Electron-Nuclear Double Resonance of F Centers in MgO†

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Electron-nuclear double-resonance measurements on F centers in MgO are reported. From these measurements, the magnetic and electric hyperfine interaction constants for sites with one nearest-neighbor Mg^{25} nucleus are obtained with high precision. We find: For the isotropic hyperfine-interaction constant, $A/h=11.03\pm0.02$ MHz; for the dipolar interaction constant, $B/h=1.33\pm0.02$ MHz; for the quadrupole interaction constant, $e^2qQ/h=5.64\pm0.01$ MHz. From the quadrupole interaction constant, it is shown that the Mg nuclei relax outward from the vacancy by an amount between 0.04 and 0.08 times the Mg–O distance. The value of e^2qQ for Sr^{87} leads to similar conclusions regarding the relaxation of nearest-neighbor nuclei of the F center in SrO.

INTRODUCTION

An electron trapped in a negative ion vacancy of MgO and analogous compounds offers an interesting variation of the well-studied F center in the alkali halides [1] The extra charge of the vacancy causes the wave function to be less diffuse and the relaxation of the environmental ions to be rather different from the alkali halides. In this paper, electron-nuclear double-resonance (ENDOR) experiments are reported which allow one to infer the gradient of the electric field at the nearest-neighbor (nn)Mg^{25} nuclei. From this gradient, some conclusions are drawn concerning the relaxation of the nn of the F center in MgO.

EXPERIMENTAL

The measurements reported here were made on two MgO crystals loaned to us by Professor J. C. Kemp of the University of Oregon. One crystal, designated I, was grown by General Electric Company and irradiated for 36 h in the Oak Ridge ORR reactor. The other crystal, designated Y3, was purchased from Norton Company and irradiated for 36 h in the center of the MTR reactor at Arco, Idaho. Sample I contained 4.9×10^{18} F centers per cc and Y3 contained 4.3×10^{18} F centers per cc. Sample I showed resonance absorption by unidentified impurities of the order of 1% as strong as the F-center resonance but only one of these fell within the F-center spectrum when the applied magnetic field was along [100]. Sample Y3 showed a rather strong Mn^{2+} spectrum which did not overlap the F-center spectrum, and a very strong $Fe^{3+}(\frac{1}{2}\rightarrow-\frac{1}{2})$ resonance which overlapped the low-field portion of the F-center resonance when the field was along [100].

The high-field half of the EPR spectrum of sample I is shown in Fig. 1(a) for the magnetic field along the [100] direction. For the entire spectrum, twelve hyperfine lines are resolved: six spaced at 4.9-G intervals which are attributed to sites with one nn Mg^{25} in the [100] and [$\bar{1}$00] directions (the $\theta=0°$ spectrum), and six other lines, twice as strong, spaced at 3.5-g intervals, which are attributed to sites with one nn Mg^{25} in one of

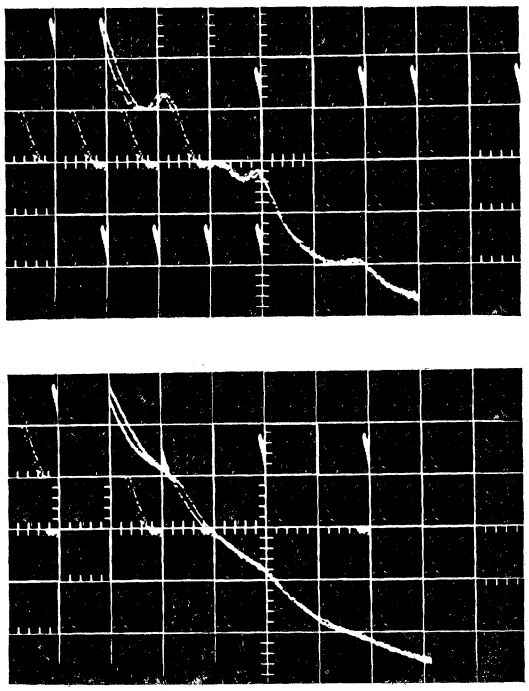

FIG. 1. A portion of the paramagnetic resonance spectrum of F centers in sample I for the magnetic field in the [100] direction. The four hyperfine lines $m=+\frac{5}{2}$, $+\frac{3}{2}$, $\theta=90°$, and $m=+\frac{5}{2}$, $+\frac{3}{2}$, $\theta=0°$ are shown. For (a), the microwave power level was 5 μW, and for (b) the power level was 240 μW. The resolved hyperfine lines saturate at lower power than the broad background.

