the present work for the bands of curves a, b+c, and d of Fig. 2

ACKNOWLEDGMENTS

Optical Absorption and Photoconductivity in the Band Edge of β-Ga₂O₃†

H. H. Tippins

Aerospace Corporation, El Segundo, California

(Received 14 May 1965)

Optical absorption and photoconductivity have been observed in the ultraviolet in single crystals of nominally pure β-Ga₂O₃. At room temperature a steep absorption edge, characteristic of a band-to-band transition, is observed at 2700 Å. The edge is shifted approximately 100 Å toward shorter wavelengths when the temperature is reduced to 77°K. Photoconductivity begins coincident with the absorption edge at 77°K, but could not be detected at room temperature. A model is proposed in which the absorption arises as a result of excitation of an electron from the oxygen $2p$ band to the gallium $4s$ band. Calculations using this model and the Born-Haber cycle are in good agreement with the observed band gap of 4.7 eV. It is suggested that the much smaller band gap of β-Ga₂O₃ as compared with sapphire is due to the reduced coordination number of the ions involved in the transition.

SEVERAL important properties of the β form of Ga₂O₃ have recently been investigated in studies of the crystal structure by Geller[1] and the optical and microwave properties of Ga₂O₃:Cr by Peter and Schawlow[2] and Tippins.[3] In this paper are reported some preliminary results on the ultraviolet absorption spectrum and photoconductivity observed in the pure crystal. A simple charge-transfer model is proposed to explain the absorption process, and calculations based on this model are in good agreement with the position of the absorption edge. Several interesting features result from the relatively complicated Ga₂O₃ crystal structure not encountered for other wide-band-gap semiconductors previously studied.

The crystals used for this investigation were obtained from boules grown by Chase[4] using the Verneuil technique. The primary cleavage planes for Ga₂O₃ are (100). The crystal cleaves easily and frequently spontaneously along these planes, which makes fabrication of samples with good optical faces oriented in an arbitrary direction almost impossible. However, with sufficient care, the cleavage planes themselves provide a satisfactory surface.

Figure 1 shows the absorption edge obtained for a sample 86 μ thick. The light is incident normal to the (100) plane. These data were recorded on a Cary model 14 spectrophotometer and are not corrected for multiple internal reflections. The low-temperature data were obtained using a cold-finger–type Dewar with quartz windows. Except for the one shoulder there is very little structure. Reducing the temperature to 77°K shifts the edge approximately 100 Å to the blue but
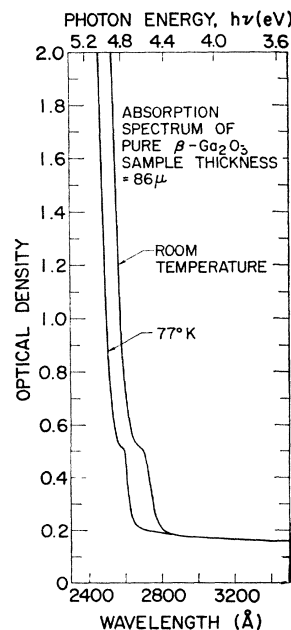

FIG. 1. Absorption edge of pure β-Ga₂O₃.

† This research was supported by the United States Air Force under Contract No. AF 04(695)-469.
[1] S. Geller, J. Chem. Phys. **33**, 676 (1960).
[2] M. Peter and A. L. Schawlow, Bull. Am. Phys. Soc. **5**, 158 (1960).
[3] H. H. Tippins, Phys. Rev. **137**, A835 (1965).
[4] A. Chase, J. Am. Ceram. Soc. **47**, 470 (1964).

does not change the shape. The absorption edge measured at liquid-helium temperature is almost identical and unshifted to that observed at 77°K.

The large absorption coefficients observed are characteristic of a band-to-band transition, and the question of whether the absorption is accompanied by photoconductivity is of interest. Photoconductivity was observed at 77°K in the region of the absorption edge using the rate-of-charge method with blocking electrodes. However, good reproducible photoconductivity data could not be obtained. The photoresponse is a sensitive function of the illumination and thermal history of the sample, its cooling rate, and the preparation of the surface through which the light enters. The photoconductivity samples were fabricated such that the cleavage planes were parallel to the field electrodes and the light entered an edge perpendicular to the electrodes. The latter edge was lapped and polished, but it was not possible to obtain a really satisfactory surface. Figure 2 shows a typical photoresponse per incident photon versus wavelength. Although these data are not completely reproducible, the response invariably begins at wavelengths much longer than that of the absorption edge, reaches a peak near the edge, and decreases to zero near 2400 Å.

