Electron Spin Resonance of Neutral Hydrogen Atoms in SrF_2 and BaF_2

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The electron-spin-resonance spectra of SrF_2 and BaF_2, each containing neutral hydrogen atoms in interstitial sites, is investigated. In all cases, the electron-proton contact hyperfine interaction is resolved. Also resolved are the smaller superhyperfine interactions with the nuclei of the eight neighboring F^- ions. It is found that the magnitude of these interactions is very sensitive to the host lattice. In particular, the super-hyperfine interaction decreases by about a factor of two as one proceeds from smallest to largest lattice parameter. It is also found that the difference between the electron-proton interaction parameter B and the corresponding quantity for the free atom is positive, and decreases from 39.9 ± 0.1 Mc/sec for CaF_2 to about 4.1 ± 0.1 Mc/sec for BaF_2, at room temperature. We have also observed forbidden transitions corresponding to simultaneous flips of the electron and an associated fluorine nucleus, and we discuss the intensity of these in terms of the effective magnetic fields acting on the F^- sites.

INTRODUCTION

ABOUT two years ago, Hall and Schumacher[1] reported a detailed description of the electron spin resonance (esr) spectrum of neutral hydrogen atoms occupying interstitial positions in CaF_2. This spectrum was especially interesting because it displayed an extremely well-resolved magnetic superhyperfine interaction between the electron, belonging to the hydrogen atom, and the eight nearest-neighbor F^- nucleii. The resultant splitting is superposed on the well-known hyperfine splitting of the hydrogenic electron interacting with its own proton,[2] and is an order of magnitude smaller. We wish to report here on a set of similarly well-resolved spectra which we have observed with host crystals of SrF_2 and BaF_2 containing atomic hydrogen. Not unexpectedly, the superhyperfine interactions are very well resolved in these cases also.

EXPERIMENTAL DETAILS

Like CaF_2, the lattices of SrF_2 and BaF_2 can be visualized as a simple cubic array of F^- ions with every alternate body center occupied by the divalent ion. Samples prepared in the fashion already described[1] will possess $10^{18}-10^{19}$ H^- ions/cc on substitutional F^- sites. After x-irradiation at room temperature, the H^- ions are converted into neutral H atoms which lodge in readily available body-centered positions, surrounded by an eightfold coordinated array[3] of fluorine ions in

[1] J. L. Hall and R. T. Schumacher, Phys. Rev. **127**, 1892 (1962).

[2] G. Breit and I. I. Rabi, Phys. Rev. **38**, 2082 (1931).

[3] In work which has not yet been published, W. Hayes and co-workers have established that the hydrogen is present before irradiation as H^- ions on substitutional sites. The evidence consists of a very detailed study of the infrared absorption spectra arising from such localized centers. In this connection be it noted that it is important that the x-irradiation be carried out at room temperature. A low temperature irradiation may produce H atoms which are frozen on F^- sites. They will possess as nearest neighbors four Ca^{2+} ions arranged tetrahedrally. Since Ca^{2+} has no nuclear moment, the only magnetic superhyperfine interaction which is possible will involve the six next-nearest neighboring F^- ions arranged in octahedral symmetry. In fact, the esr spectrum arising from such a configuration has actually been observed and resolved by the Oxford group. W. Hayes (private communication).

cubal symmetry. In SrF_2, the separation between a hydrogen atom and any one of the adjacent fluorines (assuming that the lattice is undilated) is 2.52 Å while in BaF_2 this distance is 2.68 Å. Thus, in each of these crystals the separation is considerably larger than in CaF_2 where it is only 2.36 Å. With such a range of values, it appeared desirable to measure the various parameters associated with the esr spectrum in order to learn something regarding their dependence on nearest-neighbor distance.

