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Magnetic Resonance Line Shapes at the Onset of Saturation*

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Magnetic resonance absorption line shapes and widths in Li metal and CaF_2 crystals have been measured as a function of radio-frequency power level. The measurements have been made on the Li^7 resonance in Li at 77°K and 215°K and on the F^{19} resonance in CaF_2 at room temperature. The measurements have been made from low rf power into the region of appreciable saturation, but not into the very high saturation region considered by Redfield. A decrease in δH, the peak-to-peak absorption derivative line width, was observed in both systems at sufficiently large values of H_1, the rf magnetic field. The changes of line width in Li at various values of T_1 and of characteristic motional frequency of the nuclei show good qualitative agreement with the criteria proposed in the recent theory of Tomita. Line-width data obtained by Redfield in aluminum are included for comparison. In the case of CaF_2, where the spin-lattice relaxation proceeds via paramagnetic impurities, the decrease in δH occurs at appreciably higher saturation levels than is the case in Li and Al.

INTRODUCTION

IT has been known experimentally for some time[1–5] that magnetic resonance absorption line shapes and widths for systems in which $T_1 \neq T_2$ do not in general change with rf power level in the manner predicted by the early theories.[6,7] Redfield[1] has shown that some of the difficulties in the early theories are associated with the assumption made in the Bloembergen, Purcell, and Pound theory that the complex rf nuclear spin susceptibility is simply proportional to the difference in population of the nuclear spin levels and is not affected by the presence of the rf field except insofar as the spin level populations are affected. He shows that when the rf field is large, a coherence is introduced into the magnetization by polarization of the spins along the rf field direction, so that the above assumption breaks down. Starting from more general assumptions, Redfield is able to develop a theory for the behavior of the magnetic resonance absorption and dispersion signals in the case where the rf field is of the order of magnitude of or larger than the local magnetic fields.

The decrease in δH, the peak-to-peak absorption derivative line width, and change in shape of the absorption line upon saturation observed in copper and aluminum by Abell and Knight[4] and Redfield[1] was also observed in metallic lithium.[5] This effect, particularly in Li, occurs while H_1, the rf field, is still quite small compared to local fields. (In Li the change is observable when the ratio of H_1 to δH is 1.5×10^{-3}.) Redfield's work indicated that the line narrowing might not be surprising, but made no quantitative predictions about the behavior at the onset of saturation.

We have made detailed measurements of the behavior of the Li absorption line at the onset of saturation at 77°K, 215°K, and 298°K. Measurements have also been made of the behavior of the absorption signal in CaF_2. The CaF_2 system was chosen in order to test whether the existence of the line narrowing depends on the spin-lattice relaxation process. In CaF_2 the relaxation mechanism for the F^{19} nuclei is the spin diffusion-limited relaxation by paramagnetic impurities, and this mechanism gives a nuclear spin-lattice coupling quite different from the coupling via conduction electrons in the metals. The absorption lines in CaF_2 have also been found to exhibit the decrease in δH and shape change, but at higher values of rf saturation.

Tomita[8] has recently put forth a detailed theory of the saturation behavior of the magnetic resonance lines. He develops the conditions necessary for the observation of the "saturational narrowing" and the slow saturation of the dispersion signal observed by Redfield. This theory agrees with Redfield's calculations at very large rf fields. The experimental data in Li and CaF_2 will be presented, and, where appropriate, related to to the Tomita theory.

