energy of the order of 1 ev or a little less per vacancy pair would likely be released when a vacancy cluster disappears into the perfect lattice. As the number of vacancy pairs remaining at 250°C in one cc of crystal irradiated with 1.0×10^{16} protons/cm^2 is about 5×10^{18}, one can estimate that about 0.2 cal or a little less would be evolved from this crystal in the temperature range, 250–400°C. The corresponding observed value from the stored-energy measurements[3] is about 0.6 cal. The agreement is rather poor and this discrepancy may possibly be due to energy release associated with the elimination of strains from a crystal.

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F^{19} Nuclear Magnetic Resonance Line Shapes in CaF_2†

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The F^{19} magnetic resonances have been measured in CaF_2 with the magnetic field along the [100], [110], and [111] crystal directions and these data are compared with the data of Pake and Purcell. Calculations of the second and fourth moments for the new data further confirm the theory of Van Vleck on magnetic dipole interactions in solids since improved agreement with theory is obtained in the case of the magnetic field along the [111] crystal direction. Corrections of the moments for modulation broadening were small.

THE measurements by Pake and Purcell[1] of the F^{19} magnetic resonance line shapes confirmed the theory proposed by Van Vleck[2] on magnetic dipole interactions in solids. Their data were taken in the very early days of nuclear magnetic resonance before the effect of modulation on line shapes[3] was known and, though the second moments of the resonances with the magnetic field aligned along the [100] and [110] crystal directions were in excellent agreement with theory, the result for the [111] direction was in doubtful agreement. Therefore, the experiment has been repeated using the same fluorite crystal that was used by the early investigators but employing a spectrometer of later design and correcting for modulation broadening.

A conventional single-coil spectrometer with phase-sensitive detection was used. The magnetic field was that of a permanent magnet with an inhomogeneity of 0.01 gauss over the one-milliliter sample volume. The field was modulated at 30 cps. A crystal-controlled oscillator operating at 25.81 megacycles provided the radio-frequency field. The nuclear paramagnetic absorption signal was isolated by means of a bridge network.[4] The radio-frequency signal was preamplified by a cascode amplifier[5] and then amplified and demodulated by a National HRO-7 receiver. The derivative of the absorption curve obtained from the phase-sensitive detector[6] was displayed on a Leeds-Northrup recorder. The recorder chart drive was used to sweep the magnetic field through resonance thereby assuring a constant relationship between the magnetic field and chart abscissa. This relationship was determined by amplitude modulating the oscillator at a known audio-frequency and measuring the spacing between resonances arising from several of the side-band frequencies.

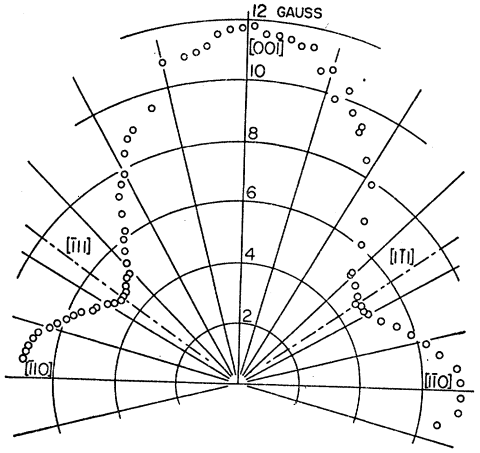

FIG. 1. F^{19} resonance width measured between points of maximum slope as a function of the magnetic field direction in a single CaF_2 crystal.

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A narrow proton resonance was used for this calibration. Thermal shielding of the magnet and the bridge with two-inch thick Fiberglas insulation allowed sweep times greater than 30 minutes without appreciable change in the bridge balance.

The crystal orientation in the magnetic field was ascertained by plotting the resonance width measured between points of maximum slope as a function of crystal rotation about a [110] crystal direction perpendicular to the magnetic field. Directions corresponding to the [100], [110], and [111] crystal directions could be aligned parallel to the magnetic field. Figure 1 shows the plot of line width *versus* crystal orientation. The line width increases rapidly as the magnetic field deviates from alignment along the [111] direction so that a small error in crystal orientation will cause appreciable error in the moments of the line shape relative to theoretical values. If one assumes that the minimum resonance width occurs with the [111] direction parallel to the magnetic field and assumes that the axis of rotation is a [110] direction perpendicular to the magnetic field, then the error in crystal orientation was less than two degrees.

The sets of line-shape data were taken under slightly different conditions though all parameters except crystal orientation were constant for each set. The radio-frequency field amplitude was below saturation levels for all data. The magnetic field was swept at 0.02 gauss/second and the modulation amplitude H_m was 0.43 gauss. Six consecutive resonances were taken for the field along each of the three directions of interest. The six curves were superimposed and reduced to a single mean curve by tracing, thereby integrating the noise. The resultant curve was then symmetrized by superimposing the two halves and tracing a mean curve. Figure 2 shows the data in the reduced form.

The second moments of the experimental curves were obtained by numerical evaluation of the integrals in Eq. (1).

$$\langle \Delta H^2 \rangle_{Av} = \int_{-\infty}^{\infty} \left(\frac{d\chi''}{d\Delta H} \right) (\Delta H)^3 \times d\Delta H \Big/ \left[3 \int_{-\infty}^{\infty} \left(\frac{d\chi''}{d\Delta H} \right) \Delta H d\Delta H \right], \quad (1)$$

where ΔH is the deviation of the magnetic field from H_0, the value it has at the center of the resonance, and $d\chi''/d\Delta H$ is obtained from the curves of Fig. 2. Correction of $\langle \Delta H^2 \rangle_{Av}$ for modulation broadening by Eq. (2),[3]

$$\langle \Delta H^2 \rangle_T = \langle \Delta H^2 \rangle_{Av} - \tfrac{1}{4} H_m^2, \quad (2)$$

gives the true second moment $\langle \Delta H^2 \rangle_T$. At the modulation amplitudes used by Pake and Purcell, and also by us for the data reported here, the modulation correction is negligible.

