

Infrared spectra of hydrogen isotopes in α -Al₂O₃

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Infrared absorption of OH⁻, OD⁻, and OT⁻ in α -Al₂O₃ at 77 K occurs at energies of 3282, 2439, and 2069 cm⁻¹, respectively. A small band at 3266 cm⁻¹ disappeared after high-temperature treatment of the crystal and was attributed to an OH⁻ ion which is perturbed by an unidentified defect. Calculations of the electrostatic potential combined with measurements of the polarization of the absorbed light indicated that the OH⁻ ion lies in the basal plane of the crystal. No evidence was found from measurements of the EPR spectrum of a γ -irradiated crystal for the presence of V_{OH}⁻ centers in α -Al₂O₃.

I. INTRODUCTION

Possible technological applications of refractory oxides in the development of new energy sources have led to much interest in and research on these materials. Its strength and high melting temperature make aluminum oxide particularly interesting as a potential first-wall material in thermonuclear reactors and for hydrogen-containment applications. In regard to the latter, the characterization of hydrogenic species in α -Al₂O₃ is important in order to determine the solubility and diffusivity of hydrogen. In this work we report our observations of the absorption of infrared light due to hydrogen, deuterium, and tritium in α -Al₂O₃.

Bates and Perkins¹ recently observed infrared absorption from these isotopes in rutile. The frequencies which they found for the absorption bands fit those of an anharmonic oscillator in which the hydrogen isotope is chemically bound to an oxygen ion forming an OH⁻ ion. Our frequency data for aluminum oxide were well fit to the same model. In addition, the results of potential-energy calculations have suggested possible orientations of the OH⁻ ion, and these results are compared with experiment.

II. EXPERIMENTAL CONSIDERATIONS

Sapphire crystals of uv grade were obtained from the Union Carbide Corporation's Crystal Products division. The crystals were cut to dimensions of 3.2 × 11.2 × 12.7 mm and polished to optical transparency. Their orientation was such that the *c* axis lay within 1° of the 12.7-mm edge.

As will be discussed in Sec. III E, the integrated intensity of the infrared absorption of the OH⁻ band indicated that the as-received crystals contained approximately 2.6 × 10¹⁵ cm⁻³ of OH⁻. For the OH⁻ measurements no further doping was necessary. Deuterium was introduced into a crystal by heating it to 1000 °C in flowing D₂ gas at a temperature of 760 Torr for 24 h. A tri-

tium-doped sample was prepared by sealing the crystal in a quartz ampoule which had been evacuated and back-filled with T₂ gas at a pressure of 140 Torr. The ampoule was heated for 4 days at 1000 °C, at which temperature the T₂ gas pressure over the sample was approximately 600 Torr.

Measurements of the intensity of the OH⁻ band as a function of polarization of the light were made using a Perkin-Elmer 621 double beam spectrophotometer. The polarizer was of the wire grid type having an extinction ratio of 100:1. All other infrared measurements were made on a Digilab FTS-20 Fourier transform spectrometer. The resolution of this instrument was about 3 cm⁻¹. In these experiments between 500 and 1000 spectral scans were made and averaged. Each single beam spectrum of the crystal was divided by the spectrum of the evacuated sample chamber. Low-temperature data were taken with the crystal mounted on the cold finger of a liquid nitrogen cryostat. All Fourier transform spectra were obtained with the crystal mounted such that the light was directed parallel to the *c* axis (i.e., so that the total path length was 12.7 mm).

III. INFRARED SPECTRA AND THEIR ANALYSIS

A. Isotope frequency shifts

Figure 1 shows the infrared absorption in crystals of α -Al₂O₃ containing hydrogen, deuterium, and tritium at a temperature of 77 K. The rather steeply sloping background apparent in the bottom spectrum of Fig. 1 is due to the high-energy edge of the α -Al₂O₃ lattice absorption which overlaps the OT⁻ band. The value of each peak frequency and its uncertainty were determined by fitting a Gaussian function to the absorption band. The values so determined are given in the column headed ν_{exp} in Table I.