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[1] A review of the work on these centers has been given by J. E. Wertz, G. S. Saville, L. Hall, and P. Auzins, Proc. Brit. Ceram. Soc. 1, 59 (1964).

the four directions equivalent to [010] (the $\theta=90°$ spectrum).[2]

The EPR and ENDOR measurements were made at Ohio University with a superheterodyne spectrometer operating near 9.6 GHz. The spectrometer is locked to the sample cavity which is a reflection cavity in one arm of a microwave bridge. A sensitivity of 6×10^{12} spins/g is achieved at room temperature with 0.1 mW of power incident on the cavity and a 1-cps bandwidth.

The ENDOR cavity consists of a TE_{012} mode rectangular brass cavity in which a 0.04-in.-wide slit was sawed longitudinally along the center of the broad sides of the cavity from a point $\frac{2}{3}$ of the cavity length from the iris on through the bottom plate. The sample was placed on the bottom plate directly over the slit. A six-turn coil was wound around the outside of the cavity from the bottom plate upward about $\frac{1}{10}$ of the cavity length. The coil is driven by General Radio Unit Oscillators. Magnetic fields of 1 g peak-to-peak are produced in the sample position with 1 W of radio frequency power at about 5 MHz.

In this cavity, the microwave frequency magnetic field in the sample position is parallel to the bottom plate and the broad side of the cavity. The low-frequency magnetic field (hereafter, the rf field) at the sample is also in this direction since it is guided by the bottom plate into the slit. Therefore, optimum operation is possible only for the static magnetic field in the direction perpendicular to the broad face of the cavity.

The cavity, coil, and coaxial feed line are shielded so that no spurious responses occur even at the 30-MHz frequency used for the superheterodyne circuits.

For high-sensitivity ENDOR experiments, the rf power is square-wave-modulated 100% at 37 Hz, and the video output of the spectrometer is narrow-band-amplified and phase-detected at the modulation frequency. The phase-sensitive demodulator is set for maximum sensitivity at the same phase as the modulation wave form. These conditions lead to a signal proportional to the steady-state ENDOR effect produced during each modulation cycle.

The rf generator is swept at a uniform dial speed and frequency markers inserted manually on the chart record of the phase-sensitive detector output. The 200-Hz accuracy of the markers far exceeds that required for this experiment.

The static magnetic field was set in the [100] direction, at the appropriate value such that the microwave field induced transitions corresponding to one of the twelve hyperfine lines. In the following discussion these transitions will be defined by the angle θ defined above and the value of the nuclear spin quantum number m. The microwave power was adjusted to produce 50% saturation of the hyperfine transition (saturation parameter $\gamma^2H_1^2T_1T_2=1$). The power required corresponds to a value $T_1T_2\cong5\times10^{-9}$ sec with the sample at 77°K.

Setting this power is complicated by the presence of a broad background under the hyperfine structure which does not saturate as easily as the resolved hyperfine lines. This property of the broad background is shown by Fig. 1(b), which is the same spectrum as in Fig. 1(a), but at a higher power level. In fact, the resolved hyperfine structure represents no more than 20% of the magnetic resonance absorption in the region several gauss either side of the main resonance peak. The background has many characteristics that one would expect of the resonance produced by exchange narrowing of the hyperfine structure.

The ENDOR response obtained from sample Y3 at 77°K while partially saturating the $m=+\frac{3}{2}$ line of the $\theta=90°$ spectrum is shown in Fig. 2. An integration time constant of 5 sec was used, and the signals correspond to only about 0.1% of the EPR signal from the individual hyperfine line being saturated. The amplitudes of these responses are representative of most of the $\theta=90°$ ENDOR transitions, but are substantially larger than the responses from the $\theta=0°$ spectrum. The 100-kHz widths are characteristic of all the ENDOR responses from sample Y3. For sample I, the linewidths are typically about 250 kHz.

