*Work supported by the National Science Foundation under Contract No. GP-5517.

†Alfred P. Sloan Foundation Fellow.

[1]P. M. Platzman and W. M. Walsh, Jr., Phys. Rev. Letters 19, 514 (1967).

[2]P. M. Platzman and W. M. Walsh, Jr., Phys. Rev. Letters 20, 89(E) (1968).

[3]See Ref. 1 or V. P. Silin, Zh. Eksperim. i Teor. Fiz. 35, 1243 (1958) [translation: Soviet Phys.—JETP 8, 870 (1959)].

[4]L. D. Landau, Zh. Eksperim. i Teor. Fiz. 30, 1058 (1956) [translation: Soviet Phys.—JETP 3, 920 (1956)].

[5]Stability requires that γ_l be positive. See, for example, P. Nozières, Theory of Interacting Fermi Systems (W. A. Benjamin, Inc., New York, 1964), p. 16.

[6]Regard ψ as a vector in the space spanned by the Y_{lm}.

[7]Mixing occurs when $\vec{k}$ is not perpendicular to $\vec{H}$. We shall describe elsewhere the rather different structure emerging in that case.

[8]This and the quadratic form of the small-k corrections were first pointed out by Silin, Ref. 3. It should be emphasized that for each m there are infinitely many distinct modes, but see also remark (b).

[9]Equation (8) of Ref. 1 is what (7) becomes when l and m are both taken to be 1. However Eq. (7) has no significance in that case.

[10]W. M. Walsh, Jr., and P. M. Platzman, Phys. Rev. Letters 15, 784 (1965).

NMR STUDY OF THE SPIN-REORIENTATION BEHAVIOR OF $Mn_{2-x}Cr_xSb$†

R. W. Houghton and W. Weyhmann
School of Physics, University of Minnesota, Minneapolis, Minnesota 55455
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Spin reorientation due to change in sign of the temperature-dependent anisotropy energy has been studied in $Mn_{2-x}Cr_xSb$ ($x = 0$ and 0.03) by nuclear spin echo measurements. The behavior of the dipole and quadrupole hyperfine interactions and T_2 is reported in the region 180 to 280°K. The data suggest the possibility that a phase transition(s) is occurring.

We have studied ferrimagnetic $Mn_{2-x}Cr_xSb$ ($x = 0$ and 0.03) in the spin-reorientation temperature region by nuclear spin-echo observations. A large change (by a factor of 2) in the quadrupole interaction upon the reorientation of the magnetization from perpendicular to parallel to the c axis is observed as a change in the modulation of the spin-echo spectrum excited at the magnetic hyperfine frequency. The results indicate a broad region of instability as the spin-reorientation region is approached and should provide a strong test of any dynamical model which might be developed.

Neutron-diffraction studies have shown Mn_2Sb to have two molecules in each tetragonal unit cell with magnetic moments of $(+2.3 \pm 0.20)\mu_B$ and $(-3.87 \pm 0.40)\mu_B$ on the two types of manganese sites, I and II, respectively.[1] Measurements by Darnell, Cloud, and Jarrett[2] show the anisotropy energy increases nearly linearly between 200 and 300°K passing through zero ($K_1 = -K_2$) at $T_f = 247$°K. For $Mn_{2-x}Cr_xSb$ ($0 \leq x \leq 0.05$), T_f monotonically decreases with increasing x down to 200°K, where a first-order transition to antiferromagnetism occurs. The magnetization is parallel to the c axis for $T > T_f$ and perpendicular for $T < T_f$.

The spin-echo measurements are made using a wide-band hybrid junction and wide-band mixer. The sample, bulk pieces or powder dispersed in paraffin, is placed in a copper block at the shorted end of a 50-Ω stainless-steel coaxial line 25 cm long. The line is capacitor tuned and critically coupled to 50 Ω. A heater and thermocouple in the copper block allow measurements to below 77°K. The oscillator is able to provide rf fields H_1 up to 3 Oe and pulses 0.5 μsec wide. The powdered sample is Mn_2Sb ground to 325 mesh (44 μ) size under a liquid. The bulk sample is $Mn_{1.97}Cr_{0.03}Sb$, cleaved into thin flakes with surfaces perpendicular to the c axis.[3] These flakes were carefully stacked into piles to maintain uniform c-axis orientation and were molded in paraffin.

Mn_2Sb at 77°K has NMR signals due to Mn at 143.7 and 126.26 MHz.[4] Applying fields up to 10 kOe increases the higher and decreases the lower resonant frequencies, and at fields greater than the demagnetization field, the slope $d\nu/dH$ agrees within measurement error with the gryomagnetic ratio of ^{55}Mn. Assuming a negative effective hyperfine magnetic field, the electronic moment associated with the lower frequency is aligned parallel to the field and is therefore the larger-moment site, II. Thus the frequencies 143.7 and 126.26 MHz are associated with sites I and II, respectively.

