S^{33} Nuclear Magnetic Resonance in Paramagnetic α-MnS

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The temperature dependence of the S^{33} nuclear magnetic resonance has been studied in the paramagnetic state of the cubic antiferromagnet α-MnS. In the temperature range of 175 to 300°K, a Curie-Weiss temperature of −630°K and a transferred hyperfine coupling constant A^{33} of $+(1.65\pm0.04)\times10^{-4}$ cm^{-1} are measured. Utilizing the Mn^{55} nuclear-magnetic-resonance data measured by Jones, the ratio of A^{33} to A^{55}, the Mn^{55} hyperfine coupling constant, is determined to be $A^{33}/A^{55}=-0.0230\pm0.0005$. A discussion is presented on the effective fraction of valence electrons which contribute to the hyperfine field.

INTRODUCTION

SINCE the initial studies by Bizette, Squire, and Tsai,[1] the magnetic properties of the cubic anti-ferromagnets MnO, α-MnS, and α-MnSe have been the subject of extensive theoretical and experimental studies.[2] Recent studies of the hyperfine interactions in the paramagnetic state of these materials have been carried out with the technique of nuclear magnetic resonance (NMR).[3,4] The NMR paramagnetic shift in the field (or frequency) arising from the transferred hyperfine interaction between the anion and the Mn atom allows the determination of the sign and magnitude of this interaction.[5] With this information and with a theoretical or an experimental value of the isotropic hyperfine coupling constant for the anion in question, it is then possible to calculate the amount of overlap of the electron orbitals.[6]

O'Reilly and Tsang[3] have studied the O^{17} shift in the paramagnetic state of an enriched sample of MnO, and they were able to determine a value for both the transferred hyperfine coupling constant and the effective fraction f_s of the 2s orbitals in the O^{2-} ion contributing to the hyperfine field. In this paper, a similar study on the S^{33} NMR temperature dependence in the paramagnetic state of α-MnS is reported.

The fractional field shift a^{33} is given by

$$\omega=\gamma^{33}H(1+a^{33}),\tag{1}$$

where $a^{33}=(H_R-H)/H$, H_R is the resonance field of a reference material, H is the resonance field of the S^{33} in the sample, γ^{33} is the S^{33} nuclear gyromagnetic ratio, and ω is the frequency. The nuclear Hamiltonian may be written as

$$\mathfrak{K}^{33}=\gamma^{33}\hbar\mathbf{I}\cdot\mathbf{H}+6A^{33}\mathbf{I}\cdot\langle\mathbf{S}\rangle,\tag{2}$$

where $\mathbf{I}$ is the nuclear spin, A^{33} is the transferred hyperfine coupling constant for each of the six manganese sulfur bonds, and $\langle\mathbf{S}\rangle$ is the time-averaged electron spin on the manganese ion. It has been shown[7] for Mn^{2+} in the ^6S ground state that

$$\langle S\rangle=\chi H/g\beta N,\tag{3}$$

where χ is the temperature-dependent paramagnetic susceptibility, g is the electronic gyromagnetic ratio, β is the Bohr magneton, and N is Avogadro's number.

From Eqs. (1)–(3), the fractional shift may be expressed as

$$a^{33}(T)=(g\beta N)^{-1}(6A^{33}/\gamma^{33}\hbar)\chi(T).\tag{4}$$

A similar expression may be derived for the Mn^{55} NMR shift,[4] and it may be combined with Eq. (4) to yield

$$a^{33}(T)/a^{55}(T)=6(A^{33}/A^{55})(\gamma^{55}/\gamma^{33}),\tag{5}$$

where A^{55} is the nuclear hyperfine interaction due to core polarization and is assumed to be temperature-independent in the temperature range of 175 to 300°K. This expression shows that a plot of $a^{33}(T)$ versus $a^{55}(T)$ not only yields directly the value A^{33}/A^{55} but also shows that a straight line through the data should pass through the origin. The latter result demonstrates the insignificance of any Van Vleck temperature-independent susceptibility which may be present.

The relationship between the effective fraction f_s of the 3s electrons belonging to the S^{2-} ion and the transferred hyperfine coupling constant A^{33} may be expressed as[6]

$$f_s=2SA^{33}/A_{3s}^{33},\tag{6}$$

where $S=\frac{5}{2}$ is the true spin for Mn^{2+} and A_{3s}^{33} is the isotropic hyperfine coupling constant for the S^{2-} ion. A_{3s}^{33}, in MHz, is given by

$$A_{3s}^{33}=(8\pi/3)(g\beta\gamma^{33}/h)|\psi(3s)|^2,\tag{7}$$

where $\psi(3s)$ is the s-wave function of the valence shell.

