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Low-Temperature Behavior of the Hyperfine Splitting and the Absolute Sign of the Hyperfine Constant[†]

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An anomalous temperature dependence of the splitting between hyperfine lines for Mn^{2+} in SrF_2 has been observed at low temperatures. This behavior is explained in terms of high electron spin polarization at low temperatures and the second-order hyperfine contribution. It is shown that for $SrF_2:Mn^{2+}$ the actual hyperfine coupling constant A is the same within experimental error at $T=77$, 4.2, and 1.3 K. In general this type of anomalous behavior of the hyperfine splitting can be used to determine the absolute sign of A for a paramagnetic ion with electronic spin $S \geq 1$ when the fine-structure splitting is vanishing or very small. For Mn^{2+} in SrF_2 the sign of A is determined to be negative.

I. INTRODUCTION

In conducting studies of the temperature dependence of the hyperfine coupling constant $A(T)$ of S -state ions in cubic crystals, it is important to make measurements of $A(T)$ in the temperature region below 77 K for the following reasons: (i) The "knee" of the curves predicted by present theories¹⁻⁵ generally falls in this region, and (ii) the presence of local modes⁶ may influence the low-temperature behavior of $A(T)$. Consequently, we intended to measure $A(T)$ of $^{55}Mn^{2+}$ in the alkaline-earth fluorides for $T \leq 77$ K, since no data have been reported in this region. In the course of these investigations, we discovered an anomalous increase in the apparent magnitude of A as the temperature was lowered. We report in this paper the results of our observations and an explanation of this anomalous behavior. At the same time, we demonstrate that these measurements can be used to determine unambiguously the absolute sign of the hyperfine coupling constant of paramagnetic ions with effective spin $S \geq 1$ when the fine-structure splitting is zero or very small.

II. EXPERIMENTAL

A series of ESR investigations were performed on a single crystal of SrF_2 containing nominally 0.5 wt % of Mn^{2+} ions at 77, 4.2, and 1.3 K at 9.3

and 31.8 GHz. The two spectrometer systems employed were a modified X-band Varian spectrometer and a modified K_a -band Strand Labs spectrometer, both of which were used in conjunction with a model HR-8 Princeton Applied Research lock-in amplifier and 1000-KHz field modulation.

The ESR spectra obtained from the crystal displayed six rather broad (~ 35 G between the two inflections of the first derivative curve) ^{55}Mn ($I = \frac{5}{2}$) hyperfine component lines, which exhibited no resolved superhyperfine structure with the fluorine nuclei. The linewidth of each hyperfine component line and the splitting between hyperfine lines were experimentally independent of the crystal orientation with respect to the magnetic field direction.

To investigate the temperature dependence of the hyperfine coupling constant A of Mn^{2+} in the crystal at low temperatures, we measured the separation (ΔH) between points of zero first derivative of the two outermost ($m = +\frac{5}{2}$ and $m = -\frac{5}{2}$) hyperfine component lines at 77, 4.2, and 1.3 K. Table I shows the measured values of ΔH at the two indicated microwave frequencies for low microwave power levels so that the ESR lines were not saturated. It is seen that ΔH substantially increases as the temperature decreases and that it depends on the microwave frequency.

Measurements of ΔH were made as a function of

TABLE I. The observed separation ΔH (in G) between points of zero first derivative of the $m = -\frac{5}{2}$ and $m = +\frac{5}{2}$ hyperfine component lines for Mn^{2+} in SrF_2 .

	77 K	4.2 K	1.3 K
9.3 GHz	512 ± 1	520 ± 1	528 ± 1
31.8 GHz	512 ± 2	516 ± 2	520 ± 2

the microwave power level. It was found that ΔH measured at 77 K showed no dependence on the microwave power level, whereas ΔH measured at 4.2 and 1.3 K decreased as the microwave power increased; at sufficiently high power levels ΔH at 4.2 and 1.3 K was the same as that at 77 K, within experimental error.