As in the case of rutile,¹ the model of an anharmonic diatomic oscillator, which consists of

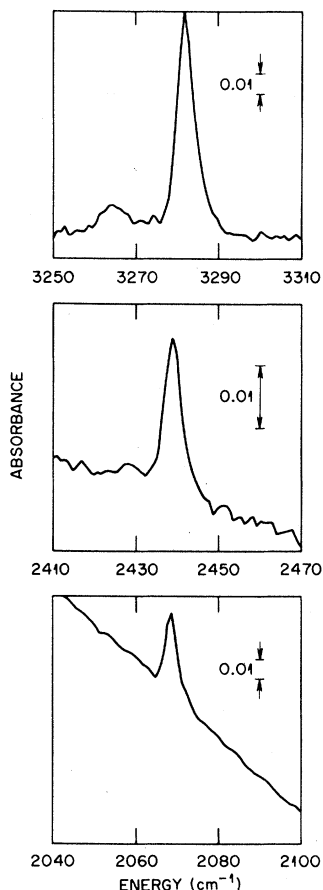


FIG. 1. OH⁻ (top), OD⁻ (center), and OT⁻ (bottom) infrared absorption bands in α -Al₂O₃ at 77 K.

the hydrogen isotope bound to an oxygen ion, yielded a very good fit of the isotopic frequencies. Herzberg² gives the energy levels for such an oscillator as

$$E_n = (n + \frac{1}{2})\rho_i\omega_e - (n + \frac{1}{2})^2\rho_i^2\omega_e x_e + \dots, \quad (1)$$

where E_n is the energy of a level of vibrational quantum number n , ω_e , and x_e are constants, and ρ_i is given by

$$\rho_i = (\mu_1/\mu_i)^{1/2}, \quad (2)$$

where μ_i is the reduced mass $m_i m_o / (m_i + m_o)$ of the oscillator of the hydrogen isotope i of atomic mass m_i , and m_o is the atomic mass of oxygen. Using the atomic masses of hydrogen, deuterium, tritium, and oxygen, (1.007825, 2.0140, 3.01605, and 15.99491 amu, respectively), we find $\rho_1 = 1.0000$, $\rho_2 = 0.7280$, and $\rho_3 = 0.6112$. Using only the first- and second-order terms of Eq. (1) we find that the frequency for the ground to first excited state transition is given by

$$\nu_i = \rho_i\omega_e - 2\rho_i^2\omega_e x_e. \quad (3)$$

We made a least-squares fit of this equation to the observed frequencies and determined the values of $\rho_i\omega_e$ and $\rho_i^2\omega_e x_e$ shown in Table I. It should be noted that the uncertainties given in Table I are large relative to the accuracy of the experimentally observed frequencies due to a rather large correlation between the parameters ω_e and $\omega_e x_e$. That is, a small increase in ω_e , for example, may be compensated for by an increase in $\omega_e x_e$ without affecting the fit very much. The frequencies calculated from these best fit parameters are given in the column labeled ν_{fit} . As is seen, in most cases these calculated frequencies are within 1 cm⁻¹ of those observed experimentally.

The quantity $D_0 = (\rho_i\omega_e - \rho_i^2\omega_e x_e)^2 / 4\rho_i^2\omega_e x_e$, also shown in Table I, represents the dissociation energy of the ion.^{2,3} The slight variations in D_0 with isotopic mass are due to differences in the zero-point energies of OH⁻, OD⁻, and OT⁻.

