Paramagnetic Spectra of E_2' Centers in Crystalline Quartz

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The electron spin resonance spectra of the E_2' center, a defect of the quartz structure, are in agreement with a phenomenological Hamiltonian for a spin state $S=1/2$. The Hamiltonian is $\mathcal{H}=\frac{1}{6}N\sum_{i=1}^{6}(\beta\mathbf{H}\cdot\mathbf{g}_i\cdot\mathbf{S}+\mathbf{S}\cdot\mathbf{A}_{ki}\cdot\mathbf{I}_{ki})$. The i subscript refers to the symmetry operations of the quartz crystal and indicates that a defect at an arbitrary point in the unit cell has an equal probability of being at five other equivalent sites which are related by the symmetry operations of the crystal. The k subscript identifies the nuclear sites with which a defect at the ith site may interact. The $k=1$ site is occupied by a proton for nearly all of the E_2' centers. $k=2$, 3, 4, 5 are Si sites. Of these sites, 4.7% are occupied by Si^{29} ($I=1/2$). The occupancy of the $k=1$ site by a proton was confirmed by substituting a deuteron for the proton. The hyperfine interaction with the proton is less than the magnitude of the interaction with the field H at the proton, i.e., $|\gamma(\mathrm{H})\beta_n H|>|A|, |B|$ where A and B are the principal values of the hyperfine interaction tensor. The angular variation of the splitting agrees with the values calculated on this basis. The hyperfine interactions with Si^{29} were not of this form. A model is proposed which is in agreement with the observations. The principal feature of the model is a Si-O vacancy with an electron trapped on the defect Si from which the O ion is missing. The proton is trapped nearby. The data for the E_2' center are compared with the data for the E_1' center.

I. INTRODUCTION

MANY of the point defects produced in quartz by irradiation are paramagnetic. The spin resonance of these defects has made possible the observation of the crystalline environment in the vicinity of the defect. Some of these defects have been shown to be defects in which Si and O atoms are missing from their normal positions in the quartz structure.[1] Other defects have been observed which have been attributed to impurities[2] and impurity complexes.[3]

The subject of this paper is a center observed in neutron- and γ-ray-irradiated quartz single crystals. Earlier work[4] had indicated a correlation of an optical band whose peak is at 2300 Å with the paramagnetic center. In this work[4] the center was labeled E_2'. It was shown that the optical band was also found in high-purity silica, and an indication that the band in the silica was paramagnetic[5] lent support to the assumption that the center in the silica was the same as the E_2' center observed in quartz single crystals. The evidence indicates that the center in γ-ray-irradiated crystals is indirectly related to one of the impurities present in the crystals studied. The present work considers the details of the electron spin resonance spectra of this center and its relation to the quartz structure. This is done through the use of a phenomenological Hamiltonian which describes the observed orientation dependence of the spectra. Hyperfine interactions were observed and are utilized in developing the geometry of the center. A comparison with another and similar center, the E_1' center[4,6] is useful in suggesting tentative models for the two centers.

In the following paper the results of an investigation of the temperature dependence of the spin-lattice relaxation of two E' centers are given. It is shown that the tentative models, which are proposed, are consistent with the observed temperature dependence of the spin-lattice relaxation.

II. EXPERIMENTAL PROCEDURE

The single-crystal specimens were cut from large synthetic and natural crystals. The synthetic crystals were of two kinds: (1) grown on a Z-plate[7] seed crystal, and (2) grown on a Y-bar seed crystal.[8] The crystal in which D was substituted for H was grown in deuterated water.[9] The natural crystals were Brazilian quartz. Most of the measurements were made on the synthetic crystals grown on a Z plate and Y bar. These were labeled GQ-9, GQ-10, CQ-11, D_2O-Q, and SQ-1. The irradiations were made in a Co^{60} source at 6×10^6 roentgens (R) per hour. The ambient temperature was ~35°C.

The electron spin resonance (ESR) was observed in a superheterodyne spectrometer in which the signal frequency (~10.3 Gc/sec) was locked on the resonant frequency of the specimen cavity. The temperature of the specimen was 300 or 78°K. The orientation measurements were made by rotating the magnetic field, H. The power level in the cavity was $\leq10^{-6}$ W in order to avoid saturation of the ESR signal.

[1] R. A. Weeks, J. Appl. Phys. **27**, 1376 (1956).
[2] J. H. E. Griffiths, J. Owen, and I. M. Ward, in *Report of the Conference on Defects in Crystalline Solids* (The Physical Society, London, 1955), p. 81; M. C. M. O'Brien, Proc. Roy. Soc. (London) **A231**, 404 (1955).
[3] J. H. Anderson and J. A. Weil, J. Chem. Phys. **31**, 427 (1959).
[4] C. M. Nelson and R. A. Weeks, J. Am. Ceram. Soc. **43**, 396 (1960); R. A. Weeks and C. M. Nelson, *ibid.* **43**, 399 (1960).
[5] R. A. Weeks and E. Sonder, Proceedings of the First International Conference on Paramagnetism, Jerusalem, Israel (to be published).
[6] R. H. Silsbee, J. Appl. Phys. **32**, 1459 (1961).
[7] Grown by General Electric Ltd., England and kindly supplied by C. S. Brown. Sawyer Research Products, Inc., East Lake, Ohio, supplied the other Z-plate crystal.
[8] Grown by Clevite Research Corporation, Cleveland, Ohio, and kindly supplied by D. Hale.
[9] The deuterated specimen was kindly supplied by J. C. King of BTL.