Employing an X-band 100-kc/sec modulation spectrometer, we have examined the esr spectrum of the hydrogen atoms in SrF_2 and BaF_2 with the magnetic field H_0 oriented in the $\langle 100 \rangle$ direction and also in the $\langle 111 \rangle$ direction. From the data, we strove to deduce the value of the components of the axially symmetric superhyperfine interaction tensor $\mathbf{T}$, the value of the hyperfine interaction with the proton B, and the g factor. All these quantities enter into the spin Hamiltonian of the form:

$$H = g\beta \mathbf{H} \cdot \mathbf{S} + B \mathbf{I}_p \cdot \mathbf{S}$$
$$+ \sum_{\alpha=1}^{8} \mathbf{S} \cdot \mathbf{T} \cdot \mathbf{I}^\alpha - g_p\beta_N \mathbf{H} \cdot \mathbf{I}_p - g_F\beta_N \sum_{\alpha=1}^{8} \mathbf{H} \cdot \mathbf{I}^\alpha,$$

where the various terms, listed in order of decreasing magnitude, have the following meaning: the first term is the electronic Zeeman splitting, the second the electron-proton hyperfine interaction, the third the electron-fluorine superhyperfine interaction and the last two terms describe the interaction of the various nucleii with the externally applied magnetic field. The summation refers to the eight nearest-neighbor fluorine nuclei, labeled by α. We have been able to obtain all these parameters in the case of SrF_2. With BaF_2 the data are, as we shall see, somewhat less complete.

SrF_2

Figure 1 shows the spectrum obtained with our samples of SrF_2 and for comparison a spectrum recorded

with a sample of CaF_2 in a similar orientation. Both spectra were obtained at room temperature. Only one half of the full spectrum is displayed in the figure, viz., that belonging to the transition $m_I = -\frac{1}{2}$, $m_S = +\frac{1}{2} \rightleftharpoons m_I = -\frac{1}{2}$, $m_S = -\frac{1}{2}$, where m_I is the component of nuclear spin of the hydrogen atom and m_S that of the electron spin, both referred to the external field direction. Another nearly identical set of lines is to be found some 500 G below these, corresponding to transitions within a manifold of substates belonging to $m_I = +\frac{1}{2}$.

It is evident that the two spectra of Fig. 1 are very similar in all respects, and that the interpretation of the SrF_2 spectrum must follow exactly that of the CaF_2 which has already received ample attention elsewhere.[1] We will content ourselves here with a brief summary of the salient features.

The nine principal lines originating from these substates are the result of the superhyperfine interaction between the electron and the neighboring F^- nuclei which splits the single free-ion levels. For an *arbitrary* direction of the magnetic field H_0 there would be, in general, 81 lines. These arise because a pair of nuclei sharing a given body diagonal have the same energy in an external field, for similar spin states. The total number of states per body diagonal is three, and with four body diagonals making unequal angles with H_0 we get $3^4 = 81$ lines. With $H_0 \| \langle 100 \rangle$, however, all eight fluorine nuclei are magnetically equivalent, and the number of lines collapses to only nine, corresponding to the number of possible values of the algebraic sum of the components of the eight spin $\frac{1}{2}$ nuclei along the direction of the effective local field. Accordingly, the central and most intense line belongs to $m_F = 0$, while all adjacent lines have m_F differing by ± 1. The local field is, or course, only approximately parallel to H_0, and is determined precisely by the values of the two components $T_{\|}$ and $T_{\perp}$ of the axial interaction tensor **T**. These two components, are measured by determining the splitting for two directions of H_0, say $\| \langle 100 \rangle$ and $\| \langle 111 \rangle$. The latter direction actually gives *two* distinct splittings: seven lines coming from the six magnetically equivalent fluorines lying on axes making an angle of 71° with H_0, and fourteen more when these seven are each split into triplets by the remaining two fluorines at 0°. With SrF_2, in contrast to CaF_2, there is not an exact factor of two relation between these two slpittings, and all 21 lines are resolved. It has been shown[1] that subject to certain approximations which remain valid also in SrF_2, the parameters $T_{\|}$ and $T_{\perp}$ may be determined from the splitting ΔH by