PERTINENT EXPERIMENTAL DETAILS

The measurements of Li were made at 5.6 Mc/sec, using a conventional Pound-Knight[9] oscillator-detector, which detects only the absorption signal. The audio output was fed into a 47-cy/sec phase-sensitive detector, using a diode bridge mixer similar to that used by Volkoff.[10] The 47-cy/sec field modulation was replaced by an 8-cy/sec modulation for one set of measurements at room temperature. A Liston-Becker dc amplifier with the input chopper removed was used for the phase-sensitive detector for these 8-cy/sec measurements. For the measurements on F^{19} in CaF_2 the rf system consisted of the transmitter, probe, and receiver unit from a Varian V-4300B crossed-coil rf spectrometer, operating at 40 Mc/sec. The audio signal from the Varian receiver was fed into the

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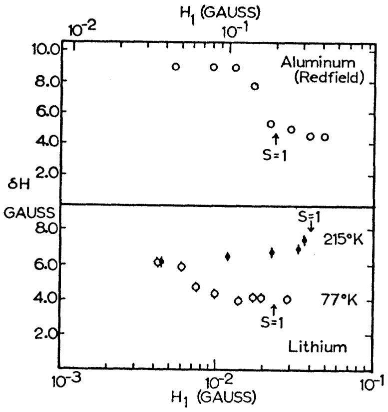

FIG. 1. The peak-to-peak absorption derivative line width, δH, is shown as a function of H_1 for lithium metal at 77°K and 215°K. Some data of Redfield taken in aluminum at room temperature are shown for comparison. $S=\frac{1}{2}\gamma^2 H_1^2 T_1 g(\nu_0)$.

47-cy/sec unit used for the lithium measurements. The author is indebted to the Cornell Chemistry Department for the use of the Varian units and their electromagnet for the CaF_2 measurements.

The Li sample used was composed of small spheres dispersed in mineral oil. The sample was prepared in the manner described previously.[11] The typical particle diameter was about 50μ. The skin depth in Li at 77°K, for an infinite plane surface, is about 20μ at 5.6 Mc/sec. The Q of the sample probe was observably lower at 77°K than at room temperature, presumably because of eddy current losses in the particles, but no asymmetry of the resonance produced by phase shift mixtures of χ' and χ'' was observed.[12,13] Redfield[14] has also noted the lack of this asymmetry with particles of Al and Cu large compared to the skin depth.

The CaF_2 crystals were obtained from the Harshaw Chemical Company and exhibited T_1 values slightly less than 1 min at room temperature.

The low-temperature measurements in Li were made by immersing the probe in liquid nitrogen for the 77°K measurements and in a turpentine-dry ice mixture for the 215°K measurements.

For Li, the magnitude of H_1 for a given rf voltage on the sample coil was determined from the variation of the amplitude of the absorption signal at exact resonance with rf level. These measurements were done at room temperature. T_1 is known from pulse measurements.[11] Moreover, since the spin system obeys the Bloch equations at low rf levels, the saturation of the peak absorption will follow the simple theory rather closely.[1]

Because of the large values of T_1 in Li and CaF_2, we found it impractical to operate with the magnetic field modulation frequency ω_m small compared to $1/T_1$. Halbach[15] has calculated the effect of large ω_m on the observed absorption derivative for systems obeying the Bloch equations. He shows the existence of a signal which is 90° out of phase with the field modulation. In the present experiments, the phase of the reference signal to the phase-sensitive detector was always adjusted so as to observe the component of signal in phase with the magnet modulation. Possible effects of the large modulation frequency are discussed below at appropriate points.

THE ABSORPTION LINE IN LITHIUM

The experimental values of δH in Li are given in Fig. 1 as a function of H_1. Comparison of values of H_1 in the coil determined by the room temperature saturation runs with values computed from coil dimensions and measured rf voltage indicates that the absolute magnitude of H_1 may be in error as much as 50%. (The effect of using metallic particles with dimensions of the order of the skin depth prevents a precise determination of the H_1 seen by the spin system.) The saturation factor S is defined to be $\frac{1}{2}\gamma^2 H_1^2 T_1 g(\nu_0)$, where $g(\nu_0)$ is the value of the normalized unsaturated absorption line-shape function at exact resonance. In calculating S, values of T_1 were obtained by interpolating between experimental values obtained at room temperature and above using pulse techniques[11] and values at very low temperatures obtained using a rapid-passage scheme.[16] The interpolation was done assuming the temperature dependence $T_1 \propto 1/T$. The value of the product $T_1 T$ obtaining at room temperature is in excellent agreement with the value given by Anderson and Redfield[16] for helium temperature, so that one may have confidence in the interpolation. A value for T_1 was also obtained experimentally at 77°K by the progressive saturation technique. The value agrees within the rather large error of the measurement with the interpolated value. Also plotted in Fig. 1 for comparison are data obtained by Redfield in Al.[17] The scale of H_1 for the Al data is chosen so that the point $S=1$ coincides vertically with $S=1$ for Li at 77°K.