B. OH⁻ and OD⁻ distributions within the crystal

From measurements of tritium diffusion in α -Al₂O₃ by Fowler *et al.*,⁴ we estimate the coefficient of self-diffusion D for deuterium to be approximately 3×10^{-10} cm²/sec for a crystal temperature of 1000 °C. Assuming a simple random-walk model for the diffusion,⁵ the rms pene-

TABLE I. Frequencies (ν), bandwidths (δ), and spectroscopic constants for OH⁻, OD⁻, and OT⁻ bands in α -Al₂O₃.^a

	T (K)	ν_{exp} (cm ⁻¹)	δ_{exp} (cm ⁻¹)	$\rho_i\omega_e$ (cm ⁻¹)	$\rho_i^2\omega_e x_e$ (cm ⁻¹)	ν_{fit} (cm ⁻¹)	D_0 (eV)
OH ⁻	300	3279.1 ± 0.4	9.3 ± 0.6	3535.7 ± 3.9	128.3 ± 2.0	3279.1	2.80 ± 0.05
	77	3282.4 ± 0.3	5.6 ± 0.4	3542.2 ± 2.3	129.9 ± 1.2	3282.4	2.78 ± 0.03
OD ⁻	300	2436.9 ± 1.4	6.8 ± 2.8	2574.0 ± 2.9	68.0 ± 1.1	2438.0	2.86 ± 0.05
	77	2438.9 ± 0.9	5.3 ± 1.6	2578.7 ± 1.7	68.9 ± 0.6	2441.0	2.83 ± 0.03
OT ⁻	300	2065.7 ± 1.1	5.6 ± 2.4	2161.0 ± 2.4	47.9 ± 0.8	2065.2	2.89 ± 0.05
	77	2068.7 ± 0.6	4.0 ± 1.0	2165.0 ± 1.4	48.5 ± 0.4	2067.9	2.86 ± 0.02

^a δ_{exp} is the full width at half-band maximum. ν_{fit} is the band energy calculated from the best-fit parameters $\rho_i\omega_e$ and $\rho_i^2\omega_e x_e$.

tration depth of the deuterium is given by $(2Dt)^{1/2}$. For the treatment time of 24 h the deuterium penetration depth is found to be less than 0.1 mm.

A series of very simple experiments has confirmed a greater deuterium concentration at the crystal surface and, in addition, has shown a concomitant decrease in the OH^- concentration. The face of the deuterium diffused crystal normal to the beam direction was 3.2 mm wide and 11.2 mm high. In one experiment we placed a mask 1.79 mm wide and 11 mm long in the center of the crystal face so that transmitted light passed through the crystal near its side faces. In a second experiment we used a mask 2.36 mm wide. In Fig. 2 the intensities of the OH^- and OD^- bands from these experiments are compared with those of an experiment in which no mask was used. The OH^- band, shown at the top of the figure, decreases in intensity as the sampled region of the crystal lies closer to the side faces. By contrast, the OD^- band, shown at the bottom of Fig. 2, increases in intensity.

Another crystal was cooked in a vacuum at 1000 °C for 24 h. The ratio of its spectrum to that of an untreated crystal showed no detectable difference in the OH^- band intensity. The diminution of the OH^- band intensity in the deuterium diffused crystal, therefore, suggests that isotopic substitution of D for H is taking place.

Admittedly, the small size of the hydrogen diffusion length makes it difficult to detect the small changes in the OH^- band intensity which may result from vacuum heat treatment. In fact, given the small value of the diffusion coefficient, it is somewhat surprising that the OD^- and OT^- bands are as intense as they are. We suspect that a slight divergence of the beam combined with total internal reflection from the crystal surfaces, where OD^- and OT^- concentrations are highest, results in disproportionately large values of the intensities of these bands. These effects, in addition to diffraction of the light around the mask, make it very difficult to use measurements of band intensity versus mask size to determine the deuterium or tritium concentration profiles.