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EXPERIMENTAL TECHNIQUE AND RESULTS

One of the major problems in NMR has been the want of sensitivity to such low abundant isotopes as S^{33} (0.76%). This problem is enhanced in solid materials where several resonance-line broadening mechanisms are present. In the case of a paramagnetic material, a principal contribution to the line broadening is the hyperfine interaction. One technique which has been proven suitable for increasing sensitivity is that of time averaging.[8] Under certain conditions[9] this technique allows the signal-to-noise to increase proportionally to the square root of the number of scans.

Using this technique, the NMR spectra of S^{33} were observed in the diamagnetic compounds ZnS and CdS.[10] This was the first known observation of this isotope in any solid. It was then pointed out[11] that the S^{33} transferred hyperfine coupling constant in α-MnS had not been measured. In conjunction with the earlier study

FIG. 2. A plot of $(a^{33}T)^{-1}$ versus T^{-1}.

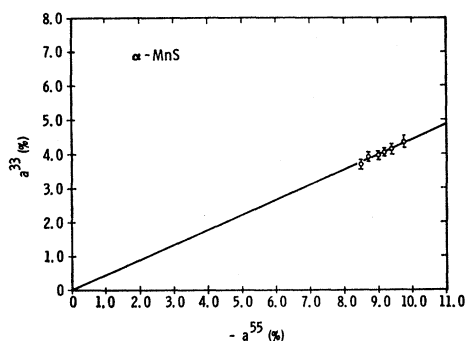FIG. 1. The S^{33} fractional field shift a^{33} versus the Mn^{55} fractional field shift $-a^{55}$. The a^{55} data were measured by Jones (Ref. 4).

of the Mn^{55} NMR in the paramagnetic state of this material (Néel temperature of 147°K), this study was undertaken. A finely divided powder sample was obtained from Jones.[11]

The measurements were made with a Varian VF-16 NMR spectrometer, a C-1024 time-averaging computer, and a V-4540 variable temperature controller. The temperature was calibrated with a copper constantan thermocouple. The frequency was set at 5.715 MHz and was monitored with a Hewlett-Packard HP-5245L frequency counter. The dispersion mode was always observed. The reference field used to measure the paramagnetic shift was determined by the S^{33} signal from

ZnS. As many as 2000 scans were taken over a period of 16 h.

No reliable line-shape or linewidth data could be obtained because the typical signal-to-noise ratio was about 3 to 1. The linewidth was observed to broaden from about 20 to about 50 G as the temperature was lowered from 300 to 175°K. The temperature was maintained to within ±1°K.

Figure 1 is a plot of $a^{33}(\%)$ versus $-a^{55}(\%)$, where the temperature is an implicit parameter and the $-a^{55}(\%)$ data are those measured by Jones.[4] A straight line intercepting the origin can be drawn through the data points and is not inconsistent with the data. This shows the assumptions made in deriving Eq. (5) are reasonable. Figure 2 is a plot of $(a^{33}T)^{-1}$ as a function of $(T)^{-1}$ and again a straight line can be drawn through the data points. This shows, from Eq. (4), that $\chi(T)$ may be represented by a Curie-Weiss law, $\chi(T) = C(T-\theta)^{-1}$, where $C=4.38$ for the Mn^{2+} ion and θ is the Curie-Weiss temperature. It should be noted that the indicated errors in the two figures are the maximum possible errors in determining the resonance field position and are representative of the linewidth.

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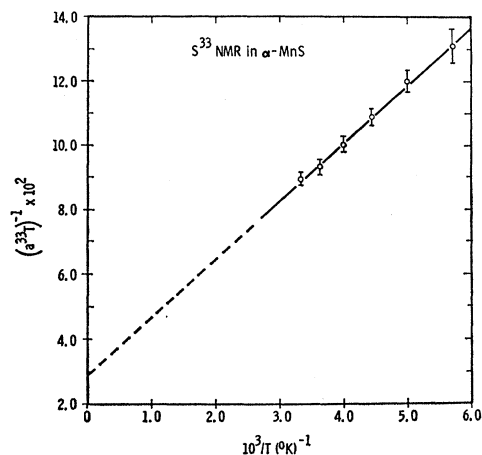[11] E. D. Jones (private communication).