The decrease in δH in Li at 77°K and in Al at room temperature occurs at approximately the H_1 level Tomita predicts. He develops the fact that this "saturational narrowing," or what he more graphically calls "forced nutational narrowing," should occur, for the case where there is no motional narrowing, when the frequency of precession about H_1, γH_1, satisfies the condition

$$\gamma H_1 \gtrsim [(1/T_2)\phi_0]^{\frac{1}{2}}, \tag{1}$$

where ϕ_0 is the motional frequency of the nuclei, and

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[12] R. E. Norberg, Phys. Rev. **86**, 745 (1952).

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[17] A. G. Redfield (private communication). The author is indebted to Dr. Redfield for communication of unpublished experimental absorption derivative curves. Quoted values of δH and the integrated width given in Table I were obtained by the present author, using Redfield's experimental data.

$1/T_2$ is the spread in precessional frequency of the nuclei produced by the dipolar broadening.

For metals, with the conduction electron relaxation mechanism, Tomita shows that, in the case where the characteristic frequency of any diffusional motion is very small, ϕ_0 becomes $1/T_1$, the flipping frequency produced by the spin-lattice relaxation processes. Equation (1) thus corresponds essentially to the condition $S\gtrsim 1$. It will be seen that in both the Al and Li data the criterion given by Eq. (1) is rather closely satisfied. It is important to point out that this "narrowing" is perhaps more properly described as a change in the line shape. The decrease in δH is produced primarily by a change in shape from the very nearly Gaussian shape at low rf level to an almost Lorentzian shape after the narrowing. The integrated widths (that is, the total area of the absorption curve divided by the peak height) have also been calculated. The results are given in Table I.

Since the effect of the wings is more important for the Lorentzian line than for the Gaussian, any systematic errors in area determination are likely to make the changes in integrated widths even less than shown in Table I. After the shape change has taken place, there is no evidence of further decrease in δH. Beyond the range of H_1 plotted, the line width will presumably begin to rise again as H_1 becomes comparable with local fields. Whether one wishes to call the effect a narrowing of the line is largely a matter of taste. It is certainly true that the line width does not increase in the region $S=1$, as predicted by the simple saturation theories.

No attempt has been made to relate the details of the line narrowing to the Tomita theory. In the range of H_1 covered, Tomita uses an interpolation formula to connect δH for the unsaturated line to the expression for δH obtaining at large H_1, that is, where $\gamma H_1 > 1/T_2$. This interpolation formula is not expected to give the details of the shape change or quantitative values for the decrease in δH.

The Li data at 215°K provide an interesting further qualitative verification of Tomita's ideas. These data were originally taken in order to experimentally determine the effect of T_1 on the level at which the narrowing occurs. T_1 changes from 0.540 sec at 77°K to 0.190 sec at 215°K. 215°K was chosen because it is the maximum temperature at which the line width remains unaffected by motional narrowing.[18] What is observed is that the forced nutational narrowing does not occur at all. Instead, there is a small broadening over the range of the data.

TABLE I. Integrated line widths (in gauss) in lithium and aluminum.