$$(\Delta H)^2 = (g\beta)^{-1}[T_{\perp}^2 + (T_{\|}^2 - T_{\perp}^2) \cos^2\theta] \qquad (1)$$

where θ is the angle made by H_0 with the $\langle 111 \rangle$ direction. In Fig. 2 we plot $(\Delta H)^2$ versus $\cos^2\theta$ for three values of θ, and in Table I we list the values of the parameters derived from the intercepts of Fig. 2, using the best
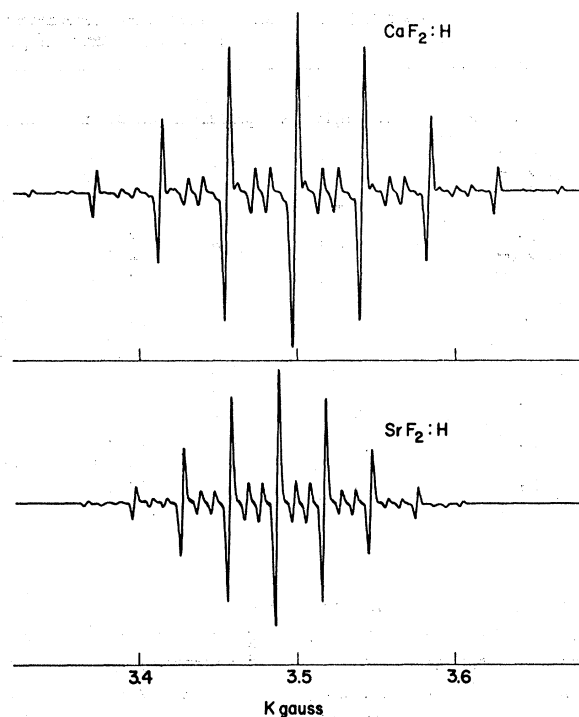

FIG. 1. High-field transitions in CaF_2:H and SrF_2:H for $H_0\langle 100 \rangle$. A similar set appears at fields some 500 G lower. The principal group of nine lines corresponds to $\Delta m_S = \pm 1$, $\Delta m_F = 0$. The "forbidden" doublets correspond to $\Delta m_F = \pm 1$.

fit. We list also the values of B and g obtained from the hyperfine splitting between the two groups. In computing B and g we have carefully determined the separation between the two lines corresponding to $m_F = 0$, and made use of the Breit-Rabi formula to obtain the final result. To achieve the maximum precision all magnetic field measurements were made with a proton resonance gaussmeter to 1 part in 10^5 or better.

In calculating the parameters B and g to the ultimate accuracy, it would be necessary to include certain second order corrections[1] arising from the fluorine hyperfine energy whose magnitude would cause a shift of ~ 0.25 Mc/sec in the position of the line $m_F = 0$.
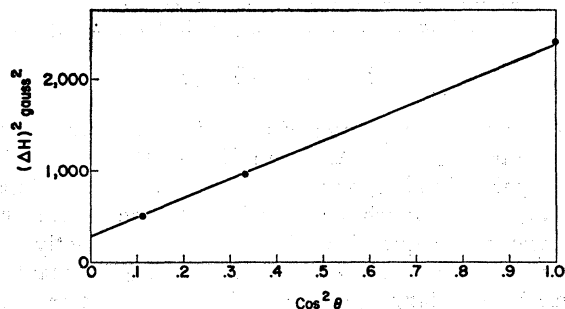

FIG. 2. Splitting of superhyperfine components versus $\cos^2\theta$, where θ is the angle between direction of H_0 and that of fluorine nuclei, with the H atom as origin.

TABLE I. Experimental values of esr parameters for hydrogen atoms in three host crystals. Values of g are given in terms of g_0, the value for the free H atom.