TABLE I. Summary of the Mn^{55} nuclear hyperfine coupling constants A^{55} and of the respective O^{17}, S^{33}, and Se^{77} transferred hyperfine coupling constants A^{17}, A^{33}, and A^{77}.

Sample	A^{55} (10^{-4} cm^{-1})	Reference	$A^{17,33,77}$ (10^{-4} cm^{-1})	Reference
MnO	-81.5 ± 2.2	4	$+2.42$(128°K)	3
			$+2.35$(300°K)	3
			$+2.46\pm0.05$	4
α-MnS	-71.8 ± 5.3	4	$+1.65\pm0.04$	present work
α-MnSe	-67.0 ± 4.5	4	$+7.2\pm0.6$	4

K E N N E T H   L E E

TABLE II. Summary of $|\psi(ns)|^2$, the calculated isotropic hyperfine coupling constants, the measured transferred hyperfine coupling constants, and the effective fractions f_s for O^{17}, S^{33}, and Se^{77}.

Anion	$\|\psi(ns)\|^2$ $(10^{24}\,cm^{-3})$	Reference	Isotropic hyperfine constant (cm^{-1})	Transferred hyperfine constant $(10^{-4}\,cm^{-1})$	Reference	f_s $(\%)$
O^{17}	51.6	12	0.154	2.46	4	0.799
$(n=2)$				2.42	3	0.786
				2.35	3	0.763
	58.8	13	0.177	2.46	4	0.695
				2.42	3	0.684
				2.35	3	0.664
S^{33}	53.5	12	0.0905	1.65	present	0.915
$(n=3)$	67.6	13	0.114	1.65	work	0.723
Se^{77}	106.5	12	0.449	7.2	4	0.802
$(n=4)$	142.0	13	0.600	7.2	4	0.600

DISCUSSION

A least-squares fit of the data points in Fig. 1 for a straight line yields an intercept of the ordinate at $a^{33}=-0.03\%$ and a mean-square deviation of 0.0003%. Since the smallest experimental error in the a^{33} data is $\pm0.1\%$, it is reasonable to draw a straight line through the origin, as shown in Fig. 1. Any Van Vleck susceptibility may therefore be neglected.

From Fig. 1 the slope of the straight line is determined to be $\Delta a^{33}/\Delta a^{55}=-0.444\pm0.009$ and from Eq. (5) it follows that

$$A^{33}/A^{55}=-0.0230\pm0.0005, \qquad (8)$$

where $\gamma^{33}=0.3265$ kHz/G and $\gamma^{55}=1.0501$ kHz/G. The error estimates are made by solving for the maximum and minimum slopes which could be drawn through the data and the origin. From the Mn^{55} NMR data,[4] $A^{55}=-71.8\times10^{-4}$ cm^{-1} was calculated and, therefore,

$$A^{33}=+(1.65\pm0.04)\times10^{-4}\,cm^{-1}. \qquad (9)$$

In the temperature range of this study, Fig. 2 shows that $\chi(T)$ may be represented by a Curie-Weiss law. Therefore, from Fig. 2 and Eq. (4), θ and A^{33} are calculated to be

$$\theta=-630°K, \qquad (10)$$

$$A^{33}=+1.63\times10^{-4}\,cm^{-1}. \qquad (11)$$

This value for A^{33} is in good agreement with that obtained from Fig. 1 and θ is in good agreement with the $-(590\pm60)°K$ result obtained by Jones.[4] Because of the errors in the a^{33} data, the results from a plot such as Fig. 2 have a larger error than those from a plot such as Fig. 1. It is therefore difficult to assign a meaningful estimated error to the results obtained from Fig. 2.

A listing of the hyperfine coupling constants measured in these cubic antiferromagnets MnO, α-MnS, and α-MnSe is given in Table I. In comparing the transferred hyperfine couplings, an unexpected result is ob-served. This is the fact that $A^{33}<A^{17}<A^{77}$. From the periodic chart of the atoms, it was initially expected that $A^{17}<A^{33}<A^{77}$. However, when the effective fractional occupancy f_s and the isotropic hyperfine coupling constant A_{3s} for S^{33} are considered, this observed result is quite reasonable.

From Eq. (7), it is seen that in order to calculate A_{3s}^{33} the atomic parameter $|\psi(3s)|^2$ must be determined. This atomic parameter has not been determined for the S^{2-} ion. Theoretical calculations have been made for the neutral ground-state atoms,[12,13] and because of the uncertainties in these calculations it is reasonable to assume that $|\psi(3s)|^2$ will not differ greatly between the neutral ground state and the divalent state.