	$S\ll 1$	$S\cong 1$
Li	7.5±0.5	6.5±0.4
Al	8.4±0.4	7.3±0.4

The characteristic frequency of the nuclear motion caused by self-diffusion can be written

$$\phi_0 = 1/\tau_c = 12D/a^2, \tag{2}$$

where τ_c is the correlation time of the nuclear motion, D is the coefficient of self-diffusion, and a is the lattice constant. At 215°K, using the experimental value of D,[11] ϕ_0 is 70 sec^{-1} in Li. The value of $1/T_1$ is 5.3 sec^{-1}. Thus, the criterion for forced nutational narrowing in Eq. (1) involves the motional ϕ_0 rather than $1/T_1$, and we would not expect narrowing until the value of H_1 is such that $S=13$. Tomita shows that, in this case, we expect the onset of some saturational broadening at $S=1$, and this is indeed observed. A quantitative comparison of the broadening with the Tomita theory is probably not useful because of the rapid field modulation used. The Halbach[15] solution for the case of a spin system obeying the Bloch equations predicts less broadening upon saturation when the modulation frequency is rapid compared to $1/T_1$ than for slow modulation. Observations on the Li resonance at room temperature, where the line is motionally narrowed but T_1 is not equal to T_2,[11] were made at modulation frequencies of 47 and 8 cy/sec. (T_1 is 0.140 sec.) The line did broaden much more slowly upon going into the saturation region with the 47-cy/sec modulation, and the difference between the observations with the two modulation frequencies agrees fairly well quantitatively with the Halbach theory. It should be noted that while $\omega_m > 1/T_1$ for the 77°K Li data in Fig. 1, the condition $\omega_m < 1/T_1$ obtained for Redfield's measurements on Al. There appears to be little effect of the modulation frequency on the narrowing and shape change for the Li 77°K data. At least, the behavior in Li agrees very well with Redfield's observations in Al.

EXPERIMENTAL DATA ON CaF_2

Experimental values of δH for the F^{19} resonance in CaF_2 as a function of H_1 are shown, for two crystal orientations, in Fig. 2. The H_1 level was calibrated by a search coil measurement at the position of the CaF_2 sample in the Varian spectrometer probe. The value of H_1 at which $S=1$ for the two crystal orientations is indicated. The point is not the same for the two orientations for two reasons: (1) $g(\nu_0)$ is different for the two orientations, and (2) T_1 is also different. T_1 was measured to be 40 sec for H_0 along the [100] direction through the crystal and 50 sec for H_0 along [110]. These T_1 data were obtained in the following way. With H_1 set in the region of appreciable saturation, the dc field was set at the position of maximum derivative signal. The field was then flipped off resonance for a specified period of time, then flipped back on and the magnetization sampled quickly, before the rf field

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could appreciably resaturate the resonance. The amount of recovery of magnetization as a function of the time off resonance is used to find the relaxation time, T_1. The different values for different crystal orientation are not unexpected, since the relaxation process is limited by spin diffusion to the residual paramagnetic impurities, and the nuclear dipolar coupling varies with direction through the lattice.

The upper limit on the range of H_1 is dictated by the available spectrometer power. It was not thought fruitful to build in more rf amplification, however, because of the difficulty of obtaining a pure χ'' signal in the region of heavy saturation.

The line narrowing is again observed and is accompanied by a change in the line shape. The nonsaturated line shapes agree with the careful measurements of Bruce.[19] In the [110] crystal orientation, the line is nearly Gaussian at low rf, while for [100], the line is more nearly square. After the narrowing, however, for both orientations the line is nearly Lorentzian in shape, particularly for the [110] orientation. Absorption line derivatives at low and high rf level are shown in Fig. 3. In Fig. 2 it will be observed that the line widths for the two orientations appear to be approaching one another at the highest rf level.

With the 47-cy/sec field modulation, the modulation was very rapid compared to T_1. As mentioned previously, in this situation one may in general expect some distortion of the line derivative curve upon passing into the saturation region. Actually, for CaF_2 neither line width nor shape changed until the narrowing, at which point one is already well into the saturation region. Interpretation of exact values of line widths at the highest rf levels is, however, complicated by the necessity of the "fast" modulation.