III. DISCUSSION

A. Analysis

For Mn^{2+} in SrF_2 the values of $|A|$ and g reported at 300 K are 101.9, and 2.0015 G, respectively, and the fine-structure coupling constant a is too small to be determined experimentally.⁷ For our purposes we shall assume that a is zero. With no fine-structure splitting, the allowed ESR transitions $|M, m\rangle \rightarrow |M-1, m\rangle$ (where M and m are the magnetic quantum numbers of the electron and nuclear spins S and I , respectively) for an isotropic hyperfine interaction occur at magnetic fields given to second order by⁸

$$H_{M,m} = H_0 - Am - (A^2/2H_0)[I(I+1) - m^2 + m(2M-1)], \quad (1)$$

where $H_0 = h\nu/g\beta$ and A is in G.

Figure 1(a) exhibits the detailed structure of the $m = -\frac{5}{2}$ and $m = +\frac{5}{2}$ hyperfine components determined by Eq. (1) for negative A . Because of the second-order hyperfine term which depends on M , each hyperfine component is split into five lines corresponding to the five possible $M \rightarrow M-1$ transitions for $S = \frac{5}{2}$. These five lines are equally spaced with a mutual separation of $5A^2/2H_0$. For the $m = \pm\frac{5}{2}$ transitions this factor is approximately equal to 8 G for $|A| = 100$ G, $g = 2$, and $\nu = 9$ GHz. At ordinary temperatures for which $kT \gg h\nu$, the electron population difference between the M and $M-1$ levels is approximately equal for all values of M ; consequently, at these temperatures (e.g., 77 K) the relative ESR intensities of the five lines are principally determined by their relative transition probabilities. These intensities form a symmetrical pattern which is centered on the $M = +\frac{1}{2} \rightarrow -\frac{1}{2}$ transition for each hyperfine component, as shown in Fig. 1(a). One should also note that, independent of the sign of A , the resonant field of the $M = +\frac{5}{2} \rightarrow -\frac{3}{2}$ transition, for example, is highest for the $m = -\frac{5}{2}$ hyperfine com-

ponent, whereas it is lowest for the $m = +\frac{5}{2}$ hyperfine component. However, the $m = +\frac{5}{2}$ hyperfine component lies at high field for $A < 0$ and it lies at low field for $A > 0$.

When the line-broadening effects arising from the unresolved superhyperfine, spin-spin, and spin-lattice interactions become so large that the five lines are not resolved, each hyperfine component displays a single broadened line, as shown by the dashed lines in Fig. 1(a). The shape of the absorption envelope of each hyperfine component is symmetric and its maximum point occurs on the $M = +\frac{1}{2} \rightarrow -\frac{1}{2}$ transition. Thus, the separation (ΔH) between the maxima of the $m = +\frac{5}{2}$ and $m = -\frac{5}{2}$ hyperfine envelopes is equal to $5|A|$, and consequently the magnitude of the hyperfine constant $|A|$ is determined by $|A| = \frac{1}{5} \Delta H$ at ordinary temperatures.