Sample	Lattice parameter, Å	T, °K	B Mc/sec	g/g_0	$T_{\parallel}$ Mc/sec	$T_{\perp}$ Mc/sec	$\Delta(100)$ Mc/sec	Reference
CaF$_2$:F Powder	5.451	300	1460.26 ±0.10	1.000106 ±0.000010	...	...	...	Hall and Schumacher[1]
CaF$_2$:H Single Crystal	5.451	77	...	1.00023 ±0.00003	173.826 ±0.300	69.025 ±0.300	115.1 ±0.1	Hall and Schumacher[1]
CaF$_2$:H Powder	5.451	300	1460.3 ± 0.1	1.00038 ±0.00003	...	...	...	Present work
CaF$_2$:H Powder	5.451	77	1465.0 ± 0.1	1.00031 ±0.00003	...	...	...	Present work
SrF$_2$ Single Crystal	5.86	300	1442.0 ± 0.2	1.00017 ±0.00003	133.0 ±0.3	46.0 ±0.3	85.5 ±0.1	Present work Present work
SrF$_2$ Powder	5.86	300	1443.6	1.00011 ±0.00003	...	...	...	Present work
BaF$_2$ Single Crystal	6.184	77	...	...	...	...	54.5 ±0.1	Present work
BaF$_2$ Single Crystal	6.184	300	1424.5 ± 0.1	1.00003 ±0.00003	...	...	55.6 ±0.1	Present work
BaF$_2$ Powder	6.184	77	1426.1 ± 0.1	1.00002 ±0.00003	...	...	...	Present work

This shift may, however, be smaller than the uncertainty which enters due to a slight misorientation of the crystal, and its inclusion would therefore appear to be pointless. To obtain even greater accuracy we have resorted to measurements on a powdered sample. The spectrum in this case consisted of just two lines, corresponding to the two proton orientations. An accurate determination of the position of these lines suffices to yield B and g. These parameters were calculated with the aid of Eqs. (25) and (26) of Ref. 1, which includes the second-order corrections referred to above, and the results are shown in Table I.

As previously mentioned, the main transitions in Fig. 1 correspond to the selection rule: $\Delta m_S = \pm 1$, $\Delta m_F = 0$. However, between each pair of lines are found also doublets, of lesser intensity. These are the "forbidden" transitions, corresponding to the selection rule $\Delta m_S = \pm 1, \Delta m_F = \pm 1$; viz., a flip of a fluorine nuclear spin simultaneously with an electron flip. It will be noticed that the strength of these transitions in SrF$_2$ is greater than for the corresponding set in CaF$_2$. This can be understood on the following grounds: The "forbidden" transitions occur because the effective field acting on the fluorine nuclei is made up of the external field plus a local field very much larger than H_0 and given by

$$\mathbf{H}_{\text{local}} = - \mathbf{S} \cdot \mathbf{T} / g_F \beta_N , \qquad (2)$$

where g_F is the g factor of the F^{19} nucleus, and β_N the nuclear magneton. Although $\mathbf{H}_{\text{local}} \gg \mathbf{H}_0$, it is in fact not parallel to $\mathbf{H}_0$, so that the direction of the total field, $\mathbf{H}_{\text{total}}$, along which we must imagine the fluorine spin states to be quantized, is not reversed exactly 180° by an electronic flip which reverses $\mathbf{H}_{\text{local}}$. In quantum-mechanical language, the initial fluorine state, characterized by quantum number m_F along $\mathbf{H}_{\text{total}}$ is not precisely orthogonal to the final state quantized along the new $\mathbf{H}_{\text{total}}$. We can make a quantitative estimate,

based on an expression by Clogston et al.,[4] of the relative probability R of the forbidden transitions. This probability is given by

$$R = \tan^2 \tfrac{1}{2} \{ \psi(m_S = +\tfrac{1}{2}) - \psi(m_S = -\tfrac{1}{2}) \} , \qquad (3)$$

where ψ is the angle between the direction of the external field $\mathbf{H}_0$ and the field, $\mathbf{H}_{\text{total}} = \mathbf{H}_0 + \mathbf{H}_{\text{local}}$, which is experienced by the fluorine nucleus. If $\mathbf{H}_{\text{local}}$ is decomposed into two orthogonal components $H_{\perp}$ and $H_{\parallel}$ where $H_{\parallel}$ is parallel to H_0 then ψ is given explicitly by

