Measurement of the Fluorine Chemical-Shift Tensor in MgF_2†

L. M. Stacey and R. W. Vaughan
Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91109

and

D. D. Elleman
Jet Propulsion Laboratory, Pasadena, California 91103

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The components of the fluorine chemical-shift tensor in MgF_2 have been measured using the recently developed multiple-pulse NMR techniques. Relative to HF the three principal values of the chemical-shift tensor are -26, -11, and $+4$ ppm.

Multiple-pulse NMR techniques have recently been developed by Waugh and co-workers,[1-3] which furnish a means of reducing the dipolar broadening in solid-state NMR spectra and thus allow measurement of NMR parameters which are much smaller than the dipolar broadening. One such quantity of particular importance is the chemical shift. Numerous efforts have been made in the past to measure the components of the chemical-shift tensor because of the information they contain on the nature of the electronic structure, or bonding, within a solid or molecule. The majority of such studies have involved the use of either the field dependency of the line or its asymmetry in polycrystalline samples[4] or measurements in liquid-crystalline solvents.[5] None of these techniques are capable of yielding the full tensor, and most are prone to large experimental errors. Single-crystal studies capable of determining the full tensor have been performed only once for each of three nuclei: on ^{13}C in the magnetically dilute system[6] $CaCO_3$ and for two heavier nuclei with larger chemical shifts,[7,8] ^{207}Pb and ^{125}Te. We wish to report here the first direct measurement of the components of the fluorine chemical-shift tensor.

Magnesium fluoride was chosen for this initial study because (1) its crystal structure is such that one predicts that the anisotropy in the chemical shift could manifest itself as a splitting of the resonance line at certain orientations in addition to a resonance shift; (2) the nature of the electronic bonding within this essentially ionic solid is simple enough to allow detailed theoretical calculations; and (3) preliminary measurements on powder samples indicated the magnitude of the anisotropy to be small and the experiment could, thus, serve to demonstrate the capabilities of the multiple-pulse technique for resolving small splittings.

The crystal structure of MgF_2 is illustrated in Fig. 1. The crystal structure is tetragonal,[9] but the fluorine-site symmetry is C_{2v}, and there are two geometrically different, although chemically equivalent, fluorine sites (I and II in Fig. 1). The main symmetry axes of the two fluorine sites fall along the [110] and [1$\bar{1}$0] crystallographic axes, and thus when the magnetic field is parallel to a [110] axis, half of the fluoride ions will have their major symmetry axes parallel to the field and half will have their major symmetry axes perpendicular to the field. This results in two resonance peaks in the NMR spectrum taken at this orientation (top spectrum in Fig. 2) with the multiple-pulse technique. The separation between these peaks is a direct measure of the difference between two of the principal elements of the chemical-shift tensor. Figure 2 illustrates the changes in the NMR spectra as the crystal is rotated with the magnetic field in the (001) plane from the [110] to the [100] axis. The splitting between the two peaks follows the expected sine

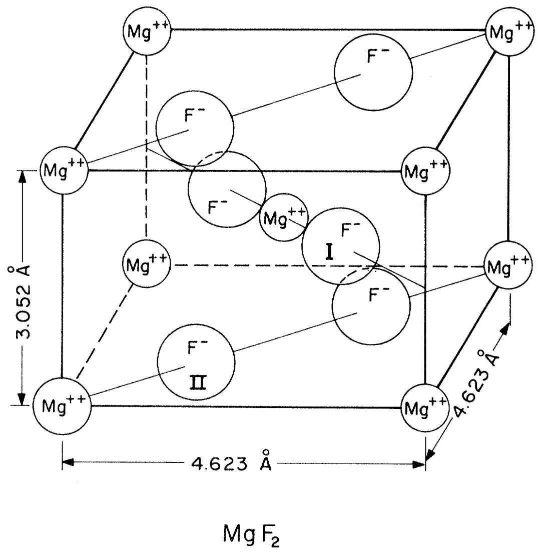

FIG. 1. Crystal structure of MgF_2.