A model, similar to the one used to interpret the fundamental absorption of the alkali halides,[5,6] has been constructed to explain the position of the Ga$_2$O$_3$ absorption edge. We assume that the highest filled band is the oxygen $2p$ band and that the absorption arises when an electron is excited to the $4s$ level of a neighboring gallium ion. Since the cations and anions both have more than one site, the structure[1] of Ga$_2$O$_3$ is of primary importance for this interpretation. There are two crystallographically nonequivalent gallium ions and three nonequivalent oxygen ions in the unit cell. Each Ga$_I^{3+}$ ion is surrounded by a distorted tetrahedron of oxygen ions (average Ga-O spacing 1.83 Å). Each Ga$_{II}^{3+}$ ion is surrounded by a highly distorted octahedron of oxygen ions (average Ga-O spacing 2.01 Å). The O$_I^{2-}$ and O$_{II}^{2-}$ ions both have three nearest-neighbor gallium ions, whereas the O$_{III}^{2-}$ ion has four nearest-neighbor gallium ions. The number and types of nearest neighbors for each of the five ions are summarized in Table I. The structure may be considered as built up from these distorted tetrahedra and octahedra.

The total energy required to remove an electron from an oxygen $2p$ level and transfer it to an unfilled $4s$ level of a gallium ion at a distance r_0 is

$$h\nu = \epsilon_+ + \epsilon_- - e^2/r_0 + \chi(O^{2-}) - I(Ga^{2+}) - \psi_{pol}, \qquad (1)$$

where ϵ_+ and ϵ_- are the magnitudes of the electrostatic lattice energies at the gallium and oxygen sites, χ is the oxygen electron affinity, I is the ionization potential

TABLE I. Ion coordination in Ga$_2$O$_3$.

Nearest neighbors of opposite sign	O$_I$	O$_{II}$	O$_{III}$
Ga$_I$	1	2	1
Ga$_{II}$	2	1	3

of Ga^{2+}, and ψ_{pol} is the polarization energy of the dipole formed by the charge transfer. The energies ϵ_+ and ϵ_- are in general determined from the Madelung constant but unfortunately this quantity has not been evaluated for the Ga$_2$O$_3$ structure. However, values of ϵ_+ and ϵ_- sufficiently accurate for our purposes can be obtained in the following way. By use of the Born-Haber cycle, the Ga$_2$O$_3$ total lattice energy is calculated from the measured heat of formation.[7] Next, it is assumed that the ratio of the total lattice energy to the electrostatic part of the lattice energy is the same for Ga$_2$O$_3$ and α-Al$_2$O$_3$. This ratio (approximately 0.82 for Al$_2$O$_3$) varies very little from one substance to another; the assumption should therefore introduce an error of a few percent at the most. We obtain in this way E_e(Ga$_2$O$_3$) $\cong$4400 kcal/mole. The contribution of the various gallium and oxygen ions to the total lattice energy is not the same because of the different coordination numbers. In fact, Templeton[8] and Kapustinsky[9] have shown that to a very good approximation the electrostatic lattice energy of an ion is proportional to its coordination number. It is therefore convenient to define a quantity φ such that $\epsilon_+ = C_+\varphi$ and $\epsilon_- = C_-\varphi$, where the C's are the coordination numbers of the ions. Thus, φ is the electrostatic energy per valence bond and can be calculated from

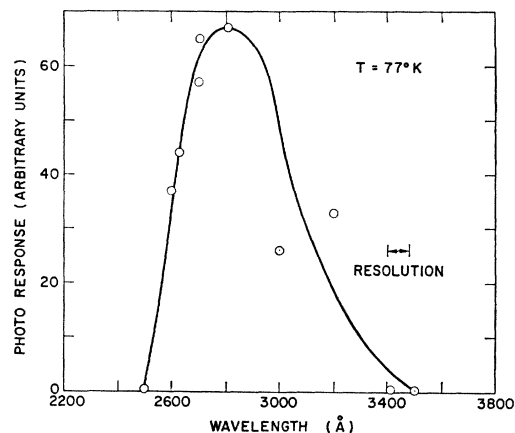$$\varphi = 2E_e/N \sum_{molecule} C_i Z_i, \qquad (2)$$

FIG. 2. Wavelength dependence of the transient photoconductivity in pure β-Ga$_2$O$_3$.