$$\psi = \tan^{-1}[-H_{\perp} m_S / (H_0 - H_{\parallel} m_S)], \qquad (4)$$

where $H_{\perp}$ and $H_{\parallel}$ are related to $T_{\perp}$ and $T_{\parallel}$ by

$$H_{\parallel} = (g_F \beta_N)^{-1} [T_{\perp} + (T_{\parallel} - T_{\perp}) \cos^2 \theta] \qquad (5)$$

$$H_{\perp} = (g_F \beta_N)^{-1} [(T_{\parallel} - T_{\perp}) \sin \theta \cos \theta]. \qquad (6)$$

Specializing these expressions for the case of $\mathbf{H}_0 \| \langle 100 \rangle$, we find that the value of $H_{\parallel}$ and $H_{\perp}$ are 26.0 kG and 12.4 kG, respectively, for CaF$_2$, and 19.2 kG and 10.3 kG for SrF$_2$. From Eq. (3) we find the ratio of two probabilities to be 2.1:1. Experimentally we find 2.2±0.1, which agrees reasonably well.

Another consequence of Eq. (3) is that the intensity ratios of the forbidden to the allowed transitions should be dependent on the externally applied field. In particular, for the present case, they should increase with field. This is borne out in our work; in the case of the low field lines (not shown in Fig. 1), the forbidden transitions are noticeably weaker.

BaF$_2$

Crystals of BaF$_2$ containing H atoms were prepared in a manner similar to those of SrF$_2$ and CaF$_2$. After x-irradiation at room temperature, they were examined

[4] A. M. Clogston, J. P. Gordon, V. Jaccarino, M. Peters, and L. R. Walker, Phys. Rev. 117, 1222 (1960).

by esr. We mention in passing that the concentration of hydrogen atoms, as measured by the intensity of the resonance, decreased markedly if the crystal was held for a few hours at room temperature. At 77°K, however, the atoms remained in their sites indefinitely. This is very different from the case of the SrF_2 and CaF_2 host lattices, where the spectrum could be observed even after the crystals had been stored for months at room temperasure. We ascribe this difference to the extreme openness of the BaF_2 lattice, which permits a considerable mobility to the H atoms, resulting ultimately in their diffusion out of the material or their recombination to form hydrogen molecules.