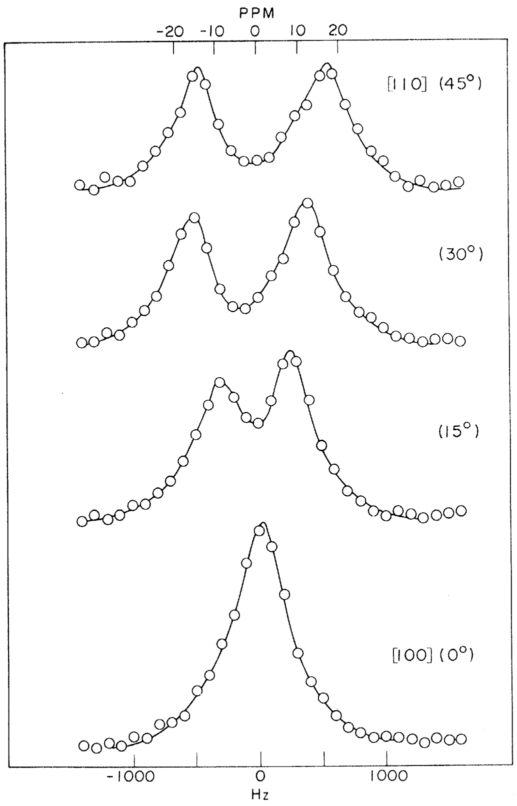

FIG. 2. Multiple-pulse spectra of a single-crystal sample of MgF_2 with the magnetic field at several orientations in the [001] plane. The angular values are the angle between the field direction and the [100] crystal axis. The abscissa at the top, in parts per million, has been corrected for the $\sqrt{3}$ scaling factor while the bottom scale corresponds to uncorrected experimental frequencies.

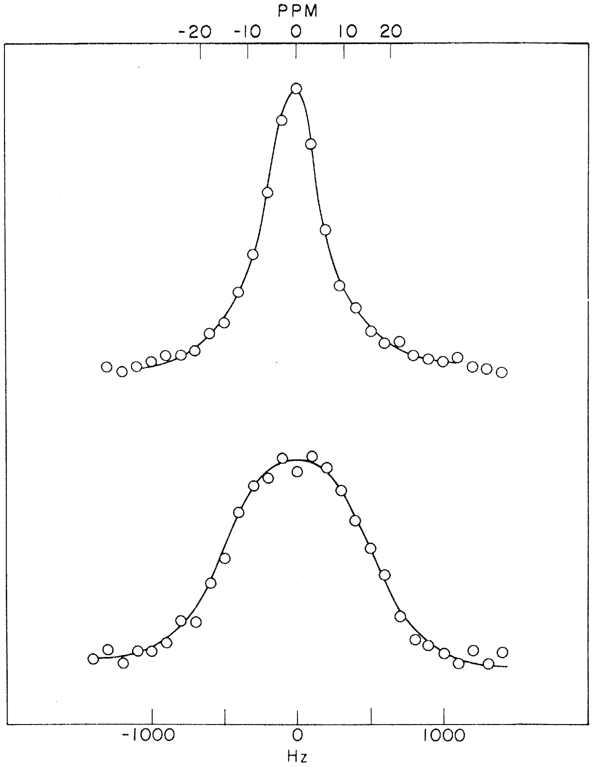

FIG. 3. Multiple-pulse NMR spectra of MgF_2. The top spectrum comes from a single crystal with the magnetic field oriented parallel to the [001] crystal axis, and the bottom spectrum from a polycrystalline powder. The scale at the top of the figure, ppm, has been corrected for the chemical-shift scaling factor $\sqrt{3}$ while the bottom abscissa indicates the experimental frequencies.

function going to zero on the [100] axis, at which point the fluorine sites appear equivalent. With the magnetic field along the [001] axis, the additional information to determine the third principal element of the chemical-shift tensor can be obtained. Such a spectrum is illustrated in Fig. 3, along with a powder spectrum for comparison purposes.