The atomic parameters $|\psi(ns)|^2$, where $n=2$, 3, and 4, respectively, for O^{17}, S^{33}, and Se^{77}, have been calculated using two different sets of wave functions. Morton et al.[12] used Hartree-Fock (HF) self-consistent–field atomic wave functions[14] and Hurd and Coodin[13] used Hartree-Fock-Slater (HFS) self-consistent solutions.[15] These latter wave functions, in general, lead to larger values of $|\psi(ns)|^2$ than the former wave functions and the values for each anion are listed in Table II. The first and second $|\psi(ns)|^2$ values listed for each anion are calculated respectively from the HF and HFS wave functions. The isotropic hyperfine coupling constants A_{2s}^{17}, A_{3s}^{33}, and A_{4s}^{77} are calculated from Eq. (7) (suitably modified for each anion) and are given in Table II. The f_s values calculated from Eq. (6) are also listed in this Table.

It is difficult, if not impossible, to assess the validity of the $|\psi(ns)|^2$ values calculated from the two different

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wave functions. However, the f_s values calculated with either of the wave functions are not unreasonable. The f_s values for O^{17} are in agreement with those calculated by O'Reilly and Tsang,[3] who used HF wave functions for the O^{2-} ion.

The important result is to note that with the measured A^{33} the f_s values for S^{33} are approximately the same as those for O^{17} and Se^{77}. This is expected because of the similarity in the crystallographic and magnetic properties of these cubic antiferromagnets. Therefore, the relatively small value for A^{33} is reasonable and consistent with the theoretical calculations.

Stopping Powers of S³², Cl³⁵, Br⁷⁹, and I¹²⁷ Ions in Mylar*

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Stopping powers of Mylar are presented for S^{32} ions of mean energy 15 to 95 MeV, Cl^{35} ions of 15 to 95 MeV, Br^{79} ions of 30 to 90 MeV, and I^{127} ions of 60 and 105 MeV. The heavy-ion beams were accelerated on the Rochester MP tandem Van de Graaff; energies were known to ±50 keV. The precision of energy-loss measurements was of the order of 2% with an estimated accuracy of ±8%. The experimentally determined stopping powers were used with the Bethe-Bloch equation and experimental proton stopping powers to calculate effective charges. The fractional effective charges for the ions investigated all fit a single smooth curve when compared with a reduced velocity variable; published values for O^{16}-ion stopping powers in carbon and aluminum yielded effective charges which fit the same curve. The effective charges for S^{32}, Br^{79}, and I^{127} are compared with the experimental most probable charge states, and are found to be less than the experimental values in all cases. This variation at its greatest is found to be 67%.

INTRODUCTION

THEORIES of heavy-ion stopping for ions of a few MeV to ∼100 MeV have met with limited success.[1,2] With a paucity of experimental stopping powers for heavy ions, and no satisfactory theory, there is a need for more data and a semiempirical means of correlating the available data, so that interpolations and extrapolations may be performed with reasonable accuracy.

Recently, Cumming and Crespo presented stopping-power data for light and heavy fission fragments in Mylar, and investigated several semiempirical means of correlating these data.[3] In this paper, we present stopping powers in Mylar for S^{32}, Cl^{35}, Br^{79}, and I^{127} ions at energies between 15 and 105 MeV. We use these data to test further a mode of correlation used for heavy-ion data in Ref. 3 and elsewhere.[4,5] The data are of interest for several reasons, among them the similarity in composition of Mylar ($C_{10}H_8O_4$) to tissue,[6] the use of Mylar as a degrader in many nuclear recoil studies,[7] and as an aid in interpretation of ion-track registration sensitivities of some nuclear-track detectors.[8]

EXPERIMENTAL

The heavy-ion beams used in this work were accelerated on the Rochester MP tandem Van de Graaff accelerator. All beams were extracted from the hydrogen duoplasmatron source using ∼5% impurities of H_2S, HBr, or HI; or in the case of chlorine, the beam was produced from several milligrams of solid NH_4Cl placed in the source. Terminal voltages up to 10 MV were used, with only single-charge states being passed around the 90° analyzing magnet. The machine was stabilized on an analyzed current of ≤5 nA. A switching magnet following the analyzer was used to deflect the beam another 45° into the "chemistry" beam line. Approximately 6 m from the switching magnet, there was a 3 mm aperture in the line, behind which was a solid-

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