The frequencies of the ENDOR responses observed at 77°K while saturating the resolved hyperfine lines are recorded in Table I. All of these transitions are observed for both sample I and Y3. In addition, three other very weak responses, not entirely reproducible, were seen from hyperfine lines which strongly overlapped background impurities, and undoubtedly arise from the background resonances. The relative intensities of the responses are not the same for the two samples. Moreover, the strengths of the ENDOR responses for Y3 are greater on the high-field side of the spectrum than on the low-field side, which is the region in which the large impurity resonance lies. Because of the narrower responses in Y3, the experimental frequencies listed in Table I, along with the estimated errors, are all from this sample. The corresponding frequencies observed in sample I are all in agreement to well within the observed linewidths.

Sample I exhibits a large nonresonant response which appears to have the characteristics of the effects produced by packet shifting by an rf field in the direction of the static field.[3] It is proportional to the saturated EPR signal and becomes much larger for static field directions parallel to the rf field. The effect is particularly large when the static field is set near the center of the hyperfine structure, and produces large baseline shifts there because the rf power varies as the frequency is swept. This effect made it impossible to observe the ENDOR spectrum of sample I while saturating the

[2] J. E. Wertz, P. Auzins, R. A. Weeks, and R. H. Silsbee, Phys. Rev. 107, 1535 (1957).

[3] E. C. McIrvine, J. Lambe, and N. Laurence, Phys. Rev. 136, A467 (1964).

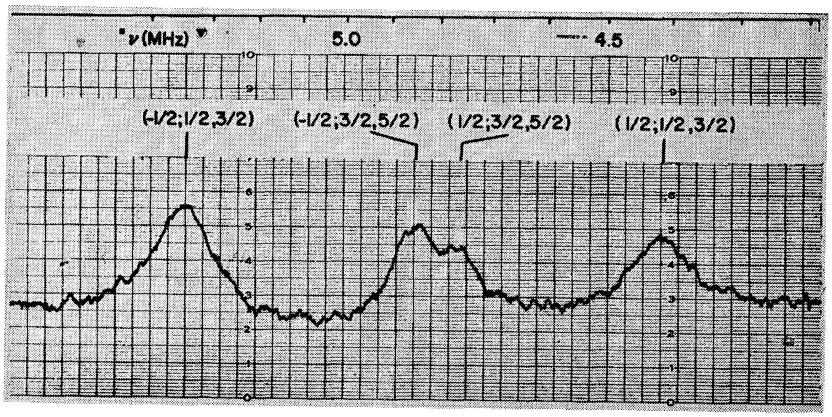

FIG. 2. The ENDOR signals obtained while partially saturating the $m=+\frac{3}{2}$ hyperfine line of the $\theta=90°$ spectrum. The integration time constant was 5 sec. The arrows and labels identify the ENDOR transitions.

$m=\pm\frac{1}{2}$ lines of both the $\theta=0°$ and $\theta=90°$ spectra. For some reason, this effect is much smaller in the sample Y3, and the ENDOR spectrum for these interior lines was obtained rather easily.

One set of data was obtained at 4.2°K using sample I. The same spectra were observed and the signal-to-noise ratio was comparable to that achieved at 77°K. Liquid helium had not been excluded from the cavity and the major source of noise was from helium gas bubbles in the liquid. Further, there was no attempt to adjust the rf modulation frequency from the 37 Hz used at 77°K. It is therefore quite possible that very superior signals can be obtained at liquid-helium temperatures.

INTERPRETATION OF THE DATA

If the possible asymmetry in the quadrupole interaction is ignored, the F-center electron interacting with one Mg^{25} nucleus in a nn position in the direction of the unit vector $\mathbf{e}$ from the center is described by the spin Hamiltonian

$$\mathcal{H}=g\beta\mathbf{H}\cdot\mathbf{S}+A\mathbf{I}\cdot\mathbf{S}+B[\mathbf{I}\cdot\mathbf{S}-3(\mathbf{I}\cdot\mathbf{e})(\mathbf{S}\cdot\mathbf{e}\,]+P[3(\mathbf{I}\cdot\mathbf{e})(\mathbf{I}\cdot\mathbf{e})-I(I+1)]-g_n\beta_n\mathbf{H}\cdot\mathbf{I}, \quad (1)$$

in which

$$P=e^2qQ/[4I(2I-1)]. \quad (2)$$

For the magnetic field along one of the cubic axes, perturbation theory is best in a representation in which both the electron and nuclear spins are quantized in the direction of the applied static magnetic field. The first-order result for the frequency of the transition from the state labeled by the electron-spin quantum number M and the nuclear-spin quantum number m to the state labeled by M and $m+1$ is given by

$$h\nu(M;m,m+1)=M[A+B(3\cos^2\theta-1)]+3P(3\cos^2\theta-1)(2m+1)-g_n\beta_nH. \quad (3)$$

In the ensuing discussion these transitions will be identified by the notation $(M;m,m+1)$.