Figures 3 and 4 show the upper field portion of the spectra obtained with BaF_2:H for two different orientations. The spectra shown were obtained at 77°K. Except for the limitation mentioned above, nearly identical spectra were obtainable at room temperature, with no apparent broadening. The number of allowed transitions shown in Fig. 3 is only 7, but the theoretical number, 9, was easily observable with an appropriate increase in gain for the outer lines. It should be noted that the "forbidden" transitions are particularly pronounced, although it is still possible to distinguish them from the allowed ones. The strong intensity of the forbidden transitions, when compared to those in SrF_2, suggest a sharply reduced T tensor. This fact is immediately confirmed when comparing the over-all splitting in the two cases. Our measurements give for the splitting Δ between principal lines in the $\langle 100 \rangle$ spectrum the ratio $\Delta(BaF_2)/\Delta(SrF_2) = 0.63$. Because of the high intensity of the "forbidden" transitions we found it difficult to obtain reliable measurements of T_{11} and $T_\perp$ from the measurements in other orientations. Figure 4, which was obtained with $\mathbf{H}_0 \| \langle 111 \rangle$, illustrates the difficulty. Moreover the difficulty is compounded when we recall that the expression in Eq. (2) is based on the approximation that a quantization of fluorine
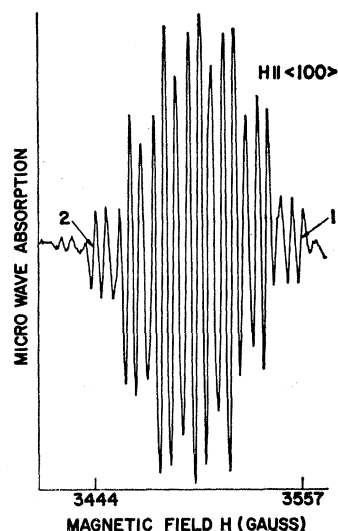
FIG. 4. High field transitions in BaF_2:H for $H_0\langle 111 \rangle$, $T = 77°K$. Note intensity of "forbidden" transitions. Between points 1 and 2 are shown 33 transitions, both allowed and "forbidden." The interval between 1 and 2 is fortuitously identical with that in Fig. 3.
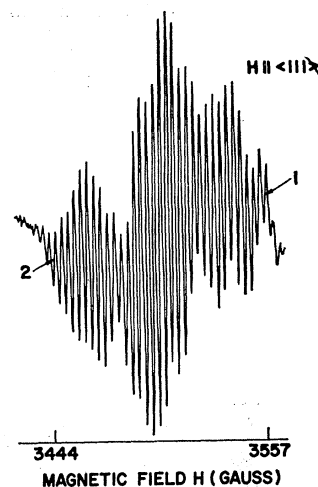
spin states along $\mathbf{H}_{local}$ is very nearly aequivalent to a true quantization along $\mathbf{H}_{total}$. This is certainly no longer the case. If we therefore content ourselves with a simple "scaling" of the values of T_{11} and $T_\perp$ by a factor 0.63, then we calculate from Eq. (3) that the relative intensity of the "forbidden" transitions in BaF_2 should be about 3.5 times as great as in SrF_2. Comparison of Fig. 1 and Fig. 3 shows that this is reasonably correct.

In order to obtain unambiguous values of B and g we have resorted in this case, too, to measurements on the powder. The values are listed in Table I. The second-order correction previously mentioned with SrF_2 was applied here too, and was estimated by "scaling" from $SrF._2$ We emphasize that the correction consists principally in a shift of the lines by $7T_\perp^2/\nu_0$, where ν_0 is the microwave frequency. In frequency units this amounts to only 0.7 Mc/sec out of 9.1 kMc/sec. In view of the size of this correction, any reasonable approximation of $T_\perp$ seems to be valid for the stated accuracy in Table I.

DISCUSSION OF RESULTS

It is immediately apparent from the numbers in Table I that the values of the parameters T_{11} and $T_\perp$ are substantially smaller for SrF_2 than for CaF_2 and presumably smallest of all for BaF_2. More important, however, the value of B, the hyperfine splitting constant, shows very clearly the effect of varying the lattice spacing. For BaF_2, the value of B, 1426 Mc/sec, is within 0.4% of the free-atom value of 1420 Mc/sec, and indicates how remarkably free the hydrogen atom really is with respect to perturbations by the crystal lattice. The trend of the g value also confirms this, giving a value closest to the free-atom value for BaF_2.

From the closeness of B and g to the free-ion values, it appears that the hydrogen atom is in a very lossely bound position and interacts but weakly with the lattice, on account of its uncharged state. It would be

FIG. 3. High-field transitions in BaF_2:H for $H_0\langle 100 \rangle$. The interval between points 1 and 2 includes only 7 of the possible 9 allowed transitions and 12 "forbidden" transitions. The values of H_0 at these points are indicated on axis $T = 77°K$
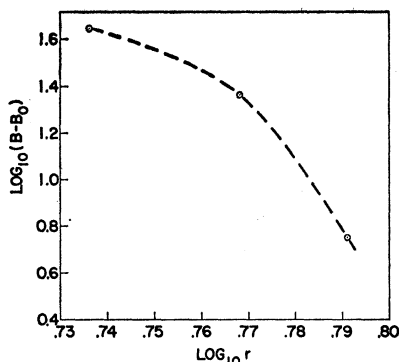
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FIG. 5. Logarithmic plot of the variation of $(B-B_0)$ versus r, where r is the lattice parameter, and $(B-B_0)$ is the deviation of the hyperfine splitting from the free atom value. The two outer points are based on measurements at $77°K$, while the middle point is from room-temperature measurements.