III. THEORY

The Hamiltonian which is used is derived from the experimental data. The significance of some of the interaction constants is considered in Sec. IV.

The Hamiltonian is that one appropriate for a paramagnetic center having an electron spin $S=1/2$ interacting with those nearby nuclei which have nuclear moments.[10] It is

$$\mathcal{H}=\tfrac{1}{6}N\sum_{i=1}^{6}(\beta\mathbf{H}\cdot\mathbf{g}_i\cdot\mathbf{S}+\mathbf{S}\cdot\mathbf{A}_{ki}\cdot\mathbf{I}_{ki}), \quad (1)$$

where N is concentration of centers, and the other terms have their usual significance. The subscript $i=1, \cdots 6$ represents the symmetry operations of the quartz lattice. The symmetry of alpha quartz implies that, except for certain lines or planes of symmetry, an arbitrary point in a unit cell is equivalent to five other points and that the points are related by the symmetry operations of the crystal. A defect possible at one of these points in the jth unit cell has an equal probability of being at any one of five other symmetry related points in the remaining unit cells of the crystal. In the absence of hyperfine interactions and for an arbitrary orientation of the crystal (excluding an orientation perpendicular to a twofold axis) paramagnetic defects at each of these symmetry related points should each exhibit a resonance absorption. In the hyperfine term the subscript k identifies a particular nuclear site with which the paramagnetic defect at a particular ith site interacts. However, the nucleus in the kth site may have zero moment, in which case the interaction is zero. In the quartz lattice the nuclei which will be of interest are Si^{29} ($I=1/2$, natural abundance 4.7%), H ($I=1/2$) present at most of the defect sites, and D ($I=1$) which was substituted for the H.

For one of the interactions with a Si^{29} nuclei $|A|$, $|B|\gg|\gamma(Si^{29})\beta_n H|$, where A and B denote the components of the hyperfine interaction tensor parallel and perpendicular to the axis of symmetry of the center. For the other interactions with Si^{29} these quantities are unknown but from the observed splittings it is probable that $|A|$, $|B|>|\gamma(Si^{29})\beta_n H|$. The interactions with H are apparently the case in which $|\gamma(H)\beta_n H|>|A|, |B|$. In this case the allowed transitions are given by[11,12]

$$h\nu=g\beta H-m_1[(g_{\parallel}/g)A\cos^2\theta+(g_{\perp}/g)B\sin^2\theta], \quad (2)$$

and where the symbols have their usual significance.[11]

IV. EXPERIMENTAL RESULTS

A. Primary Structure

After irradiating the quartz crystals described above and with the magnetic field H directed along the c axis of the crystals, a large number of lines are observed at room temperature and additional lines appear at 78°K. The principal features of these spectra at 300°K are two lines 0.4±0.1 gauss apart and of approximately equal intensity. These lines are found at a g_{eff} of 2.0008±0.0003 and 2.0010±0.0003. A set of four lines spaced 5.5 G apart and of approximately equal intensity are observed with a g_{eff} of 2.0020±0.0003. At 78°K a complex group of lines are also observed at lower fields. The principal component of this group of lines is probably the "Al" center which has been described.[2] The number of other lines and their relative intensities are found to vary from crystal to crystal. The two lines $g=2.0008$ and $g=2.0010$ in the synthetic crystals, *CQ* and *GQ* series, were of approximately equal intensities for equal γ-ray dose. The four-line system did not exhibit this equality of intensity. In the *SQ* series the intensity of the two lines was ~5 times less than in the CQ and GQ crystals.

The independence of these two systems of lines has already been described.[4] On the basis of the growth of the two-line systems with irradiation, its disappearance with bleaching light and with heating and the correlation with a single optical absorption band (2300 Å) a common symbol was adopted for this system. It was called the "E_2'" center.