There are ten nuclear transitions for each type of site with one nn Mg^{25}. In the presence of a quadrupole interaction, these transitions are only accidentally degenerate. Experimentally, ten distinct ENDOR transitions are observed for $\theta=90°$, and nine for $\theta=0°$, one of the responses in the latter set being distinctly broader than the rest. The initial phase of the analysis utilizes the transitions observed when the $m=\pm\frac{5}{2}$ hyperfine lines of the two spectra are saturated with

TABLE I. Calculated and observed ENDOR frequencies. The experimental errors listed refer to the estimated accuracy of determining line centers. The calculated frequencies are obtained from the parameters listed in the text and Eq. (1). Root-mean-square deviations between observed and calculated frequencies are listed for each set of calculated frequencies. The rms deviation for the measured frequencies is calculated from the estimated experimental errors.

Transition	Observed frequency (MHz) $\theta=90°$	Calculated frequency (MHz) To first order	Calculated frequency (MHz) To second order
	Part A, $\theta=90°$		
$(+\frac{1}{2};\frac{3}{2},\frac{5}{2})$	4.77±0.01	4.80	4.74
$(-\frac{1}{2};\frac{3}{2},\frac{5}{2})$	4.86±0.01	4.90	4.84
$(+\frac{1}{2};\frac{1}{2},\frac{3}{2})$	4.42±0.01	4.37	4.40
$(-\frac{1}{2};\frac{1}{2},\frac{3}{2})$	5.36±0.01	5.32	5.35
$(+\frac{1}{2};-\frac{1}{2},\frac{1}{2})$	4.05±0.01	3.96	4.05
$(-\frac{1}{2};-\frac{1}{2},\frac{1}{2})$	5.80±0.01	5.74	5.80
$(+\frac{1}{2};-\frac{3}{2},-\frac{1}{2})$	3.62±0.01	3.54	3.63
$(-\frac{1}{2};-\frac{3}{2},-\frac{1}{2})$	6.18±0.01	6.17	6.20
$(+\frac{1}{2};-\frac{5}{2},-\frac{3}{2})$	3.06±0.01	3.11	3.10
$(-\frac{1}{2};-\frac{5}{2},-\frac{3}{2})$	6.53±0.01	6.59	6.57
rms Deviations	0.01	0.06	0.02
	Part B, $\theta=0°$		
$(+\frac{1}{2};\frac{3}{2},\frac{5}{2})$	4.24±0.01	4.26	4.25
$(-\frac{1}{2};\frac{3}{2},\frac{5}{2})$	9.44±0.01	9.43	9.42
$(+\frac{1}{2};\frac{1}{2},\frac{3}{2})$	5.10±0.02	5.11	5.10
$(-\frac{1}{2};\frac{1}{2},\frac{3}{2})$	8.58±0.01	8.59	8.58
$(+\frac{1}{2};-\frac{1}{2},\frac{1}{2})$	5.97±0.05	5.96	5.96
$(-\frac{1}{2};-\frac{1}{2},\frac{1}{2})$	7.75±0.02	7.74	7.74
$(+\frac{1}{2};-\frac{3}{2},-\frac{1}{2})$	6.85±0.05	6.80	6.81
$(-\frac{1}{2};-\frac{3}{2},-\frac{1}{2})$		6.89	6.89
$(+\frac{1}{2};-\frac{5}{2},-\frac{3}{2})$	7.67±0.03	7.65	7.66
$(-\frac{1}{2};-\frac{5}{2},-\frac{3}{2})$	6.01±0.02	6.04	6.05
rms Deviations	0.03	0.03	0.02

