Diffusion Narrowing of Nuclear Magnetic Resonance Linewidth of F^{19} in $CaF_2:Sm^{2+}$

WM. J. VEIGELE AND A. W. BEVAN, JR.
Martin Company, Aerospace Division of Martin-Marietta Corporation, Denver, Colorado
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Nuclear magnetic resonance linewidths of F^{19} in a synthetic $CaF_2:Sm^{2+}$ single crystal and natural CaF_2 single crystals have been measured over a temperature range from 88 to 668°K and over a range of H_1 from 2.0 to 29 mG. Up to temperatures of about 400°K results are in agreement with existing theories of saturational narrowing. At higher temperatures the line narrowed in the samarium-doped crystal but not in the natural crystals. This narrowing was attributed to a decrease of the fluorine dipole interaction due to fluorine interstitial diffusion. An activation energy $E=0.26$ eV was calculated.

I. INTRODUCTION

THE fluorine nuclear magnetic resonance (NMR) in single crystals of calcium fluoride has been studied previously by continuous wave and transient methods at room and low temperature.[1] The experimental work reported in this paper is on the high-temperature dependence of the F^{19} linewidth. Additional measurements of linewidth at low temperatures and for different values of H_1 such that $S=\gamma^2H_1^2T_1T_2>1$ are also reported.

II. EXPERIMENTAL APPARATUS

A Varian wide line NMR spectrometer operating at about 16.2 Mc/sec and associated 12-in. electromagnet at a field of about 4.04 kG were used. The temperature was controlled with a Varian variable temperature accessory and was monitored with a copper-constantan thermocouple. The field was measured with a Varian F-8 fluxmeter, using protons, whose frequency was read with a H-P 524C counter. The lines recorded were first derivatives of absorption signals. The modulation was at 80 cps and one G amplitude. H_0 was scanned at 1 G/min. All measurements were made with H_0 parallel to [100]. The amplitude of H_1 was measured with a small coil in the rf probe.

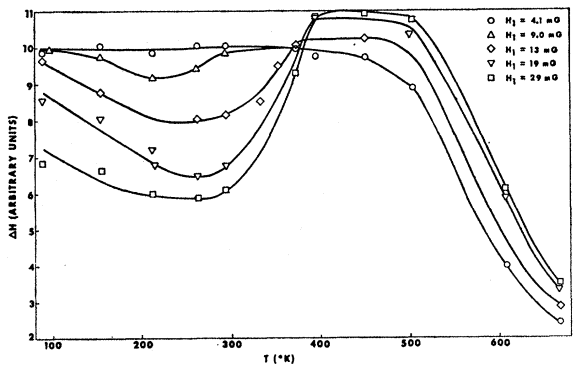

FIG. 1. Linewidth of F^{19} in $CaF_2:Sm^{2+}$ single crystal versus temperature at different H_1.

[1] I. Solomon and J. Ezratty, Phys. Rev. **127**, 78 (1962); W. I. Goldburg, *ibid.* **128**, 1554 (1962), and references in these papers.

III. CRYSTAL SAMPLES

Three samples were used: A natural fluorite colorless crystal, a natural fluorite medium-dark purple colored crystal, and a synthetic CaF_2 crystal doped with 0.05% Sm^{2+}, obtained from Semi-Elements Company, Saxonburg, Pennsylvania. Crystals of CaF_2 doped with Sm^{2+} are known to contain[2] about 20% Sm^{2+} and 80% Sm^{3+}. The purple crystal bleached to a pink color during the high-temperature measurements.

IV. EXPERIMENT AND RESULTS

NMR linewidths of the F^{19} nucleus in the three crystals were obtained over a temperature range from 88 to 668°K and for H_1 from 2.0 to 29 mG and are shown in Figs. 1 and 2. The linewidths are in arbitrary units. At low H_1 the linewidths for all crystals agreed, within experimental error, with those of Bruce.[3] In Fig. 3 are shown line shapes for the Sm-doped crystal at different T and H_1.

For temperatures below about 400°K the results, for all crystals, are in agreement with theories of saturational narrowing of Tomita[4] and Redfield.[5]

Above 400°K the line in the Sm-doped crystal nar-

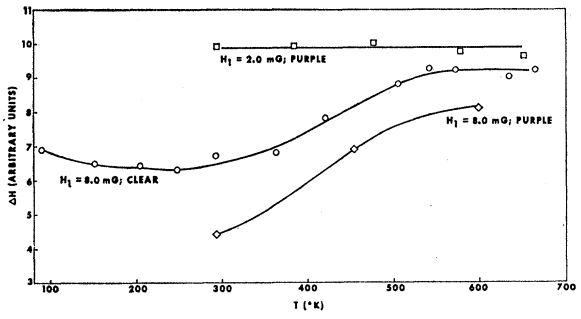

FIG. 2. Linewidth of F^{19} in natural CaF_2 single crystals versus temperature at different H_1. Linewidths are arbitrary for each curve so that placement of one curve relative to another on this figure is arbitrary.