The forced nutational narrowing takes place at values of H_1 such that $S \cong 100$ in CaF_2, whereas in Li the narrowing is well developed at $S \cong 1$. Equation (1) cannot be expected to apply to a system such as F^{19} in CaF_2, where the spin-lattice relaxation is by spin diffusion from paramagnetic impurities. The interpretation of the quantity ϕ_0 is ambiguous. In the first place, there is not a well-defined single spin-lattice transition probability, $1/T_1$, for each nucleus. Moreover, the spin-lattice relaxation involves the dipolar interactions responsible for the line width, and the method by which Tomita develops the criterion expressed in Eq. (1) does not cover this case.

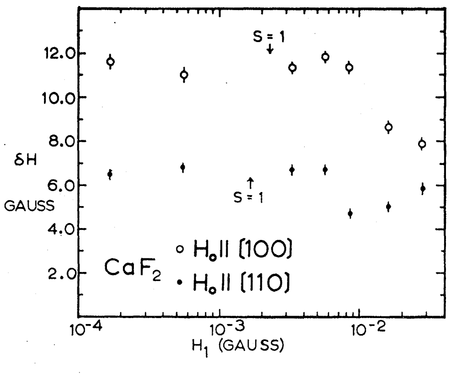

FIG. 2. The peak-to-peak absorption derivative line width, δH, is shown as a function of H_1 for a single crystal of CaF_2 at room temperature. Data taken at two crystal orientations are given. $S=\frac{1}{2}\gamma^2H_1^2T_1g(\nu_0)$.

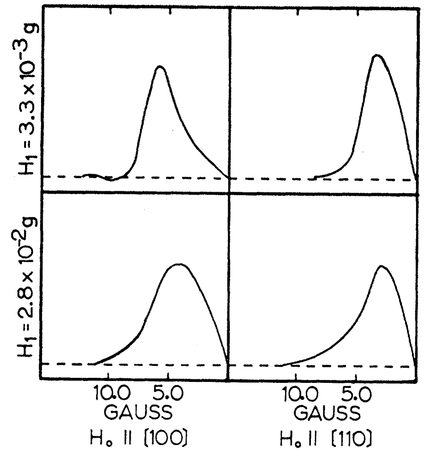

FIG. 3. Reproductions of half of the experimental derivative curves taken in CaF_2 at the two crystal orientations used are given for two values of H_1. In the original curves, the noise swath was about twice the width of the line drawn in the figure for the low H_1 setting, and about equal to the width of the line for the high H_1 setting. Peak amplitudes of the curves were adjusted to approximately the same value for the purposes of shape comparison.

SUMMARY

The measurements of line width and shape as a function of H_1 in Li at 77°K and Redfield's measurements in Al show that the forced nutational line narrowing sets in when $\gamma H_1 \gtrsim [(1/T_2)\phi_0]^{\frac{1}{2}}$, in qualitative agreement with the results of Tomita's theoretical treatment, where for the metals $\phi_0 = 1/T_1$. The so-called narrowing results primarily from a change in the line shape from the unsaturated shape determined by the nuclear dipolar interactions to a nearly Lorentzian shape in the high rf field region. The measurements in lithium at 215°K, where the motional frequency ϕ_0 is determined by diffusional motion of the nuclei rather than by the electron-induced relaxation processes, show a broadening rather than a narrowing in the same range of H_1. The lack of the narrowing again bears out qualitatively the Tomita relation given as Eq. (1). This relation would predict the narrowing to occur at a much higher value of H_1 because of the high value of ϕ_0. The competing saturational broadening tendency wins out in the region $S \cong 1$.

The line-narrowing and change to Lorentzian line shape are also observed for the F^{19} resonance in CaF_2,

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[19] C. R. Bruce, Phys. Rev. **107**, 43 (1957).

but at higher H_1 levels relative to the condition $S=1$ than is the case in the metals. The spin-lattice relaxation process is limited by spin diffusion to paramagnetic impurities, and the situation does not correspond to any of the cases treated by Tomita.