microwave power. One anticipates that the strongest ENDOR responses will be produced when those nuclear transitions are driven which connect directly with one of the levels involved in the microwave-frequency transition which is being saturated. For saturation of the $m=+\frac{5}{2}$ hyperfine line (the high-field line since the sign of A is known to be negative), these prominent transitions should be $(+\frac{1}{2};\frac{3}{2},\frac{5}{2})$ and $(-\frac{1}{2};\frac{3}{2},\frac{5}{2})$. In fact, only two prominent responses are observed for saturation of each high-field and low-field line of the two hyperfine spectra. The expected frequencies are the absolute values of Eq. (3), since the hyperfine interaction is dominant. Since the sign and magnitude of the nuclear moment of Mg^{25} is known, $(g_n\beta_n/h)=-26.0$ Hz/g,[4] the sums and differences of these pairs of frequencies give, respectively, the hyperfine interval and the quadrupole interaction constant. Independent results are obtained for each pair. Therefore, the strong ENDOR responses from the high- and low-field lines of each hyperfine structure yield two values for $A+2B$, two values for $A-B$, and four values for P. Best values of A, B, and P from these results were used to calculate all 20 ENDOR frequencies to first order.

These first-order frequencies are compared with experiment in Table I. The experimental frequency has been associated with that transition for which the theoretical frequency is nearest to the observed frequency. The agreement is reasonable, but for $\theta=90°$ the errors are larger than the experimental accuracy, as can be seen from the rms deviation in the last row of the table.

These errors can be substantially reduced by applying higher order corrections. To the accuracy of the data, there are two relevant corrections: the second-order hyperfine correction, which is as large as 25 kHz for some of the transitions, and the second-order quadrupole correction for the $\theta=90°$ spectrum only, which is as large as 90 kHz for one of the transitions. This last correction is important even though the quadrupole interaction is small because the levels mixed differ in energy only by the hyperfine interval. The addition of these corrections leads to the calculated values recorded in Table I, and substantially reduces the rms deviation between calculated and experimental frequencies for the $\theta=90°$ spectrum. The final deviations are consistent with the experimental error, and are well within the linewidth for each of the transitions.

This procedure yields the hyperfine constants

$$-A/h=11.03\pm0.02 \text{ MHz},$$
$$-B/h=1.33\pm0.02 \text{ MHz},$$
$$P/h=0.141\pm0.001 \text{ MHz}.$$

The results for A and B agree with our EPR measurements and those of earlier investigators,[2] but are more accurate.

[4] F. Alder and F. C. Yu, Phys. Rev. 82, 105 (1951).

Examination of the observed responses shows that the ENDOR mechanisms are not straightforward. When the interior hyperfine lines are saturated, responses are obtained corresponding to nuclear transitions not directly connected to the saturated levels. However, the largest ENDOR responses are always obtained for those nuclear transitions directly connected to the pair of saturated hyperfine levels, and in the case of the $m=\pm\frac{5}{2}$ levels of both spectra any other responses are extremely weak. The extra responses which are observed for saturation of the $m=\pm\frac{3}{2}$ and $m=\pm\frac{1}{2}$ hyperfine lines are always those corresponding to transitions between pairs of levels near the center of the hyperfine structure. In fact, the $(M;\frac{3}{2},\frac{5}{2})$ and $(M;-\frac{3}{2},-\frac{5}{2})$ transitions do not appear as additional responses. These features can be plausibly explained on the following basis. First, the strong background under the resolved hyperfine structure makes it difficult to saturate a given hyperfine line without saturating adjacent lines via spin-spin processes, and this effect would be most pronounced near the center of the spectrum. Second, there is fairly significant direct overlap between several of the hyperfine lines, such as the $m=+\frac{1}{2}$ and $m=-\frac{1}{2}$ lines of both spectra, and the $m=\pm\frac{5}{2}$ lines at $\theta=90°$ with the $m=\pm\frac{3}{2}$ lines at $\theta=0°$, making it possible to observe directly some additional responses. Finally, saturation of an interior hyperfine line can produce saturation of adjacent lines if the relaxation process in which the electron-spin and nuclear-spin change simultaneously is quite rapid. This relaxation rate should be faster for the interior lines of the hyperfine structure and would give rise to additional responses corresponding to nuclear transitions coupling pairs of levels once removed toward the center of the hyperfine structure. This situation appears to be realized in the case of ENDOR responses from the $m=\pm\frac{3}{2}$ lines of the $\theta=90°$ spectrum, which are both well separated from the other hyperfine lines. In both cases, only two significant extra responses are obtained, and they are the $(M;-\frac{1}{2},\frac{1}{2})$ transitions. It is plausible to attribute these two extra responses to the last mechanism mentioned, and to expect that the ENDOR spectrum in a sample free of the background resonance would exhibit these effects.

