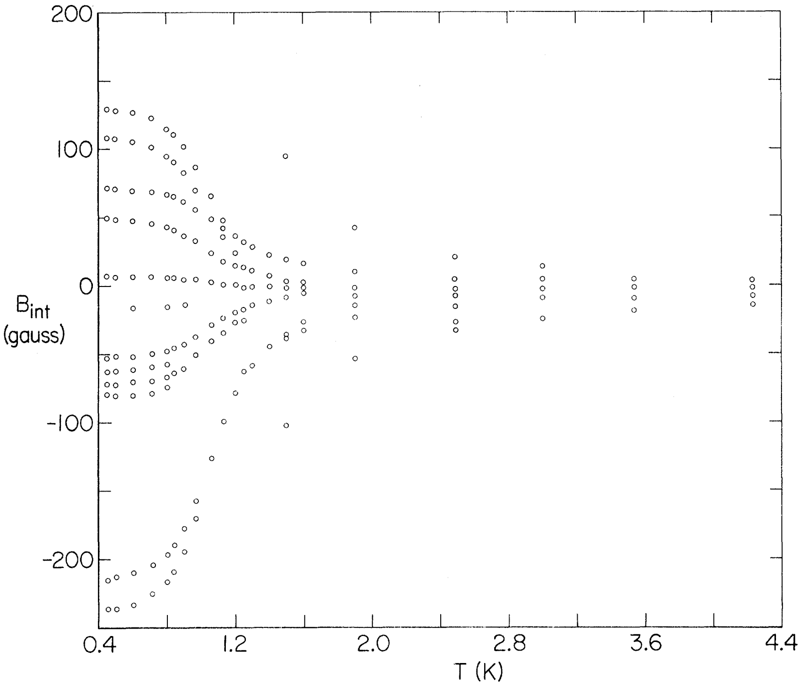

FIG. 2. Internal fields at proton sites of TMMC below 4.4 K with the external field applied along the crystallographic *c* axis.

periments. Also, not all lines of the resonance spectrum had the same intensity.

As the temperature is decreased the resonance spectrum cannot be explained by proton-proton interactions only, since the interactions with the Mn^{2+} spins become dominant. In the present experiment the external magnetic field was applied along the crystallographic *c* axis, which is along the chain of antiferromagnetic spins and perpendicular to the spin directions. The applied field used in these experiments is small compared to the intrachain exchange field, and if one assumes a reasonable value for the anisotropy field, primarily dipolar in origin, it is calculated that the spins are tipped out of the basal plane by less than 0.5°. Since the applied field is small compared to the intrachain exchange field and is perpendicular to the spin directions, the applied field, in first order, will have no effect on the ordering between the chains. The *gradual* increase in the contribution from the Mn^{2+} spins is to be contrasted with the sudden change expected if the Mn^{2+} spins undergo a cooperative transition. The effective fields experienced by the protons due to the Mn^{2+} spins are proportional to their thermal averages over a time comparable to the inverse resonance linewidth. For a three-dimensional antiferromagnet, this thermal average is just the sublattice magnetization.

The dipolar fields at the proton sites due to the Mn^{2+} spins are very sensitive to the proton coordinates, and since they are unknown we are unable to make a quantitative fit to the data shown in Fig. 2. In spite of this we can draw two qualitative conclusions. Firstly, the magnitude of the local fields can be easily accounted for by just the dipolar field of the Mn^{2+} spins. Secondly, our calculations show that a random arrangement of antiferromagnetic linear chains gives rise to a spectrum consisting of many more lines than we have observed experimentally.

Two other features of the proton spectrum are deserving of comment. Magnetic-field-rotation experiments showed that the spectrum had its simplest form when the field was applied along the *c* axis. Secondly, as shown in Fig. 2, there is an asymmetry in the internal field about zero. One might expect such an asymmetry to occur when the dipolar fields are comparable in magnitude with the externally applied field. Contrary to our observations, which cover the range 3.9–6.3 kG, one would expect this effect to show a magnetic field dependence. This can be resolved only by detailed calculations using the true (presently unknown) proton coordinates.

Measurements have also been made at temperatures between 0.3 and 4 K of the ac susceptibility, both parallel and perpendicular to the *c* axis, as a function of applied magnetic field in the range 0–22 kG. The only notable feature was a peak at 11.5 kG which appeared at temperatures below 0.8 K when the field was applied perpendicularly to the *c* axis. Accurate measurements on this peak could be made only below 0.6 K, where it was found that its position was independent of temperature. The origin of this peak is unclear but if one assumes that it is due to some kind of spin-flop state, then the anisotropy field is calculated to be approximately 150 G. No anomaly was observed when the field was applied along the *c* axis.

IV. CONCLUSIONS

At temperatures above 6 K the proton NMR spectrum can be accounted for entirely by proton-proton interactions. This indicates that although the Mn^{2+} spins are in antiferromagnetic linear chains, their fluctuations are sufficiently rapid that they do not contribute to the proton cw spectrum. All hindered rotations of the TMA group have ceased below 39 K. In the temperature region of 39 to 50 K, the spectrum can be fitted only by assuming an orientation of the TMA group which is in conflict with the published room-temperature x-ray data. Above 50 K additional rotations prevent further conclusions being drawn concerning the crystal structure.

Below 6 K, our experiments show that the Mn^{2+} spins do not undergo a cooperative magnetic transition, but rather there is a continuous diminution of fluctuations in the crystallographic *ab* plane until order has been attained between chains below approximately 0.8 K. Since the proton positions are unknown, however, our measurements are unable to determine the ordered arrangement at low temperatures.

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