The spin-echo spectrum is modulated by the quadrupole interaction. Abe, Yaruska, and Hirai[5] analyzed the results of a 90°-90° exciting rf pulse pair and found that $\tau\Delta\nu_Q = 1$, where τ is the modulation period and $\Delta\nu_Q$ the quadrupole splitting. Marginal oscillator measurements of site II at 77°K by Hihara, Koi, and Tsujimura[6] yielded $\Delta\nu_Q = 0.47$ MHz, while we measure 0.475 ± 0.010 MHz indicating that the above analysis is satisfactory for our system.

In Fig. 1 we show results of spin-echo measurements on sites I and II near T_f. At each temperature, the measurements were made at a single frequency determined by maximizing the spin-echo signal by cyclically adjusting all the tuning "knobs." The spin-echo amplitude is given by

$$A(t) = [c + b\cos(\tau t + \delta)]e^{-t/T_2},$$

where $t = 0$ at the beginning of the second rf pulse, the percent modulation is $100(b/c)$, and T_2 is

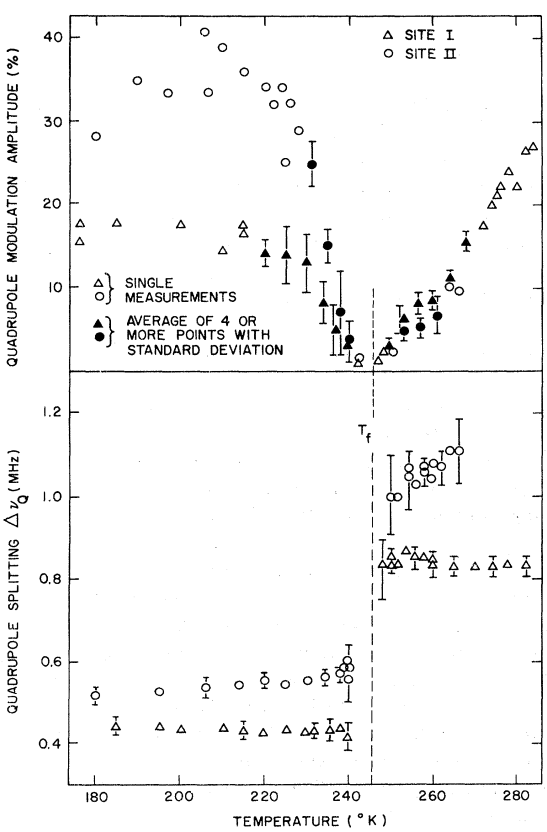

FIG. 1. Quadrupole modulation of spin-echo spectrum in the spin-reorientation region for two manganese sites, I and II. (Estimated errors are shown for $\Delta\nu_Q$).

the transverse relaxation time. The two striking features are the disappearance of the modulation at T_f and the apparent discontinuity of $\Delta\nu_Q$ at T_f. No distinct modulation can be detected in the region 245 to 246°K, so we have indicated the approximate location of the presumed T_f ($245 \pm \frac{1}{2}$°K) by the dotted line.[7] The modulation was too small to measure its frequency inside the reorientation region[8] ($T_f \pm 3$°K), but the frequency did not visually appear to change until T_f was passed. The temperature dependence of the quadrupole modulation is independent of the rf-field amplitude over a 10:1 ratio. For $Mn_{1.97}Cr_{0.03}Sb$ we find T_f at 220°K, which we expect from the anisotropy measurements,[2] and a narrower transition region (our powder samples presumably have more strains and inhomogeneities). Otherwise, the behavior is identical to that of our powder sample of Mn_2Sb. Applying an external field up to 1 kOe perpendicular to the c axis in this sample increases T_f and broadens the region over which the modulation is unobservable.

It is important to note that the modulation amplitude decreases with no measurable shift in the quadrupole frequency. No modulation was observable near T_f. There was no evidence of a superposition of a modulation characteristic of the opposite orientation, i.e., of double or half frequency, when outside the reorientation region. If the magnetization were uniformly rotating from one direction to the other, we would have expected to see a continuous change in the quadrupole frequency associated with any change in the modulation amplitude. Our only proposal at this time is that the magnetization is spatially unstable in this region. From the experimental data present-

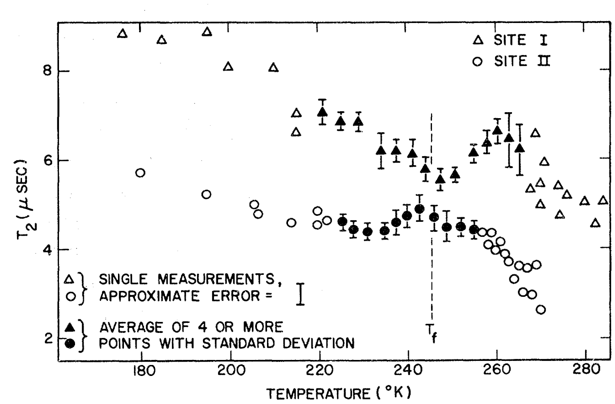

FIG. 2. Transverse spin relaxation time, T_2, in the spin reorientation region for the two manganese sites.