In Fig. 1 the spectrum of the E_2' center is shown as a function of rotation about a twofold, [11·0], axis. At orientations away from the c axis as many as six lines are observed, whereas one would expect only three lines to be observed for this rotation axis and for an $S=1/2$ state. The spin-lattice relaxation measurement showed that these two lines could be inverted independently and thus the possibility of an $S=1$ state was eliminated (see following paper). The separation of these lines (c axis$\|\mathbf{H}$) was measured at 24.0 Gc/sec and was found to be

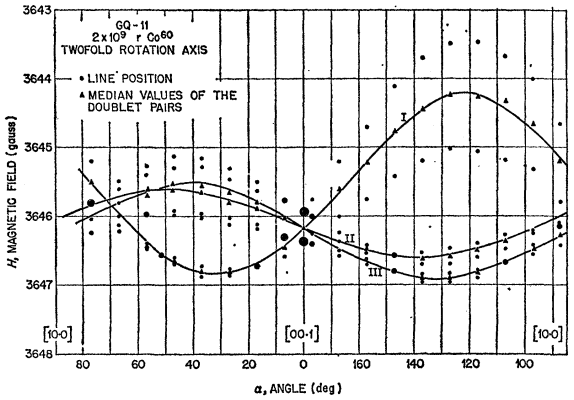

FIG. 1. Spectra of the E_2' center for a rotation about a twofold axis. Each point (line position) is the average of two methods, (reference 1) oscilloscope trace with superimposed proton resonance (reference 2), chart recording of derivative and monitoring the field with a proton resonance. The number of circles around each point indicates the relative intensity of each line. The proton resonance frequency was measured with a Hewlitt-Packard frequency counter Model 524C. The curves were calculated from the g tensor. The squares are the median values of each pair of lines associated by crossover points.

[10] A. Abragam and M. H. T. Pryce, Proc. Roy. Soc. (London) **205**, 135 (1951).
[11] H. H. Woodbury and G. W. Ludwig, Phys. Rev. **124**, 1083 (1961).
[12] J. A. Weil and J. H. Anderson, J. Chem. Phys. **35**, 1410 (1961).

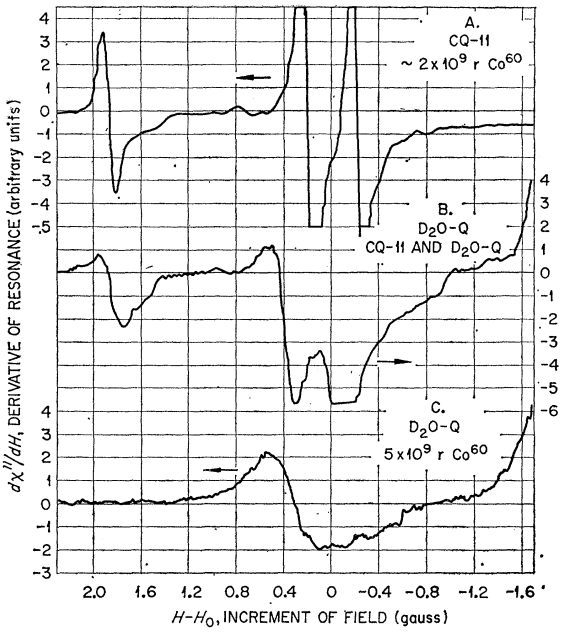

FIG. 2. The spectra in the vicinity of the E_2' center in the CQ crystals and in the deuterated crystal are shown. In (a) only the CQ crystal is in the cavity, in (c) the deuterated crystal. The values for the magnetic field, determined by the proton resonance were within ± 0.1 Oe. In (b) both crystals were placed in the cavity, the CQ crystal on top of the D_2O-Q crystal. The modulating field was ~ 0.07 G peak to peak.

field independent. It was, therefore, evident that the splitting was due to a hyperfine interaction with a nearby nuclei whose spin $I=1/2$. This nuclei must be present at nearly all of the centers.

Of the impurities which are known to be present in these crystals[13] only H has an appropriate nuclear spin. The hypothesis that the splitting was due to an interaction with a proton was tested by comparing the E_2' resonance in crystals grown in H_2O with the resonances observed in a crystal grown in D_2O. The results of this comparison are shown in Fig. 2. In Fig. 2(a) the E_2' resnance is shown and one of the lines of the four-line system appears on the high-field side of the E_2' resonance. In Fig. 2(c) one of the resonances observed in the deuterated crystal which falls at the same field as the E' center is shown. Both crystals were then placed in the cavity and aligned so that their c axes were approximately parallel. The result is shown in Fig. 2(b), and it is apparent that the resonance in the deuterated crystal occurs at the same field as the E_2' resonance.

The substitution of D for H at the E_2' center should have the following results: (a) The center of the spectrum occurs at the same field; (b) the spin of D is $I=1$ and, therefore, three lines should be observed; (c) the nuclear moment of D, $\mu_D<\mu_H$, the moment of the proton, and the splitting should be proportionately less; (d) with field inhomogeneity the three lines would not be resolved, and a broad line should be observed with its peak midway between the E_2' centers in H_2O grown crystals. The observed spectrum is in agreement with these predictions. A reasonable conclusion is that the E_2' center interacts with a nearby proton (or deuteron) which is present at most of the E_2' sites.

In the CQ and GQ crystals a third line is observed midway between the lines of the E_2' doublet [see Fig. 3(a)]. The spin-lattice relaxation of this line differs from that of the E_2' doublet (see following paper). Although an analysis of this line has not been made, it is assumed that it is due to an E_2' center at sites from which H is missing. Its intensity is approximately 5% of the intensity of the primary doublet.