[2] W. Kaiser, C. G. B. Garrett, and D. L. Wood, Phys. Rev. **123**, 766 (1961).
[3] C. R. Bruce, Phys. Rev. **107**, 43 (1957).
[4] K. Tomita, Progr. Theoret. Phys. (Kyoto) **19**, 541 (1958).
[5] A. G. Redfield, Phys. Rev. **98**, 1787 (1955).

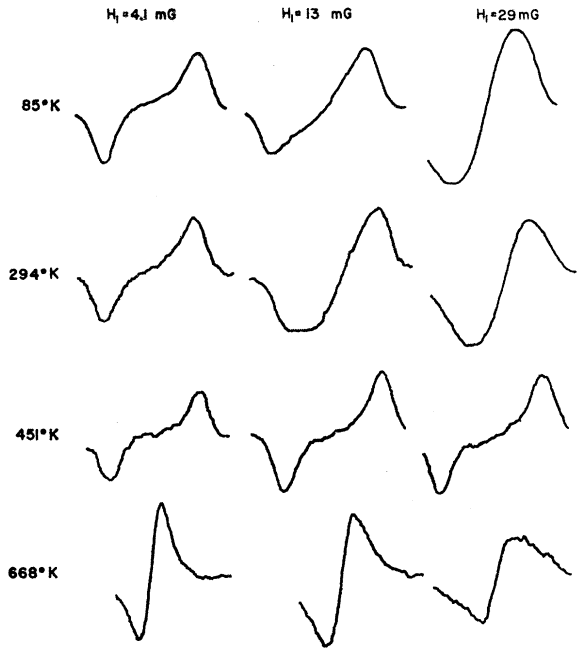

FIG. 3. Line shapes of F^{19} in CaF_2:Sm^{2+} single crystal at different T and H_1.

rowed. This was not observed in the natural crystals.

Although it appears the Sm is responsible for the narrowing, it is not through a change in the static dipole ($\mathbf{I}\cdot\mathbf{S}$) interaction because the linewidth of the synthetic and natural crystals are the same at room temperature indicating that the ($\mathbf{I}\cdot\mathbf{S}$) contribution is small. The Sm^{3+} probably caused fluorine interstitials. O'Connor and Bostick[6] have shown that Sm^{3+} is charge compensated by an interstitial F^- ion in one of the vacant octahedral holes surrounding a cation site. The high-temperature F^{19} NMR line narrowing is thought to be due to a decrease in the nuclear dipole contribution to the linewidth caused by interstitial diffusion averaging.

For CaF_2:Sm we plotted $\ln\Delta H$ against $(1/kT)$ from the $H_1=4.1$ mG curve and from the slope in the high-temperature region calculated an activation energy $E=0.26$ eV. This is of the order for interstitial diffusion. The accuracy of this calculation could be improved if observations at higher temperature were available.

ACKNOWLEDGMENTS

We wish to thank Dr. W. H. Tanttila for helpful discussions during the experiment.

[6] J. R. O'Connor and H. A. Bostick, J. Appl. Phys. **33**, 1868 (1962).

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Hyperfine Structure of Erbium-169*

WALTER M. DOYLE† AND RICHARD MARRUS
Lawrence Radiation Laboratory and Department of Physics, University of California, Berkeley, California
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The hyperfine structure of radioactive Er^{169} ($T_{1/2}=9.4$ days) has been studied in the $^3H_6$ electronic ground state by the atomic-beam magnetic-resonance method. The apparatus used was of sufficient accuracy to measure the nuclear dipole moment directly through its interaction with the external magnetic field. The results are $A=725.46(31)$ Mc/sec, $g_J=-1.16381(5)$, and $g_I=+5.55(27)\times10^{-4}$, where A is the magnetic dipole interaction constant and the electronic and nuclear g factors, g_J and g_I, are given in units of Bohr magnetons. The nuclear magnetic moment inferred from g_I and corrected for diamagnetic shielding is $\mu_I=+0.513(25)$ nm. This value of μ_I is consistent with that obtained from A using the $\langle 1/r^3\rangle$ value given by Lindgren.

INTRODUCTION

ABOUT thirty-five nuclear moments in the rare-earth region have been determined from paramagnetic-resonance and atomic-beam data. Because of the paucity of direct information about the moments, it has been necessary in most cases to infer their values from the measured interaction constants by means of theoretical calculations involving considerable uncertainty. Much of this uncertainty arises from the sensitivity of $\langle 1/r^3\rangle$ to the form of the electronic wave function. In order to obtain information concerning the $\langle 1/r^3\rangle$ values we have undertaken to measure, by atomic-beam magnetic resonance, the hyperfine-structure constant A and the magnetic moment μ_I of Er^{169}.

EXPERIMENTAL METHOD AND RESULTS

Prior work on erbium-169 had determined the ground-state spin ($I=\frac{1}{2}$) and the electronic angular momentum ($J=6$).[1] The hyperfine structure of such a

* This work was done under the auspices of the U. S. Atomic Energy Commission.
† Present address: Hughes Aircraft Corporation, Culver City, California.

[1] A. Y. Cabezas, I. Lindgren, and R. Marrus, Phys. Rev. **122**, 1796 (1961).