If the relation $|A| = \frac{1}{5} \Delta H$ is used in deducing $|A|$

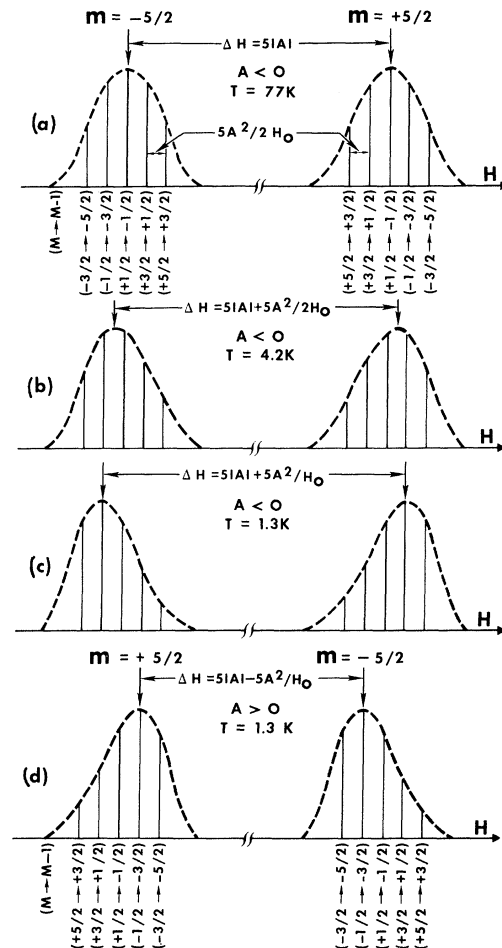


FIG. 1. Detailed structure of the $m = +\frac{5}{2}$ and $m = -\frac{5}{2}$ hyperfine components for $S = \frac{5}{2}$ and $I = \frac{5}{2}$ expected for (a) $A < 0$, $T = 77$ K; (b) $A < 0$, $T = 4.2$ K; (c) $A < 0$, $T = 1.3$ K; and (d) $A > 0$, $T = 1.3$ K.

from the measured values of ΔH at 77, 4.2, and 1.3 K (Table I), the resultant $|A|$ exhibits a temperature dependence which is different from that expected on the basis of data taken above 77 K for the same system⁹ and which cannot be explained, even qualitatively, by theoretical predictions based on the orbit-lattice interaction¹⁻⁵ as well as the local-phonon contribution.⁶ In addition, if the relation $|A| = \frac{1}{5} \Delta H$ was valid at low temperatures, then $|A|$ would depend on the microwave frequency and power level in the same manner as that observed for ΔH (Table I). As will be shown in the following paragraphs, the determination of $|A|$ from $\frac{1}{5} \Delta H$ is not at all valid at low temperatures.

At very low temperatures, the electron spin system becomes highly polarized so that the population difference between two adjacent levels M and $M - 1$ is substantially different for a different value of M . As a result, the relative ESR intensities of the five lines of each hyperfine component will be different from those shown in Fig. 1(a) for $T = 77$ K. Figures 1(b) and 1(c) illustrate the case of $A < 0$ calculated for $T = 4.2$ and 1.3 K, respectively, for $\nu = 9$ GHz. Since the $m = +\frac{5}{2}$ and $m = -\frac{5}{2}$ hyperfine components are interchanged if A is positive, the relative intensity distribution of the five lines associated with the low-field hyperfine component for $A > 0$ will be the same as that of the high-field hyperfine component for $A < 0$. This difference can be seen in Figs. 1(c) and 1(d) for $T = 1.3$ K.

It is important to note in Figs. 1(b) and 1(c) that the peaks or maxima of the hyperfine absorption envelopes (indicated by arrows in the figure) shift as the temperature decreases. From the figure this shift is estimated to be $5A^2/4H_0$ (~ 4 G) for $m = +\frac{5}{2}$ or $m = -\frac{5}{2}$ from 77 to 4.2 K, and it is about the same amount from 4.2 to 1.3 K. Consequently, for $A < 0$, the peak-to-peak separation (ΔH) between the $m = -\frac{5}{2}$ and $m = \frac{5}{2}$ hyperfine envelopes will be increased by about 8 G from 77 to 4.2 K [Fig. 1(b)] and by another 8 G from 4.2 to 1.3 K [Fig. 1(c)]. If A is positive, ΔH will be decreased by the same amounts for the same temperature changes [see, for example, Fig. 1(d)]. It is clear that at low temperatures ΔH is not given by $5|A|$ as in the case of the ordinary temperatures.

The magnitude of the predicted effects on ΔH will depend critically on the microwave power level as well as on the microwave frequency employed to induce ESR transitions. If the microwave power level is so high that the electron spin system becomes saturated, the effects would be reduced and eventually become unobservable at very high power levels. The microwave frequency dependence arises from two competing mechanisms. The higher the microwave frequency, the smaller the magnitude of the second-order hyperfine-interaction term, but

the larger the degree of electron spin polarization (considering the microwave frequency to be held constant in the ESR experiments). These mechanisms combine to reduce the expected change in ΔH by approximately a factor of 2 for an increase in operating frequency from 9.3 to 31.8 GHz. That is, for $|A| = 100$ G, $g = 2$, and $\nu = 31.8$ GHz, the value of ΔH is expected to increase by about 4 G from 77 to 4.2 K and by an additional 4 G from 4.2 to 1.3 K. Even if a fine-structure splitting is present, provided it is small compared to $5A^2/2H_0$, the analysis presented here is equally applicable. Also, since each unresolved superhyperfine line is composed of a five-line pattern similar to that shown in Fig. 1, the validity of the above analysis is unaffected by the superhyperfine structure.