C. OH^- satellite band at 3266 cm^{-1}

Changes in the spectra in the region of the OH^- band for temperatures of 77 and 300 K are illustrated in Fig. 3. We are uncertain of the origin of the small band near 3266 cm^{-1} , which we designate the *s* (for satellite) band. The peak heights, energies, and widths of the OH^- and *s* bands were found using a least-squares fit of Gaussian functions to the data. The integrated intensities *A* of the bands were calculated from

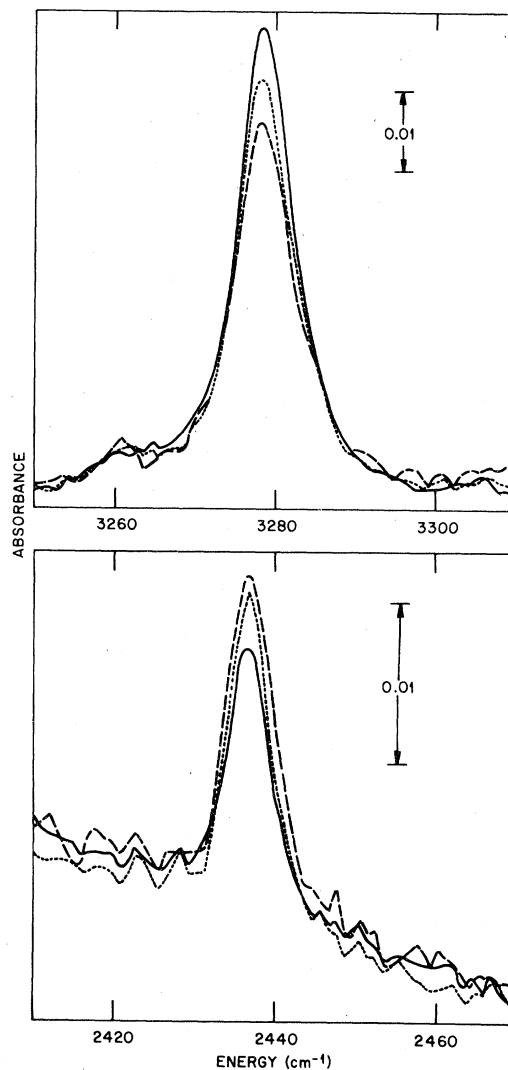


FIG. 2. Changes in OH^- and OD^- infrared absorption band intensities when the light path through the central portion of the crystal is blocked by masks of widths 0.0 mm (—), 1.79 mm (---), and 2.36 mm (- - -).

$$A = a\delta\sqrt{\pi}/2(\ln 2)^{1/2}, \quad (4)$$

where *a* is the peak height and δ is the full width at half-band-maximum. The parameters so determined are given in Table II.

The closeness of the satellite-band energy to that of the OH^- band suggests an association between the species which causes the satellite band and the OH^- ion. The satellite band could arise, for example, either from an OH^- ion in a different orientation from those OH^- ions which cause absorption at 3279 cm^{-1} or from an OH^- ion which is perturbed by a nearby defect. If such an association exists, one might expect the

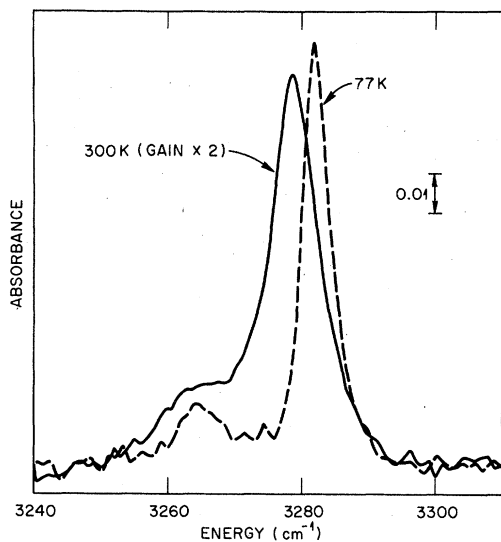


FIG. 3. Comparison of the infrared absorption spectra in the region of the OH^- band for temperatures of 77 and 300 K.

temperature dependence of the two bands to be similar. Although the results shown in Table I indicate that the energy of the satellite band is unchanged with temperature, the uncertainty in the measured value makes it impossible to rule out a temperature effect similar to that of the OH^- band.