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X-Ray Diffraction and Magnetic Measurements of the Fe-Cr Spinels[*]

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X-ray diffraction intensity measurements and magnetic moment measurements were made on the spinel system $\text{FeFe}_{2-x}\text{Cr}_x\text{O}_4$, $0\leq x\leq 2$, for the purpose of finding structural details in this system which were unknown. The x-ray measurements covered the entire composition range, and the magnetic measurements covered the range from $x=0$ to $x=1.2$. From the x-ray measurements the oxygen parameter of each sample was deduced. These parameters indicated inverse spinels for low values of x, partially inverse spinels for intermediate values of x, and normal spinels for $x=1.3$ to $x=2$.

The magnetic measurements indicated inverse spinels for $x=0$ to $x=0.3$. It was inferred from the magnetic measurements that the spins of cations on the B sites are not all parallel, at least for large x and probably for $x>0.5$. Hence, the arrangement of cations on the A and B sites for a spinel in this composition range could not be deduced from its saturation magnetic moment. Estimates of the relative strengths of the magnetic interactions in various composition ranges and a prediction of the variation in saturation magnetic moment with composition in the range $x=1.3$ to $x=2$ were made.

I. INTRODUCTION

THIS paper deals with an investigation of the system $\text{Fe}^{2+}(\text{Fe}_{2-x}\text{Cr}_x)^{3+}\text{O}_4$, $0\leq x\leq 2$. These compounds, known as the Fe-Cr spinels, were synthesized by Yearian *et al.*,[1] and their graph of lattice parameter a *vs* the composition variable x is reproduced in Fig. 1. Recently Francombe[2] has measured the lattice parameters of the Fe-Cr spinels from room temperature down to −183°C, and although his results at room temperature differ slightly from those given in Fig. 1, the general form of the variation of lattice parameter with composition is the same. In order to discuss the unusual features of this graph and to outline the nature of this research, a brief description of the spinel structure will be given.

The general formula of an oxide spinel is $XY_2\text{O}_4$. In the 2-3 spinel class, to which the Fe-Cr spinels belong, X is divalent and Y is trivalent. As a first approximation the spinel structure can be described as a face-centered cubic (fcc) lattice of oxygen ions with cations located in certain of the interstices. This lattice contains tetrahedral and octahedral interstices with four and six oxygen ions, respectively, as nearest neighbors. For simplicity, these interstices are commonly called A and B sites, respectively. There are 64 A sites and 32 B sites in the unit cell although only 8 A sites and 16 B sites are occupied. If the occupied A sites contain only divalent ions, the cation arrangement is called normal whereas, if they contain only trivalent ions, it is called inverse. Cation arrangements intermediate between these extremes are also possible. The approximation in this description of the spinel structure is that the oxygen lattice is not, in general, strictly fcc, although the spinel structure as a whole is fcc. In order to specify accurately the positions of the oxygen ions in the unit cell, an oxygen parameter u is used ($u=\frac{1}{4}+\delta$, where δ is the ratio of the distance between the center and a corner of a filled tetrahedron to the body diagonal of the unit cell). The positions of all ions in the unit cell of a spinel can be specified if the lattice parameter, oxygen parameter, and cation arrangement are known.

Yearian *et al.*[1] interpreted the unusual form of the lattice parameter graph in Fig. 1 to be the result of the transition from the inverse cation arrangement of

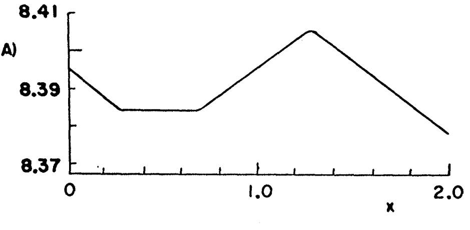

FIG. 1. Lattice parameters of the Fe-Cr spinels.

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