The change observed in ΔH (see Table I) and its response to the microwave frequency and power level are quite consistent with the preceding analysis. (Although the hyperfine envelopes should display an asymmetry in line shape at the low temperatures as can be seen in Fig. 1, such an asymmetry was not detected experimentally, apparently a result of the slight overlap between adjacent hyperfine envelope lines.)

B. Temperature Dependence of A

As shown by the preceding analysis, the dependence of ΔH on temperature below 77 K arises principally from the combined effect of the high electron spin polarization at low temperatures and the second-order hyperfine splitting, rather than any temperature dependence of the hyperfine coupling constant itself. It is therefore concluded that the magnitude of A is practically the same at 77, 4.2, and 1.3 K.

Recently there has been considerable interest in the temperature dependence of the hyperfine coupling constant of S -state ions in solids including Mn^{2+} in the alkaline-earth fluoride crystals.⁹⁻¹¹ As was already mentioned, it is important to measure the temperature dependence of the hyperfine constant $A(T)$ at low temperatures for the purpose of comparing the data with various theoretical models¹⁻⁶ for $A(T)$. In such investigations, the effect treated here should be carefully considered in deducing $A(T)$ from ESR data taken at low temperatures, since this effect manifests itself as an apparent change in the magnitude of A .

C. Absolute Sign of A

Experimental determination of the absolute sign of the hyperfine coupling constant has always been a separate and important part of ESR investigations. It was shown in Sec. IIIA that the sign of A for Mn^{2+} in SrF_2 is determined to be negative from the $in-$

crease in ΔH at low temperatures.

The usual ESR method¹² of determining the absolute sign of A for $S \geq 1$ consists of (i) the determination of the sign of A relative to that of the fine-structure coupling constant, and (ii) the determination of the absolute sign of the fine-structure coupling constant by investigating the ESR spectrum at a very low temperature. This indirect method is effective only when both the hyperfine and fine structures are experimentally resolved.

When the fine-structure splitting is very small or vanishing, it is usually not possible to determine the correct sign of A by this indirect method. However, by measurements of the hyperfine splitting at low temperatures and an analysis similar to the one presented here for $\text{SrF}_2:\text{Mn}^{2+}$, the absolute sign of A can be determined unambiguously for both S -state and non- S -state ions with electronic spin $S \geq 1$, even if the fine-structure splitting is zero or

very small.

IV. CONCLUSIONS

An anomalous increase in the splitting between hyperfine lines for Mn^{2+} in SrF_2 has been observed at low temperatures and is explained in terms of the high electron spin polarization expected below 4 K. The importance of this effect is stressed in view of the recent interest in the changes in A itself produced at low temperatures by lattice vibration and expansion and by local modes. Finally, the observation of this effect makes possible the direct determination of the sign of A for paramagnetic ions with $S \geq 1$ when the fine-structure splitting is negligible.

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Hyperfine Splitting of a Localized Moment in a Metal

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The hyperfine splitting of the erbium localized moment resonance in silver metal has been observed for nominal concentrations of 28-, 65-, 86-, and 1500-ppm solid solution Ag:Er alloys. A hyperfine coupling constant $A = 75 \pm 1.0$ Oe was found to fit the individual line positions to within experimental accuracy (± 5 Oe). The magnetic-resonance bottleneck is discussed; it is argued that this bottleneck is absent for these measurements, and is the reason for the failure of previous attempts to observe such hyperfine splittings in transition-metal alloys.

I. INTRODUCTION

We wish to report the first observation of hyperfine splitting of the magnetic resonance of a localized moment in a metal. The magnitude of

the splitting, combined with the resonance g value, leaves no doubt as to the orbital occupation number of the observed moment. The fact that previous measurements (on transition-metal alloys) have failed to observe hyperfine splittings, whereas for