tempting to try an evaluation of B, g, T_{11}, and T_1 from first principles, using slightly modified free-hydrogen-atom wave functions. Hall and Schumacher have attempted this for CaF_2 assuming a purely ionic model for the F^- ions, and imposing only a simple modification of the hydrogen-atom wave function in order to satisfy the requirements of the Pauli principle. However, as their results have already shown, such a model, ignoring as it does other interactions with the crystalline surroundings (such as van der Waals forces and dielectric effects), is expected to give only $\sim30\%$ agreement with theory for the values of T_{11} and T_1, and a much poorer prediction for the departure of B from the free atom case. Therefore, regarding the variation of T_{11} and T_1 with increased lattice spacing, we can only point out that this is in the right direction; viz., both quantities decrease as the lattice expands. We can, however, make a somewhat more precise statement regarding the dependence of B on the distance r between the H atom and neighboring F^- ions. If we assume, as seems reasonable, that $(B-B_0)\sim1/r^n$, where B_0 is the free-atom value of 1420 Mc/sec, then a logarithmic plot of the data available in Table I should yield a straight line with slope n. Instead, we obtain Fig. 5. It is obvious from this that such a simple power law will not suffice, if r is taken as the natural lattice spacing. Viewed somewhat differently we may hold the data of Fig. 5 as evidence of considerable local distortion in the lattice due to the presence of the hydrogen atom. If we assume that the effect of the distortion is appreciable *only* for CaF_2, then the slope of the curve at large r approaches a value of $n=27$. It is worth noting, in this connection, that Blum and Benedek[5] have reported a value of $n=16$ based upon measure-

ments under hydrostatic pressure, p, of the quantity, $(B-B_0)^{-1}\partial(B-B_0)/\partial p$, combined with data on the compressibility of the lattice. Their measurements were made on CaF_2. Thus, one might say that the discrepancy between these two values of n is more apparent than real, since it is *a priori* not justifiable to assume that the local compressibility around the H atom is identical with the average compressibility of the lattice. Such an assumption would be especially questionable with CaF_2, and it is reasonable to expect that high pressure measurements performed on BaF_2 would give larger values of n.

Turning now to the variation of g values with lattice parameter, we note first a slight discrepancy between our values for CaF_2 powder, which we remeasured, and those reported in Ref. 1. We can assign no reason for this discrepancy except perhaps a systematic error of ~1 G in the magnetic field determinations of either investigator. This however seems unlikely. Our proton resonance probe was located physically at a distance of about 1.5 in. from the position of the sample, but a check of the field gradients indicates that the maximum error we could incur from this separation is only ~0.1 G. Regarding the variation of g with lattice parameter, we note that our value exceeds the free atom value by about 3 parts in 10^4, for CaF_2, 1 part in 10^4 for SrF_2 and that the difference vanishes (within experimental error) for BaF_2. The trend of the change is as expected, but not the sign of the shift. It has already been pointed out[6] elsewhere that the effect of the fluorine ion wave functions should be to produce strong spin-orbit forces which yield a *negative* shift in g. This is evidently contrary to our observations.

Finally, we would like to point out one particularly anomalous set of measurements, viz., the value of the splitting $\Delta(100)$ in BaF_2 at two temperatures. As seen from Table I, this quantity undergoes a decrease of about 2% in cooling from 300 to $77°K$. The direction of this change is opposite to that reported[1] for CaF_2 and the magnitude is astonishingly large. We offer no physically plausible explanation for these values, and until a satisfactory theoretical basis for calculating the super hfs interactions exists, these results must remain an interesting paradox.

ACKNOWLEDGMENTS

[5] H. Blum and G. B. Benedek, Bull. Am. Phys. Soc. **8**, 619 (1963).

[6] F. J. Adrian, Phys. Rev. **107**, 488 (1957).