As noted above, the strongest ENDOR lines correspond to only about 0.1% of the EPR signal from the hyperfine line being saturated. A simple model, in which the nuclear transition is completely saturated, predicts a 17% effect. A large part of the discrepancy may be due to inadequate rf field. The ENDOR signal still increases rapidly with power at the highest level attainable with the General Radio oscillator. The microwave field in the cavity is about 16×10^{-3} g, and the rf field 1 g at best. Therefore, if the linewidth of the nuclear transition is the same as the packet width for the microwave frequency transitions, one calculates that the nuclear transitions are being driven about ten times more slowly than the electronic transitions. It is possible that

the width of the nuclear transition is even broader than the packet width, and that a major part of the intensity reduction can be accounted for in this simple manner. An additional reduction in intensity probably occurs because of the role played by the paramagnetic impurities and the broad background in the details of the ENDOR process.

THE ELECTRIC FIELD GRADIENT AT Mg^{25} SITES

The value of P obtained above implies $e^2qQ/h=+5.64$ MHz. Lurion[5] quotes the value $+0.22\times10^{-24}$ cm^2 for Q. We deduce that the electric field gradient at the nearest-neighbor sites is

$$q_1=+3.40(2/R_1^3),$$

where R_1 is the Mg–O distance, 2.10 Å.

The result of the gradient calculation given by Feuchtwang[6] for F centers in the alkali halides, when extended to doubly charged vacancies, becomes

$$q_1=q_1(\text{pol})(1-\gamma_\infty)-[(B/g_n\beta_n\beta)-(4/R_1^3)]+(2-C_1)(-\gamma_\infty)(2/R_1^3). \quad (4)$$

The definition of the symbols is given in Ref. 6. For Mg^{25}, $\gamma_\infty=-4.7$[7] and $(B/g_n\beta_n\beta)=2.64(2/R_1^3)$. C_1 measures the amount of the F-center electron charge within the vacancy. It is always less than one, but it may approach unity rather closely for doubly charged vacancies. Feuchtwang found $C_1=0.7$ from one set of wave functions for the F center in LiF. A reasonable guess is $C_1=0.85$ for MgO.

With these numbers, the value of q_1(pol), the gradient which arises from lattice distortion, can be estimated. We find:

$$q_1(\text{pol})=-(2/R_1^3)[0.132+(1-C_1)(0.825)],$$

and therefore with our guess for C_1, we obtain

$$q_1(\text{pol})=-0.254(2/R_1^3),$$

a rather large negative value.

The value of e^2qQ for Sr^{87} nn of Fcenters in SrO has been reported by Culvahouse, Holroyd, and Kolopus.[8] The optical double resonance measurement[9] of the quadrupole moment of Sr^{87} was overlooked by those authors, and they used estimates of q_1(pol) to find a value for the quadrupole moment of Sr.[87] Using the known quadrupole moment one finds that for SrO

$$q_1=+37.4(2/R_1^3),$$

which should be compared with the value $+52$ $(2/R_1^3)$ given as a lower limit in Ref. 8. Utilizing this better value of q_1, we find that for SrO

$$q_1(\text{pol})=-(2/R_1^3)[0.190+(1-C_1)(0.99)],$$

and if we assume $C_1=0.95$ (since the distance R_1 is 2.57 Å in this case, rather larger than the value for MgO) we find

$$q_1(\text{pol})=-0.240(2/R_1^3).$$

These results show that q_1(pol) is definitely negative and rather large for both SrO and MgO.

The estimate for q_1(pol) used in Ref. 8 was between 0 and $+0.70(2/R_1^3)$ This error resulted from the failure to consider the possibilities arising from a rather large outward shift of the nn of the F center. For all inward displacements up to 10% of R_1, the lattice polarization gradient at the nearest-neighbor position produced by displacement of the nn is positive.[6] The contribution of the next-nearest-neighbor (nnn) oxygen is also positive for inward shifts. Intuitively, it seems certain that if the positive nn ions shift inward, the negative nnn ions will also shift inward. Therefore it seems likely that the nn must move outward so as to provide a negative gradient, and that the oxygens may move inward some. The amount of outward motion of the nn nuclei which produce the required gradient is of the order of $0.05R_1$. If the oxygens were to move inward significantly, the positive gradient produced by that displacement would require a larger outward displacement of the nn. In the unlikely event that the oxygens move out, a smaller outward displacement of the nn magnesium ions would account for the observed gradient. Throughout this discussion, the effect of core polarization and the displacements of neighbors more distant than the next nearest have been ignored. In view of the uncertainty about the motion of the oxygen ions, the most that one can say about the relaxation of the nn of the F centers is that they definitely relax outward for the centers in SrO and MgO. The probable value is between $0.04R_1$ and $0.08R_1$. Kemp and Neely[10] found from an energy minimization process that the outward displacement should be about $0.05R_1$.