The intensity of the satellite band is greatly reduced following high temperature treatment of the crystal. Figure 4 shows the spectrum of an as-received crystal superposed on that of the same crystal after annealing at 800°C for 48 h. If the satellite band is due to a hydrogenic species, is this species removed from the crystal (perhaps by conversion from OH^- to H or H_2) or converted to the OH^- center producing the main peak? Our data do not provide an unambiguous answer. The integrated intensity of the OH^- band grew by only about 10% after annealing, but in the as-received crystal the satellite-band intensity is approximately 30% of that of the OH^- band. A change in the oscillator strength of the satellite-band species as a result of physical

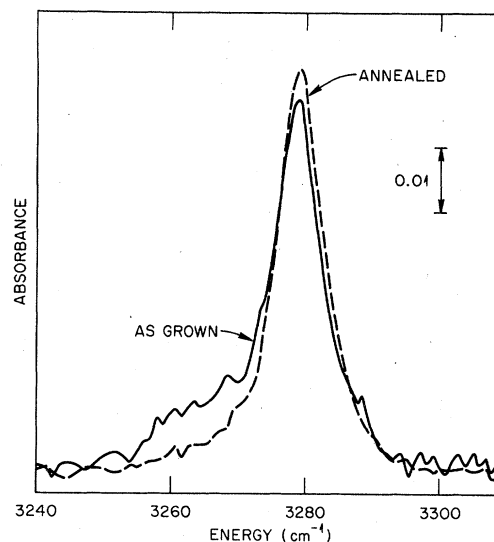


FIG. 4. Comparison of the infrared absorption spectra in the region of the OH^- band of an as-grown crystal and a crystal which was held at a temperature of 800°C for 48 h. The intensity of the satellite band at 3266 cm^{-1} is reduced as a result of this heat treatment.

changes which take place during annealing could account for this discrepancy.

D. Orientation of the OH^- ion

In order to learn something about the orientation of the OH^- ion within the crystal we measured the polarization of the absorbed light. For these measurements the crystal was mounted with its c axis perpendicular to the beam direction. The OH^- band shape was recorded for 10° increments of the angle θ between the polarization of the light and the basal plane. The chart recorder data were digitized on a programmable calculator, and the computer program subtracted the background and integrated the result using Simpson's rule. The intensities as a function of angle are shown in Fig. 5. We made two to four measurements of the band intensity for most angles. In addition to uncertainty in the background, a slight instability in the apparatus contributed to the un-

TABLE II. Comparison of energies (ν), bandwidths (δ), and intensities (A) of the OH^- band with its satellite s .^a

T (K)	ν_{OH} (cm^{-1})	δ_{OH} (cm^{-1})	A_{OH} (cm^{-2})	ν_s (cm^{-1})	δ_s (cm^{-1})	A_s (cm^{-2})
300	3279.1 ± 0.4	9.3 ± 0.6	0.81 ± 0.07	3265.6 ± 1.8	14.1 ± 3.5	0.27 ± 0.09
77	3282.4 ± 0.3	5.6 ± 0.4	1.05 ± 0.10	3265.9 ± 2.7	11.8 ± 5.0	0.27 ± 0.05

^a δ is the full width at half-band maximum. The intensity A is $\int \alpha(\nu) d\nu\text{ cm}^{-2}$, where $\alpha(\nu)$ is the absorption coefficient.

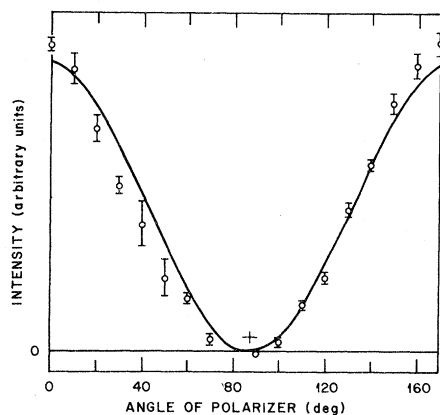


FIG. 5. Integrated intensity of the OH^- band vs polarization of light. At an angle of approximately -3° the polarization of the light is perpendicular to the c axis.

certainties in the data points shown.