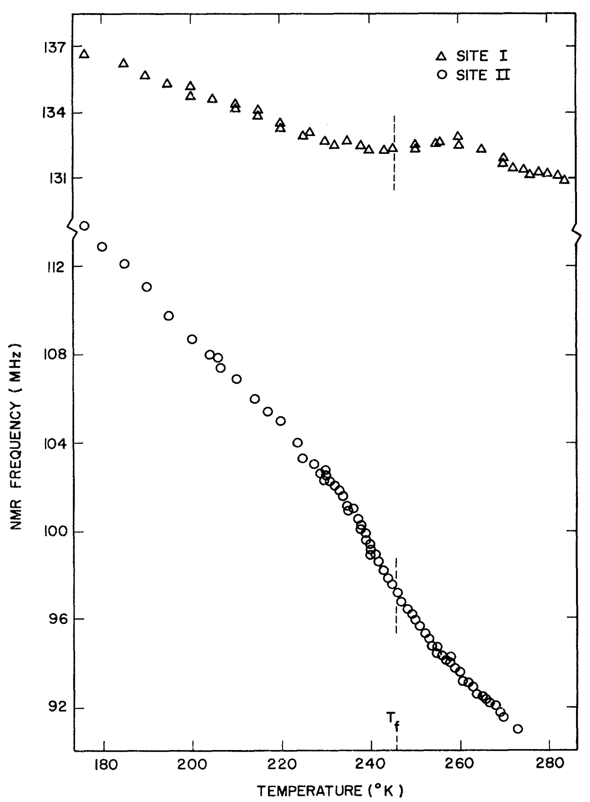

FIG. 3. Resonant frequency for maximum echo amplitude. (Approximate error is given by the size of the data points.)

ed here, we can draw no definitive conclusions; however, the data presented in Fig. 1 strongly suggest fluctuations in the orientation of the magnetization and thereby the existence of a phase transition(s).[8,9]

In Fig. 2 we show measurements of T_2 for the two Mn sites. We find anomalous but small peaks above and below T_f. Above 260°K the spin-echo amplitude is rapidly decreasing, and reliable measurements are impossible above about 270 and 280°K for sites II and I, respectively. At temperatures down to 77°K, T_2 increases monotonically. In the temperature region 77 to 280°K, T_1—the longitudinal relaxation time—decreases monotically. The minor changes in T_1 and T_2 in the reorientation region are not adequate to explain the anomalous drop in the modulation amplitude. Also, any fluctuations that may exist are not causing gross changes in the relaxation times.

The frequency measurements, shown in Fig. 3, are also interesting. By drawing straight lines through the high ($T > T_f + 15$°K) and low ($T < T_f - 15$°K) temperature data, one notices that a shift in frequency occurs on passing through the reorientation region. There is no similar shift in the magnetization, so we are probably measuring here an anisotropic hyperfine interaction. The frequency measured is that of the echo, not the oscillator pulses.

We shall report on all of these measurements in greater detail elsewhere, with extension of all the data to the liquid-helium temperature region.

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[2]F. J. Darnell, W. H. Cloud, and H. S. Jarrett, Phys. Rev. 130, 647 (1963).

[3]We are grateful to H. S. Jarrett for providing us with some bulk samples of $Mn_{2-x}Cr_xSb$.

[4]E. Hirahara, unpublished data (1963) from A. M. Portis and R. H. Lindquist, in Magnetism, edited by G. T. Rado and H. Suhl (Academic Press, Inc., New York, 1965), Vol. II(A).

[5]H. Abe, N. Yaruska, and A. Hirai, J. Phys. Soc. Japan 21, 77 (1966).

[6]T. Hihara, Y. Koi, and A. Tsujimura, J. Phys. Soc. Japan 17, 1320 (1962).

[7]Measurements using a cw tunnel-diode spectrometer have been made in our laboratory by Mr. Javed Aslam and corroborate the spin-echo results at temperatures above and below T_f. Near T_f only an unsplit line about 1 to $1\frac{1}{2}$ MHz wide is observed. The positions of maximum spin-echo and cw responses are at nearly but not exactly the same frequencies.

[8]H. Horner and C. M. Varma, succeeding paper [Phys. Rev. Letters 20, 845 (1968)], suggest the existence of two second-order transitions.

[9]R. C. LeCraw et al., J. Appl. Phys. 39, 1019 (1968), have observed nonresonant absorption over a broad frequency range near T_f in $TmFeO_3$ and other rare earth orthoferrites.