In Fig. 1 it will be noted that the positions of the lines observed for a rotation about a twofold axis show crossovers at angles less than π. For the pair of lines showing the largest anisotropy this crossover was verified by a careful observation of the two lines on an oscilloscope, the crossover occurring at 17° and 52°. Similar crossovers were observed for the other two sets of lines and were found at (147°, 107°) and (147°, 90°). The separation of these pairs of lines are plotted in Fig. 3. If the maximum separation observed is taken as an approximate value for the A term in the hyperfine interaction tensor and the maximum separation after crossover is taken as the value of the B term, then $A<0<B$ or $A>0>B$. The absolute values of these interaction con-

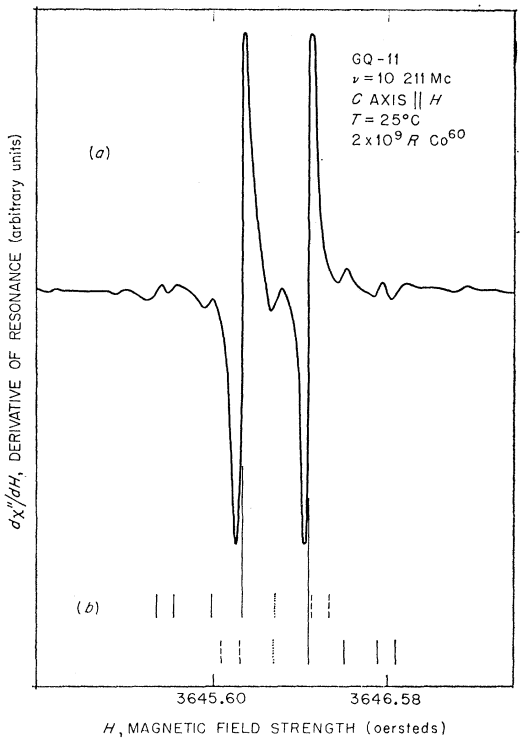

FIG. 3. Weak lines on either side of the primary doublet of the E_2' center. In (a) the derivative curves of the resonant absorption are shown, in (b) the lines in (a) are shown schematically. The well-resolved lines are shown as solid lines, the dashed lines would be present for a hyperfine interaction with three spin $I=1/2$.

[13] A. Kats, thesis, Delft, 1961 (unpublished).

TABLE I. g tensor eigenvalues and directions and the Si—Si direction.[a]

	$g_{\parallel}$	$g_{\perp}$
axis	2.0022±0.0001	2.0006±0.0001
θ	61°±3°	
ϕ	−4°±3°	
Si—Si		
θ'	53°	
ϕ'	−7°	

[a] θ and θ' are with respect to the [00·1] direction and ϕ and ϕ' are with respect to the [10·0] direction in the basal plane.

stants are $\leq 10^{-4}$ cm^{-1}. The absolute value of $|\gamma_H\beta_n H| \approx 5\times10^{-4}$ cm^{-1} and thus $|\gamma_H\beta_N H| > |A|, |B|$. The quantizing field for the proton is the laboratory field, H. In this case Eq. (2) is valid. From Fig. 1 an estimate of the anisotropy of the g tensor can be made indicating that

$$g_x/g \approx g_y/g \approx g_z/g \approx 1, \quad (3)$$

where g_x, g_y, and g_z are the eigenvalues of the g tensor. In this case the effect of the anisotropy on the hyperfine splitting is not detectable and the unperturbed line position is the median value, shown as squares in Fig. 1.

The g tensors can now be found by utilizing the symmetry properties of the quartz crystal. They are given in Table I.

The appropriate principal directions for the other five g tensors are obtained by setting $\theta'=\theta$, $\phi'=\phi\pm120°$ and $\theta'=180°-\theta$, $\phi'=-\phi\pm120°$ or $-\phi$. The errors are based on the scatter in the results for the three sets of doublets observed for rotation about a twofold axis. The values of $g_{\parallel}$ and $g_{\perp}$ are relative to the line positions for c axis parallel to H at which g_c is taken to be 2.0009. The observed linewidths represent a spread in g value of $\pm1\times10^{-5}$. No estimate of the magnitude of systematic errors has been made.

B. Additional Hyperfine Lines

In addition to the primary lines discussed above additional lines have been observed which appear to be related to the E_2' center. One set of these lines is shown in Fig. 3(a) for a c-axis orientation. Three lines on the low-field and three on the high-field side of the primary doublet are clearly resolved. A seventh line is resolved midway between the doublet. It is shown in the following paper that this line is independent of the primary doublet. Since these lines are symmetrically displaced about the primary doublet and their separation from each other is not uniform they are assumed to arise from independent sources. As will be shown below they could not arise from "forbidden" transitions as a result of quadrupolar interactions. In Fig. 3(b) a schematic reconstruction of these lines is shown in which it is assumed that they are produced by a hyperfine interaction of the E_2' center with nearby nuclei, other than H, whose spin $I=1/2$. In all of the crystals in which these weak lines could be detected the ratio of their intensity to the intensity of each component of the primary doublet was ~0.03.