The data were fit using the function

$$A = a_1 \cos^2(\theta + a_2) + a_3, \quad (5)$$

where a_1 , a_2 , and a_3 were adjusted. The parameter a_2 accounts both for possible deviation of the actual polarizer transmission axis from the dial reading and for possible misalignment of the crystal c axis; a_2 turned out to be about -3° . As Fig. 5 shows, the curve clearly reaches zero for $\theta = 90^\circ$. Because the dipole moment of the ion lies along the OH^- bond, we conclude that the OH^- ion lies in the basal plane.

We have made an approximate calculation of the potential of the OH^- ion in the crystal using a procedure similar to that described by Bates *et al.*⁶ The three possible orientations found by the calculation are shown in Fig. 6. In the aluminum oxide molecular unit the three oxygen atoms form an equilateral triangle, the plane of which is the crystal basal plane, with the two aluminum atoms directly above and below the center of the triangle.⁷ One orientation of the OH^- ion, labeled $\text{H}^+(1)$ in Fig. 6, has the proton lying in the basal plane in a direction directly away from the center of the oxygen triangle. The other two orientations, labeled $\text{H}^+(2)$ and $\text{H}^+(3)$, are such that the O-H bonds make angles of $+13^\circ$ and -13° , respectively, to the basal plane. The projections of the bonds onto the basal plane are at 30° from the nearby O-O bonds.

The parameters used in the above calculation are now known well enough to be able to trust the calculated values of the minimum potential energy. However, if the OH^- ions lie in orientation (2) or (3), it would be possible to observe the OH^- band for any polarization. The cross above the angle of 87° in Fig. 5 shows the minimum intensity

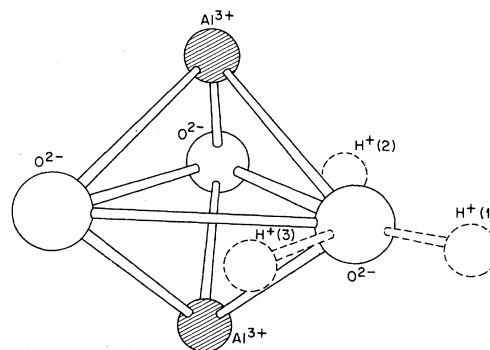


FIG. 6. Aluminum oxide molecular unit. The dashed circles show possible orientations of the proton of the OH^- ion based on calculations of the potential energy.

expected for these orientations. The curve clearly passes through zero, so we are led to conclude that the OH^- ion lies in orientation (1).

We considered the possibility that the OH^- satellite line at 3266 cm^{-1} might be an OH^- ion in one of the other orientations. If this orientation were metastable with respect to orientation (1), then annealing might cause reorientation into (1), thus reducing the satellite-band intensity. An OH^- defect in one of these other orientations would be expected to show a measurable absorption of light polarized parallel to the c axis. However, an as-received crystal showed no indication of this band for light having such polarization. Thus, this band behaves as expected of a band associated with a defect that anneals out rather than with a defect that reorients.

E. OH^- concentration

Johnson *et al.*⁸ were able to determine the total hydrogen concentration, n_{H} , in TiO_2 by exchanging deuterium for hydrogen and measuring the change in mass of the crystal. Unfortunately, the weakness of the OH^- infrared band in Al_2O_3 indicates that the hydrogen concentration is so small as to make this method impractical for this material.