CONCLUSIONS

It has been demonstrated with the aid of ENDOR measurements that the motion of the nn of the F center in MgO is definitely outward and quite large The same conclusion has been reached for the F center in SrO by using the value of the quadrupole moment determined by optical resonance[9] and the EPR data of Culvahouse *et al.*[8], on the F center in SrO. These results are in close accord with the theoretical results of Kemp and Neely.[10] If the gradients at the nnn sites could be obtained, a definitive answer can be obtained for the relaxation of the nnn and nn ions. Such measurements cannot be made with the oxides, but might be possible in sulfides. Better ENDOR signals than those obtained with the

[5] A. Lurion, Phys. Rev. **126**, 1768 (1962).
[6] T. E. Feuchtwang, Phys. Rev. **126**, 1616 (1962).
[7] This is the value for Na^+ given by R. M. Sternheimer and H. M. Foley [Phys. Rev. **102**, 731 (1956)].
[8] J. W. Culvahouse, L. V. Holroyd, and J. L. Kolopus, Phys. Rev. **140**, A1181 (1965) .The factor $4I(I+1)$ in Eqs. (5) and (6a) of this paper should be replaced by $4I(2I-1)$. The calculations in this paper were done with the correct equations.
[9] G. zu Putlitz, Z. Physik **175**, 543 (1963).
[10] J. C. Kemp and V. I. Neely, Phys. Rev. **132**, 215 (1963).

samples used in the present investigation will be required. It seems likely that very superior signals may be obtained using larger samples with smaller neutron irradiations. The signal may also be enhanced by use of an optimum rf modulation frequency with the sample at 4.2°K, or perhaps at 20°K.

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Correlation of the Optical and Electron-Spin-Resonance Absorptions of the H Center in KCl†

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It has been shown that the optical H band and the ESR H spectrum arise from the same center, the H center, in KCl. Similar to the Cl_2^- (or V_K) center, the H center has two optical transitions: A strong and highly σ-polarized transition giving rise to an absorption band at 336 nm, and a much weaker transition, which is very weakly σ-polarized, giving rise to an absorption band at 522 nm. The disorientation temperature of the H center has been found to be (10.9±0.3)°K.

I. INTRODUCTION

IT was found by Duerig and Markham[1] that x-irradiation of 5°K produced an absorption band in KCl crystals, with a peak at 345 nm, which they called the H band. Compton and Klick,[2] through the use of polarized-light bleaching experiments, showed that the optical dipole moment of the transition responsible for the H band absorption lies along a ⟨110⟩ direction. Känzig and Woodruff,[3] using electron spin resonance (ESR) techniques, found that after x-irradiation at 20°K a paramagnetic species was produced which involves an interstitial. The ESR spectrum indicates that this species consists of a Cl_2^- molecule ion located at a single negative ion site; the positive hole has additional interaction with two adjacent Cl^- ions and the complex, consisting of four collinear chlorine nuclei, has its axis along a ⟨110⟩ direction. Känzig and Woodruff attributed this ESR signal to the presence of H centers in the crystal. Although there probably is little doubt that the center studied by Känzig and Woodruff is the H center and is associated with the H band studied by compton and Klick, there have at times been questions regarding this association.

Since the H center is of such fundamental importance in the study of color centers, the present work was undertaken to test directly whether the H band in KCl arises from an optical transition of the H center observed in the ESR spectrum, and at the same time to obtain more detailed information concerning its optical absorption spectrum, methods of production, and orientation properties.