The experimental measurements were performed using perfluorobenzene as a reference, and relative to this material the three principal components of the chemical-shift tensor in MgF_2 are +13, +28, and +43, ±1 ppm. Using chemical-shift values reported for C_6F_6 and HF,[10] the values can be computed relative to the fluorine shift in HF and are −26, −11, and +4 ppm. One principal value of the MgF_2 chemical shift is thus actually slightly diamagnetically shielded relative to the strongly diamagnetically shielded HF.

Comparison with HF allows an estimate of the absolute chemical shift in MgF_2 since the chemical shift in HF has been estimated by using calculated values of the diamagnetic term for the fluoride ion and the fluorine atom together with experimental data on spin-rotation interaction constants.[11,12] Thus, the total value of the principal values for the fluorine chemical-shift tensor can be estimated by adding a value of +425 ppm [12] to the above three values relative to HF.

The ionic nature of the bonding in MgF_2 makes a detailed calculation of the chemical-shift tensor feasible, and this is being done at this time using essentially the technique of Ikenberry and Das,[13] but generalized to noncubic symmetry. The results of this calculation and additional experimental results on the alkaline-earth fluorides will be published elsewhere.

The single crystal of MgF_2 was obtained from Harshaw and orientated with standard x-ray techniques. The spectrometer operated at 56.4 MHz and utilized a four-pulse cycle[3] with a total cycle time of 36 μsec. C_6F_6, SrF_2, and CaF_2 were used to tune the spectrometer and check the chemical-shift scaling factor. The linewidths of polycrystalline CaF_2 taken at the same time as the MgF_2 data, 210-230 Hz, can be used to estimate the instrumental resolution.

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Generality of the Singular Diameter of the Liquid-Vapor Coexistence Curve[*]

N. D. Mermin[†] and J. J. Rehr[‡]
Istituto di Fisica "G. Marconi," Università di Roma, Roma, Italy

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It is argued that except in special cases the diameter of the liquid-vapor coexistence curve should have a temperature derivative at least as singular as the constant-volume specific heat. No assumptions are made about the equation of state near the critical point other than the hypothesis of Griffiths and Wheeler that the only direction in the μ-T plane "singled out by the nature of the phase transition itself is a direction parallel to the coexistence curve."

Green, Cooper, and Levelt Sengers[1] have proposed a generalization of the parametric equation of state of Schofield[2] which, when combined with a suggestion of Griffiths and Wheeler,[3] implies in general that the derivative of the coexistence-curve diameter, $d\rho_d(T)/dT = (d/dT)\frac{1}{2}[\rho_L(T) + \rho_V(T)]$, is at least as singular as the constant-volume specific heat.[4] We wish to point out that this conclusion is independent of the equation of state proposed in Ref. 1, following from the Griffiths-Wheeler hypothesis alone.

We start with an exact equation for the constant-volume specific heat in the two-phase region:

$$C_V(\rho, T) = T[\dot{s}_d + \dot{\mu}\dot{\rho}_d + \ddot{\mu}(\rho_d - \rho)], \tag{1}$$

where s_d is the entropy-density diameter, $s_d = \frac{1}{2}(s_L + s_V)$, $\mu(T)$ gives the coexistence curve in the μ-T plane, and a dot denotes temperature differentiation. It can be shown by a straightforward extension of Fisher's proof[5] of the Rushbrooke inequality that the specific-heat singularity in the two-phase region has the same strength whether the critical point is approached along the critical isochore or along the diameter.[6] Thus,

$$C_V(\rho_c, T) \approx C_V(\rho_d(T), T) = T(\dot{s}_d + \dot{\mu}\dot{\rho}_d), \tag{2}$$

where by $a \approx b$ we mean that a/b approaches a finite nonzero limit as $T \to T_c$.

Now Griffiths and Wheeler[3] have suggested that in considering the pressure as a function of μ and T near the critical point, the only significant direction in the μ-T plane for systems lacking special symmetries is that of the coexistence curve. Suppose then that we adopt variables $x(\mu, T)$ and $y(\mu, T)$ that are regular functions of μ and T, such that lines of constant y intersect the coexistence curve at nonzero angles, and the coexistence curve itself is given by $x = x_c$ (so that lines of constant x are "asymptotically parallel to the coexistence curve"). If we differentiate