In addition to these lines, two additional pairs of lines are observed for the c-axis orientation with one pair 193.5 G above and the other pair 218.5 G below the primary doublet. The separation of each of these pairs of lines is the same as the primary doublet, 0.4 G. The positions of these lines as a function of orientation could only be measured at certain orientations of the crystal because of experimental difficulties. For these orientations (17°, 60°, 77°, 147°) the separation of pairs of these lines could be matched with pairs from the primary doublet. It was assumed that these were due to a hyperfine interaction of a center with a nucleus of spin $I=1/2$. An estimate of the isotropic part of the interaction gave a value of $A'\sim400\times10^{-4}$ cm^{-1}. When the second-order shift in the center of gravity,[10] $[A^2/2H_0][I(I-1)-M_I^2]$, was calculated by assuming that H_0 was the field midway between the primary doublet, the center of gravity was within 1 G of the assumed value of H_0. This result is a partial confirmation of the value of I, and the assumption that these lines are due to hyperfine interactions of nuclei with $I=1/2$ with the E_2' center. The anisotropy in the hyperfine interaction was $\sim50\times10^{-4}$ cm^{-1}. The ratio of the intensities of each of these lines to each component of the primary doublet was 0.03.

In view of the two pairs of lines with splittings of 7 and 8 G which have been observed for the E_1' centers, a careful search was made for lines with similar splittings that were related to the E_2' centers. None were observed.

C. Growth of the E_2' Center in Various Crystals

The E_2' center could not be detected for Co^{60} γ-ray doses less than $\sim3\times10^7$ R in the GQ and CQ specimens. For larger doses the increase in intensity was approximately proportional to dose up to a dose of $\sim2\times10^9$ R. Irradiations to higher doses were not made. At a dose of 2×10^9 R the concentration was $\sim5\times10^{16}$ cm^{-3}. The concentration in the SQ crystals was a factor of 5 less than in the CQ and GQ crystals for the same dose. The concentration of the "Al" center[2] was also at least 5 times less intense than in the CQ and GQ crystals. Other paramagnetic centers which were observed in these other crystals were either decreased by at least this factor or not observed. An analysis of the impurities in these crystals by flame spectrophotometry[14] showed that the total impurity concentration of those impurities observed was at least 3 times less in the SQ crystal than in the CQ and GQ crystals. These are tabulated in the Appendix. The one impurity which is not tabulated is hydrogen and it has been shown that the hydrogen concentration is of the order of 10^{18} to 10^{19} cm^{-3} in some synthetic and natural crystls.[13,15]

[14] Performed by the Analytical group at Oak Ridge National Laboratory.

[15] H. O. Bambauer, G. O. Brunner, and F. Laves, Schweiz. Mineral. Petrog. Mitt. 42, 221 (1962).

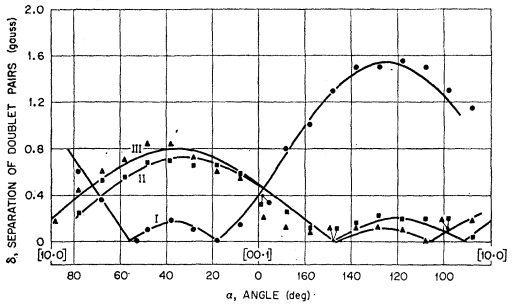

FIG. 4. The separation of the doublet pairs of the primary doublet as a function of angle with respect to the magnetic field for a rotation about a twofold axis perpendicular to the field. The data points were taken from Fig. 1. The curves were calculated by a procedure described in the text from Eq. (2).

In the natural crystal the E_2' center was also observed but there were other lines, not observed in the synthetic crystals, present in the region of the E_2' center. As has been reported,[4] the E_2' center was observed in a natural crystal after a low-temperature neutron irradiation.

V. DISCUSSION

The comparison of the crystals grown in H_2O with the one grown in D_2O furnishes convincing evidence that the doublet structure of the E_2' center is due to a hyperfine interaction of the paramagnetic defect with a nearby proton. The magnitude of this interaction is less than the interaction of the applied field with the proton. In this case the quantizing field at the proton is the applied field, and the analysis of Woodbury and Ludwig[11] and Weil and Anderson[12] is applicable. If the maximum observed value of this splitting (Fig. 4) is assumed to be the difference of the first and second principal values of the hyperfine interaction tensor, $A-B=1.55$ G and the second and third principal values are $B=-0.2$ G, then curve I, Fig. 4 is the calculated angular dependence of the splitting. Curve I is in good agreement with the points determined from Fig. 1. If these values of A and B are subjected to the symmetry operations of the crystal while maintaining the same twofold rotation axis, curves II and III (Fig. 4) are calculated. These two curves are in good agreement with the observed splitting of the other two sets of doublets. On the basis of this agreement a tentative identification with the g tensor is made, $A\approx\pm 1.35$ G parallel to $g_{||}$ and $B\approx\mp 0.2$ G parallel to $g_{\perp}$.