II. EXPERIMENTAL PROCEDURE

A. Optical Measurements

The crystals used in these experiments were cleaved from large single crystals which were either grown in air by the Kyropoulos method or were purchased from the Harshaw Chemical Company. The crystals prepared in this laboratory were grown from melts containing a mixture of 0.1 to 1.0 g of NaCl with about 100 g of KCl. The cross sectional dimensions of the cleaved crystals were about 8×14 mm² while the thicknesses of the crystals varied from 1 to 12 mm. Color centers were produced by exposure to a 2000-Ci Co^{60} γ-ray source. Absorption spectra were obtained by using a Cary 14R recording spectrophotometer. Polarized light was produced through the use of either an Ahrens or Glan prism; the Glan prism permits measurement of optical absorption spectra down to about 220 nm since it has no absorbing cement and is limited only by the absorption of calcite itself. The source of bleaching light was an HBO-500 high pressure mercury arc lamp in conjunction with interference and sharp cutoff filters.

B. ESR Measurements

The crystals used in the electron spin resonance investigation were 3×3×20 mm³ in size and were taken from the same source crystals used in the optical work. Color centers were produced by irradiation at 77°K

* Based on work performed under the auspices of the U. S. Atomic Energy Commission.
[1] W. H. Duerig and J. J. Markham, Phys. Rev. 88, 1043 (1952).
[2] W. D. Compton and C. C. Klick, Phys. Rev. 110, 349 (1958).
[3] W. Känzig and T. O. Woodruff, J. Phys. Chem. Solids 9, 70 (1958).

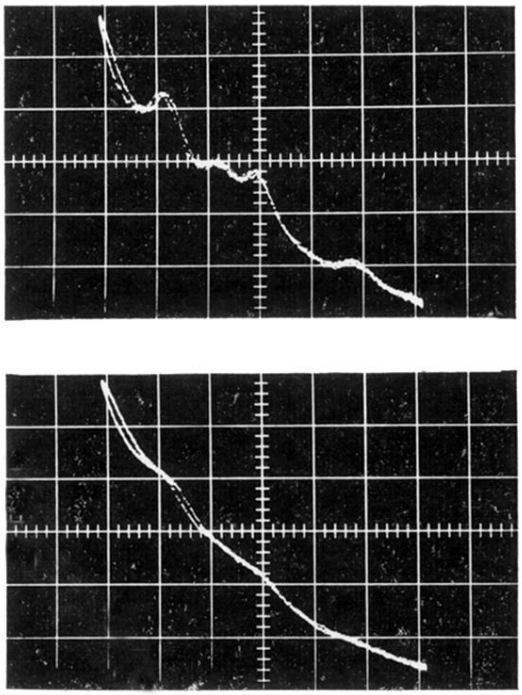

FIG. 1. A portion of the paramagnetic resonance spectrum of F centers in sample I for the magnetic field in the [100] direction. The four hyperfine lines $m=+\frac{3}{2}$, $+\frac{1}{2}$, $\theta=90°$, and $m=+\frac{3}{2}$, $+\frac{1}{2}$, $\theta=0°$ are shown. For (a), the microwave power level was 5 μW, and for (b) the power level was 240 μW. The resolved hyperfine lines saturate at lower power than the broad background.

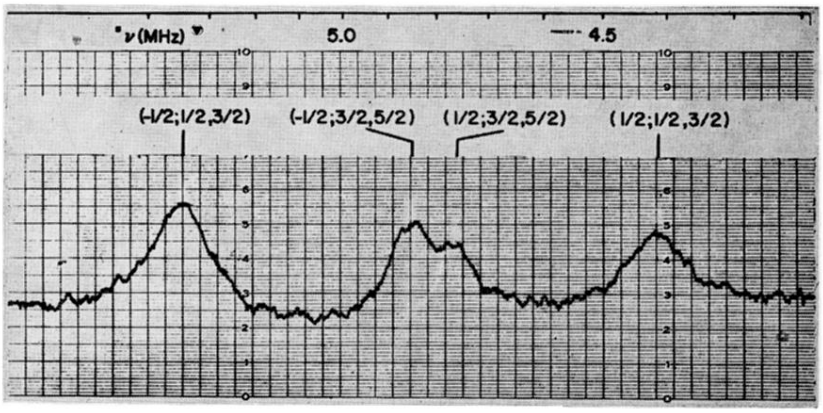

FIG. 2. The ENDOR signals obtained while partially saturating the $m=+\frac{3}{2}$ hyperfine line of the $\theta=90°$ spectrum. The integration time constant was 5 sec. The arrows and labels identify the ENDOR transitions.