In Table I the data presented above and the data of Pake and Purcell are compared with theoretical values of the root mean second moments calculated by Van Vleck. The error was estimated under the assumption that the curves are in doubt by one-fourth of the noise amplitude and hence that the error increases with the resonance width. The numerical integrations of the second moments were checked using the Nordsieck mechanical differential analyzer at the University of Illinois. The $d\chi''/d\Delta H$ functions of Fig. 2 were fed into the analyzer which drew χ'' curves on an output table and produced values for the integrals of Eq. (1) on counters. A typical set of the χ'' curves in Fig. 3 clearly shows the change of line shape with crystal orientation and, in particular, the non-Gaussian character of the line shape.

The root mean second moment for the [111] direction of set 3 is not listed in Table I since the magnetic field was misaligned about 10 degrees off the [111] crystal direction. The root mean second moment for this field direction is 1.76±0.03 gauss which illustrates the importance of crystal orientation near the [111] direction.

In Table II the root mean fourth moments, which are calculated from the data in a manner similar to the second moments, are compared with theory. Again the correction for modulation broadening is small. The theoretical values were obtained from Eq. (24) of Van Vleck,[2] by considering only the 26 nearest neighbors of a simple-cubic lattice. The contribution of nuclei at

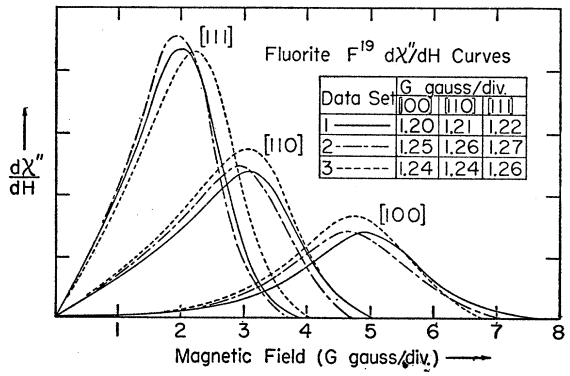

FIG. 2. Derivatives of F^{19} absorption lines in a single CaF_2 crystal with the magnetic field along the [100], [110], and [111] crystal directions.

TABLE I. Root mean second moments of the F^{19} absorption line in CaF_2 for the magnetic field H along the [100], [110], and [111] crystal directions.

Direction of H	$\langle \Delta\nu^2 \rangle^{\frac{1}{2}}$ in gauss				
	Data 1	Data 2	Data 3	Pake and Purcell[a]	Theory[b]
[100]	3.49±0.20	3.51±0.30	3.47±0.17	3.68±0.20	3.60
[110]	2.17±0.07	2.20±0.07	2.26±0.07	2.25±0.20	2.24
[111]	1.52±0.03	1.59±0.06	···	1.77±0.20	1.53

[a] See reference 1.
[b] See reference 2.

TABLE II. Root mean fourth moments of the F^{19} absorption line in CaF_2 for the magnetic field H along the [100], [110], and [111] crystal directions.

Direction of H	$\langle\Delta\nu^4\rangle^{\frac{1}{4}}$ in gauss			
	Data 1	Data 2	Data 3	Theory[a]
[100]	4.17±0.15	4.19±0.21	4.13±0.11	4.31
[110]	2.65±0.05	2.68±0.08	2.76±0.06	2.73
[111]	1.88±0.03	1.96±0.05	···	1.88

[a] See reference 3.

the remaining lattice sites is negligible relative to experimental error because Eq. (24) converges very rapidly with the separation of the interacting nuclei. From this calculation the ratio of the root mean fourth moment to the root mean second moment is 1.20, 1.22, and 1.23, respectively, for the magnetic field along the [100], [110], and [111] crystal directions, whereas Van Vleck gives 1.25 for the [100] direction. The ratio of experimental moments for each set of data corresponding to the [100] direction in Tables I and II is 1.19 which is in good agreement with the theoretical value 1.20 given here. Likewise the experimental and theoretical ratios are in excellent agreement for the [110] and [111] directions. However, this agreement is not surprising since the ratio is not a very sensitive criterion of line shape, varying only from 1.16 for a rectangular shape to 1.32 for a Gaussian shape, and since the second moments are in good agreement with theory.

In conclusion, the data presented here are in excellent agreement with theory. The spectrometer sensitivity allowed the comparison to be extended to fourth moments without appreciably increasing experimental errors due to loss of the wings of the resonance in noise. The new value for the second moment with the magnetic field along the [111] crystal direction is in better agreement with theory than are the corresponding data of Pake and Purcell.

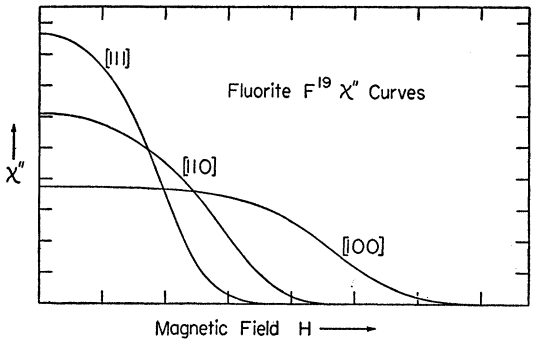

FIG. 3. F^{19} absorption lines in CaF_2 with the magnetic field along the [100], [110], and [111] crystal directions. These curves are obtained by integration of data set 2 in Fig. 2 and have the same abscissa.

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