The spin-lattice relaxation at constant temperature, the independent inversion of each component of the primary doublet (see following paper) and the doublet produced by an interaction with the nearby proton support the hypothesis that the spin state of the E_2' center is $S=1/2$. Since no interactions were observed with nuclei of $I>1/2$, the weak lines observed on either side of the principal doublet (Fig. 3) are assumed to be due to an interaction with at least three nearby nuclei of $I=1/2$. Besides the proton the only other nuclei known to be present in quartz with this spin are Si^{29}. The natural abundance of this isotope is 4.7%. For three equally probable sites near the E_2' center the intensity ratio of each hyperfine line produced by these interactions to the unperturbed line is 0.03. This value is in very good agreement with the observed intensity ratio. The schematic representation of these interactions are shown in Fig. 3(b) and is in agreement with the identification of Si^{29} as the source and in which the Si^{29} interaction is superimposed on the interaction with the proton. As was indicated in Sec. IV, it is probable that $|A|, |B|>|\gamma(Si^{29})\beta_n H|$.

As has been indicated above, one other set of lines was observed to be due to E_2' center, and their intensity ratio to the unperturbed doublet is that expected from interaction with another Si^{29}. These lines exhibit a large isotropic component and their center of gravity with a second-order correction falls at the primary doublet. On the basis of a few data points, the principal values of the anisotropic part appeared to be parallel to the directions of the principal values of the g tensor. If this interaction is due to a Si^{29}, then the Si^{29} hyperfine lines should be split by the same amount as the primary doublet. For the orientation at which measurements were made the splitting was observed to be equal to that of the primary doublets.

Taking the isotropic part of this strong hyperfine interaction as 400×10^{-4} cm^{-1}, the density of the wave function at the Si nucleus was found to be $|\psi(0)|_{\text{exp}}^2 \sim 10\times10^{24}$ cm^{-3}.[16] An estimate,[17] of the value of $|\psi_{3s}(0)|^2\sim 38\times10^{24}$ cm^{-3} for a $3s$ electron on a free Si atom compares favorably with the experimental value. The relatively large value of $|\psi(0)|_{\text{exp}}^2$ is consistent with a hydrogenic model in which the wave function is in a relatively small orbit about a Si ion. Watkins and Corbett[18] have made an estimate for their "B center" in silicon of $|\psi_{3s}(0)|^2\approx 24\times10^{24}$ cm^{-3}. This value is in even better agreement with $|\psi(0)|_{\text{exp}}^2$.

On the basis of these considerations it is assumed that the E_2' center is a Si with an incomplete orbital in which an electron is trapped. Nearby is a proton which produces the primary doublet. For such a defect an estimate of $g_{||}-g_{\text{free electron}}$ can be made. Again, noting the similarities to the "B center" in silicon[18] we expect $\Delta g_{||}\approx 0$ as observed.

Due to the complexities of the quartz structure, the above data are inadequate for developing a detailed model of the defect. However, a comparison of the characteristics of this defect, the E_2' center, with the E_1' center will be of value in defining the limits of such a model. The differences in the optical and thermal properties of the two centers have already been noted.[4] The comparison will be confined to their paramagnetic

[16] $|\psi(0)|_{\text{exp}}^2=\text{I.P.}/[(16\pi/3)\gamma(Si^{29})\beta_n\beta]$, where I.P. = isotropic hyperfine interaction, γ = nuclear g factor of Si^{29}, β_n = nuclear magneton, and β = Bohr magneton.

[17] W. Kohn and J. M. Luttinger, Phys. Rev. **97**, 883 (1955).

[18] G. D. Watkins and J. W. Corbett, Discussions Faraday Soc. **31**, 86 (1961).

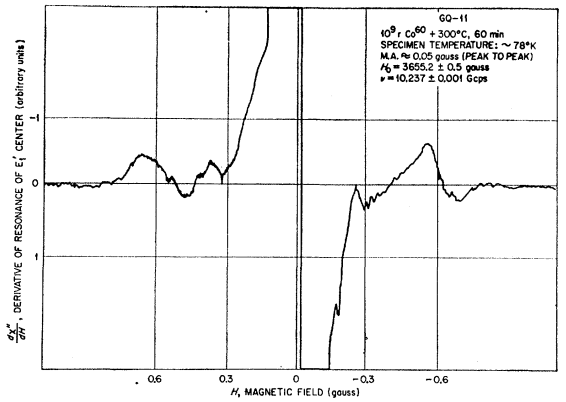

FIG. 5. Two sets of doublets on either side of the E_1' center. One set with a splitting of 1.2 G is clearly resolved. Their intensity is 3% of the intensity of the unperturbed line. The second set has a splitting of ~0.6 G. It is not possible to make an estimate of their relative intensity. The sweep of the magnetic field across the line was slightly nonlinear. The modulation amplitude was ~0.05 G peak to peak.

properties. The anisotropy of the g tensors are similar and the deviations from the free-electron g value are of the same sign and differ only slightly in magnitude. The small g shift implies a small spin-orbit interaction and an orbitally nondegenerate ground state for both centers.[19] The strong hyperfine interactions that have been attributed to a Si atom at the defect site[6] differ only by ~10% in magnitude.