It is possible, however, to make an approximate estimation of the hydrogen concentration using the optical parameters for TiO_2 . In addition to measuring the mass differences of their sample, Johnson *et al.* measured the integrated intensity A_{H} of the OH^- band for a sample of known hydrogen concentration n_{H} . This permitted them to determine the oscillator strength f for the transition from Smakula's equation⁹

$$n_{\text{H}} f = (A_{\text{H}} \mu c^2 / \pi e^2) 9n / (n^2 + 2)^2 \quad (6)$$

where μ is the reduced mass of the OH^- ion (equal to 0.9481 amu), c is the speed of light, e is the charge of an electron in esu, and n is the index

of refraction of the host crystal at the wavelength of the transition. Using this equation Johnson *et al.* obtained a value 3.8×10^{-2} for the oscillator strength of the OH⁻ ion for measurements at room temperature.

Bates and Perkins¹ observed the room temperature OH⁻, OD⁻, and OT⁻ bands in TiO₂ at frequencies of 3276, 2437, and 2065 cm⁻¹, respectively. These values are very close to those we have found (3279, 2437, and 2066 cm⁻¹) for α -Al₂O₃. By contrast, the values of the OH⁻ frequency in the alkali halides observed by Wedding and Klein¹⁰ were significantly higher. These frequencies were found to be above 3600 cm⁻¹ for all host crystals. Because of the closeness of the OH⁻ band energies in TiO₂ and α -Al₂O₃, we assume that its oscillator strength in α -Al₂O₃ is not very different from that in TiO₂. However, Johnson *et al.*⁸ point out that because the static dielectric constant of TiO₂ is very large ($\epsilon = 173$), there may be significant local distortion around the defect. Therefore, the Lorentz-field correction, given by the factors $9n/(n^2 + 2)^2$ of Eq. (4), may not be a very good approximation, and hence the oscillator strength obtained by Johnson *et al.* may be somewhat inaccurate. With this possible error in mind we can estimate the OH⁻ concentration in α -Al₂O₃ using Eq. (4) with the index refraction¹¹ at 3279 cm⁻¹ of $n = 1.711$. The result is $n_H = 2.6 \times 10^{16}$ cm⁻³.

F. Charge compensation and the OH⁻ defect

The OH⁻ stretching vibration occurs at 3296 cm⁻¹ in MgO crystals.¹² Following x irradiation of this crystal at 77 K the 3296-cm⁻¹ band intensity is reduced and another band appears at 3323 cm⁻¹. There is a correlation in intensity between this latter band and ESR signals from the V_{OH}⁻ center, which has a structure represented by OH⁻-[Mg²⁺]-O⁻, where [Mg²⁺] is a Mg²⁺ vacancy and O⁻ is an oxygen ion which has captured a hole. Such a defect is electrically neutral. It was concluded that the 3296 cm⁻¹ band arises from an OH⁻ ion adjacent to a magnesium vacancy; that is, the band arises from a V_{OH}⁻ center, which is negatively charged. It is widely believed¹³ that charge compensation is provided by impurities. For example, Fe³⁺ substituting for Mg²⁺ is frequently suggested.

Turner and Crawford^{14,15} have also observed the 3279-cm⁻¹ band (the energy of which they report as 3278 cm⁻¹) in α -Al₂O₃. Following room-temperature γ irradiation of the crystal they observed an attenuation of this band similar to that of the 3296-cm⁻¹ band in MgO. Also similar to MgO, a new band appeared in the irradiated sam-

ple at 3316 cm⁻¹. Reasoning by analogy with MgO, they speculated that the 3279 cm⁻¹ band in α -Al₂O₃ was due to an OH⁻ ion adjacent to an aluminum vacancy and that the 3316-cm⁻¹ band was due to such a defect which had captured a hole. They called the latter defect a V_{OH}⁻ center.

If this model were correct, the OH⁻ ion would lie along the oxygen-aluminum-vacancy direction, and would therefore make an angle of 42° to the basal plane. For this bond orientation we estimate the ratio of the minimum to maximum intensities of the band-versus-polarization angle of the light to be 0.62. Figure 5 shows that this ratio is actually 0.0 to within experimental error. Thus, the OH⁻-aluminum-vacancy model is inconsistent with our polarization data.