It is the comparison of the weak and very weak hyperfine interactions with nearby Si atoms in addition to their optical and thermal properties that shows the distinct differences between the two centers. As was noted above, doublets with separations between 5 and 10 G were not observed for the E_2' center although they have been found for the E_1' centers. The very weak hyperfine interactions observed for the E_2' center can be interpreted as arising from an interaction of the defect electron with a Si^{29} in one of three neighboring positions. Since the observations on the very weak hyperfine interactions of the E_1' center have not been given before, they are shown in Fig. 5. One pair of doublets is well resolved while another pair is partially resolved in the wings of the unperturbed line. The separation of the well-resolved pair is ≈1.2 G and the separation of the other pair is ≈0.6 G. These separations are approximately the same as for two of the three sets of doublets observed for the E_2' centers. The intensity of the pair with the largest splitting compared to the unperturbed line is 0.03. They are assumed to arise from two nearby sites which are occupied by Si. In view of the similarities of the defect electron wave functions of the two centers noted above, the separation of these neighboring Si atoms from the defect site should be approximately the same in the two cases.

Silsbee[6] has suggested that the weak hyperfine interaction ($A \approx 7$ G) of the E_1' center with two nearby Si atoms is due to an exchange mechanism through two oxygen atoms which have bonds with the defect Si and the two giving the weak interaction. The above comparison of the very weak hyperfine interactions suggests that these interactions may be the ones arising from the mechanism proposed by Silsbee. In this interpretation of the data, the defect Si atom of the E_2' center is bound to three oxygen atoms; the defect Si of the E_1' center to two. The weak hyperfine interactions of the E_1' center are left unexplained.

The first requirement of a model for the E_2' center is that one of the four oxygens normally bonded to the defect Si be missing since the defect Si could not trap an electron if all four bonds were completed. A second requirement follows from the first. If the defect were an oxygen vacancy, then "weak" hyperfine interactions should be observed with the two adjacent Si nuclei. Since these interactions were not found and the electron is localized on only one Si, it is concluded that one of the nearest neighbor Si sites is also vacant. The defect is on the basis of this reasoning a Si—O vacancy. The excess charge due to the remaining O ions around the Si vacancy may be compensated by the monovalent and divalent cation impurities usually present. The nearby proton is one of these impurities. If Si vacancies are present in the crystals prior to irradiation, then positive ion impurities are necessary for charge compensation. The observed variation in the concentration of E_2' centers in the three synthetic crystals for constant γ-ray dose was approximately proportional to the total cation impurity concentration. Also, as was pointed out above, the concentration of hydrogen in these materials was unknown although there was reason to believe[13,15] that it was between 10^{18} and 10^{19} cm^{-3} in the four varieties of quartz. In Fig. 6 a model of the E_2' center is shown which is in agreement with the experimental facts. Such a model would also prescribe the principal directions of the g tensor. $g_{||}$ should be along the Si—Si direction. Referring to Table I, reasonable agreement with this requirement is observed.

Since large γ-ray doses are required to produce appreciable concentrations of the E_2' center, it is probable that ion displacement is required. The displacement of Si^{4+} ions by such irradiation should be at least one half

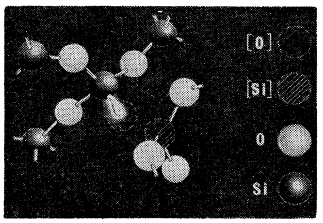

FIG. 6. Proposed structural model for the E_2' center in crystalline quartz. The crystal ball model is shown as viewed about 30° from a [10·0] axis. Regular lattice positions of the silicon and oxygen ions are indicated even though static relaxation is expected. The locations of the impurities are not shown.

[19] L. M. Roth and B. Lax, Phys. Rev. Letters **3**, 217 (1959); L. M. Roth, Phys. Rev. **118**, 1534 (1960).

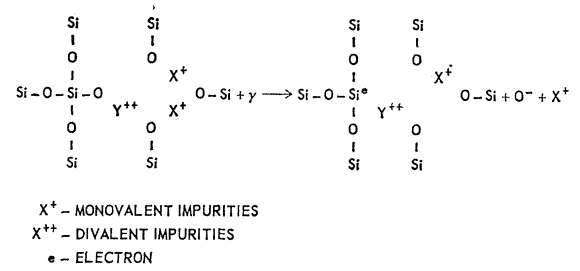

FIG. 7. A proposed model for the generation of E_2' centers by γ irradiation. Complete charge compensation for the Si vacancy is shown for the unirradiated and irradiated state. Because of the relative ease with which monovalent impurities can move along the c-axis channels, such compensation may not occur. This compensation is also determined by the charge state of the other defects since the concentrations of these have always exceeded the concentration of the E_2' centers.

as likely as the displacement of O^{--} ions. If there are Si vacancies in the crystal displacement of O^{--} ions at such sites should have an even higher probability. In Fig. 7 a plausible sequence of events is shown by which the E_2' center can be produced by γ-ray irradiation. Additional support for this process is found from the calculation of the number of O ions displaced by 2×10^9R of Co^{60} γ rays. Oen and Holmes[20] have given the displacement cross sections for O ions. The number displaced is calculated to be $\sim10^{16}$ cm^{-3}.

The third line observed midway between the two E_2' lines, with the c axis parallel to H, exhibits the same functional dependence of the spin lattice relaxation as the two major lines below ≈15°K, but above this temperature there is a difference in the temperature dependence of the spin-lattice relaxation. The similar spin-lattice relaxation below 15°K and the missing T^3 term (see following paper) above 15°K, may be explained in a plausible manner by assuming that this line is a form of the E_2' center from which the proton is missing.

Considering the weak hyperfine interaction of the E_1' center with two nearby Si^{29}, a plausible model is an O divacancy. In this model the weak hyperfine interaction arises from the two nearest-neighbor Si through the oxygen vacancies. Such a defect could trap four or two electrons in a nonparamagnetic state, and such a nonparamagnetic state has been observed indirectly.[4] The paramagnetic state is then the three or one electron state. The requirements of the theory on the temperature dependence of the spin-lattice relaxation are also met by this model (see following paper). Although these models are consistent with the available data, those data are not sufficient to remove all ambiguities, particularly with respect to the defect electron wave function, which are inherent in the models, as Silsbee[6] has pointed out. In Fig. 8 a tentative model of the E_1' center is shown.

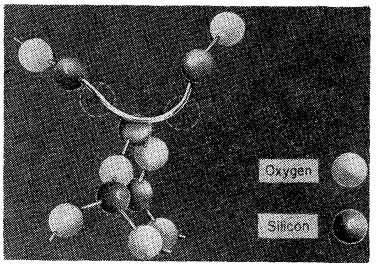

FIG. 8. Proposed structural model for the E_1' center in crystalline quartz. The crystal ball model is shown as viewed along the [10.0] axis. Regular lattice positions of the silicon and oxygen ions are indicated even though static relaxation of the lattice around the defect is expected. The locations of the interstitial impurities are not shown.

VI. CONCLUSIONS

The principal values of the g tensor of a defect of the quartz structure have been found. The principal values of the g tensor and their directions are in reasonable agreement with a proposed model. Hyperfine interactions are observed and explained on the basis of interactions with a Si atom at the defect site and with three other nearby Si atoms. A proton, present in the vicinity of nearly all of the E_2' centers, is the source of a very weak splitting. A comparison of the paramagnetic spectra of this center, the E_2' center, with the E_1' center shows many similarities and suggests a modification of an interpretation that had been given for some of the observed hyperfine interactions.

ACKNOWLEDGMENTS

Discussions with J. G. Castle and D. Feldman have been particularly helpful in developing a model for the E_2' center. H. C. Schweinler has been most helpful in discussions about the problems of analyzing the ESR data in terms of the quartz structure. I thank R. H. Silsbee for pointing out an error in the (form of the) Hamiltonian.

APPENDIX: IMPURITIES OBSERVED IN QUARTZ CRYSTALS

Impurity	GQ	CQ	SQ	NQ
Al	35[a]	70	5	50
Ca	15	7	ND	5
Cu	5	1	ND	1
Fe	4	3	5	1
K	<2	<2	10	
Li	<0.2	<0.2	ND	
Na	200	80	30	<40
Mg	1	0.8	ND	50

[a] Units are parts per million by weight. ND=not detected.

[20] O. S. Oen and D. K. Holmes, J. Appl. Phys. **30**, 1289 (1959).

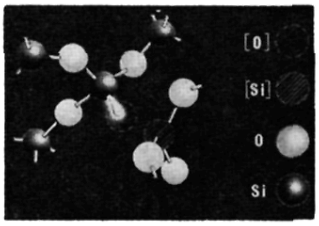

FIG. 6. Proposed structural model for the E_2' center in crystalline quartz. The crystal ball model is shown as viewed about 30° from a [10·0] axis. Regular lattice positions of the silicon and oxygen ions are indicated even though static relaxation is expected. The locations of the impurities are not shown.

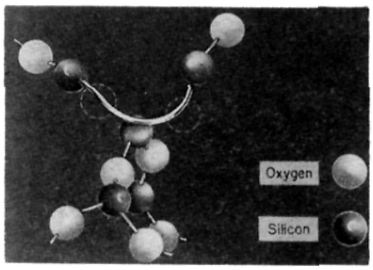

FIG. 8. Proposed structural model for the E_1' center in crystalline quartz. The crystal ball model is shown as viewed along the [10.0] axis. Regular lattice positions of the silicon and oxygen ions are indicated even though static relaxation of the lattice around the defect is expected. The locations of the interstitial impurities are not shown.