Furthermore, we have failed to find evidence from magnetic resonance experiments for the V_{OH}⁻ center following either room-temperature or low-temperature γ irradiation. A sample was irradiated at 77 K with γ rays from a ¹³⁷Cs source for 30 min corresponding to a total dose of about 2×10^5 R. Without warming the sample, we measured the electron paramagnetic resonance spectrum and found no trace of the V_{OH}⁻ center. We then irradiated the sample at 300 K for 2 h with 2-MeV electrons from a Van de Graaff accelerator for a total dose of $\sim 4 \times 10^{17}$ electrons/cm². Immediately following this treatment we irradiated the sample for another 30 min at 77 K in the γ -ray source as described above. (Irradiation at low temperature was necessary in order to observe possible atomic hydrogen which is expected to be unstable at higher temperatures.¹⁶) No EPR signals from either the V_{OH}⁻ center or atomic hydrogen were detected.

We observed an EPR line produced by room-temperature irradiation similar to that reported by Gamble *et al.*¹⁷ Electron-nuclear-double-resonance (ENDOR) experiments on a sample at 4.2 K were performed, but no hydrogen nuclei were found to be associated with the radiation damage center. It was possible to observe many strong ENDOR signals from Al³⁺ ions having hyperfine interactions with an unidentified impurity ion which we suspect is Fe³⁺, although a careful determination was not made.¹⁸ It was also possible to observe a weak, distant ENDOR signal¹⁹ at the hydrogen nuclear Zeeman frequency from hydrogen located at some distance from the impurity. The low intensity of this signal was not inconsistent with our estimate of the hydrogen concentration from the optical measurements. Thus, we concluded that the sensitivity of the apparatus was sufficient to permit detection of a paramagnetic V_{OH}⁻ center if it were present. The results of these experiments bring into question

the validity of the V_{OH^-} -center model.

If an OH^- ion replaces an O^{2-} ion, a net charge of +1 is left in the vicinity of the ion. Müller and Günthard²⁰ observed that the valence of Ni^{3+} or Co^{3+} in $\alpha-Al_2O_3$ may be reduced to 2+ by cooking the sample in hydrogen gas at high temperatures. Such a reduction could account for the charge compensation of the OH^- ion. However, Müller and Günthard also observed a broad infrared absorption band at significantly lower energies (about 3000 cm^{-1}) than the 3279 cm^{-1} which we observed. They attributed this absorption to a hydrogen-bonded group of the type $O-H \cdots O$. Thus, the defect or impurity which allows charge compensation of the OH^- ion remains unidentified.

IV. CONCLUDING REMARKS

Our observations of the OD^- and OT^- bands show that hydrogen diffuses into $\alpha-Al_2O_3$ by combining with O^{2-} ions. Polarization of light measurements on OH^- show that these ions lie in the basal plane. These experiments provide a basis for understanding the microscopic processes involved in diffusion mechanisms of H, D, and T.

A question which remains, however, is whether the hydroxyl ion is the only form in which hydrogen exists within $\alpha-Al_2O_3$. The EPR experiments showed no evidence of atomic hydrogen which, as

a paramagnetic defect, would be expected to produce magnetic resonance signals. Another possible form is molecular hydrogen H_2 , which would be undetectable by infrared absorption measurements. The frequency of the stretching mode of the free H_2 molecule²¹ is about 4160.2 cm^{-1} . This mode of H_2 has been observed²² in solids in the range of 4142 to 4152 cm^{-1} . We were unable to observe Raman scattering of visible light in the region 3500 to 4200 cm^{-1} where the H_2 molecule in $\alpha-Al_2O_3$ might be expected to have its stretching frequency. However, Raman scattering is not a sensitive probe for impurities at low concentrations. We were also unable to see Raman scattering from the OH^- ion which was present in small concentrations. Thus, we are not able to rule out the possibility of molecular hydrogen being present in small amounts.

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