[5] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, Inc., London, 1948).

[6] F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940).

[7] *Handbook of Chemistry and Physics* (Chemical Rubber Publishing Company, Cleveland, Ohio, 1963).

[8] D. H. Templeton, J. Chem. Phys. **21**, 2097 (1953) and **23**, 1826 (1955).

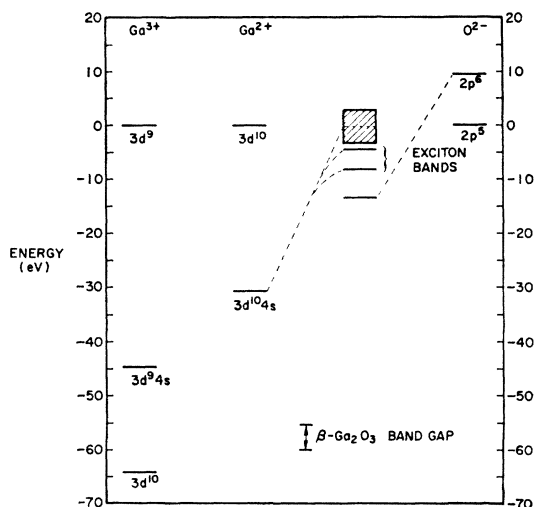[9] A. Kapustinsky, Z. Phys. Chem. **B22**, 257 (1933).

FIG. 3. Energy-level diagram for β-Ga$_2$O$_3$. The displacement of the free-ion energy levels for a tetrahedral Ga$_I^{2+}$ and threefold coordinated O^{2-} when the lattice is formed is indicated by the dashed lines. The optical-band-edge energy is shown on the same scale and should be compared with the energy of the first exciton transition.

where N is Avogadro's number and Z_i is the valence of the ions. The value of φ obtained in this way is 7.6 eV. From Eq. (1) and the above, we note that the threshold energy for absorption involves those ions with the lowest coordination number, namely the tetrahedral gallium and one of the threefold coordinated oxygen ions. It should be noted that the φ obtained here is a certain average of the φ's for the positive and negative ions. If a separate φ_+ and φ_- were determined for the cations and anions, the values would be expected to be somewhat different. However, it can be shown that the error introduced in the calculation of the transition energy using this averaged φ is less than 0.1φ.

Figure 3 shows how the energy levels of the free ion are shifted due to the electrostatic energy to form the crystal energy levels. The diagram is drawn for tetrahedrally coordinated gallium ions and threefold coordinated oxygen ions. The ψ_{pol} term is not taken into account in this figure. The energy level of O^{2-} relative to the normal state of O$^-$ is shown at the right of Fig. 3. The lattice potential at the position of the negative ions is positive so that the levels of the O^{2-} are depressed as indicated by the dashed line. For the threefold coordinated oxygens this shift is 3φ. The energy levels of Ga^{3+} and Ga^{2+} as determined spectroscopically are shown at the left of the figure. The change of the Ga^{2+} $4s$ level produced by the lattice potential is indicated by the dashed line and amounts to 4φ for the tetrahedrally coordinated gallium. In addition to the shift of the energy levels, the discrete levels of the free ions broaden into bands in the crystal, characteristic of band structure. The width of approximately 6 eV indicated for Ga $4s$ band is just a rough guess and is intended only to illustrate that a broadening is expected to occur.

The oxygen $2p$ level would also be expected to broaden, perhaps as much as several eV. The levels just below the gallium $4s$ band correspond to the first exciton bands. Their approximate positions were computed from the separation of the threefold coordinated oxygen ions from their first and second nearest-neighbor gallium ions. This is the term $-e^2/r_0$ in Eq. (1).

The observed band gap of 4.7 eV for Ga$_2$O$_3$ is shown in Fig. 3 on the same energy scale for comparison with the admittedly rough calculations. We would expect the absorption to correspond to the first exciton transition, for which the calculated ΔE is 5.3 eV. This latter figure does not take into account ψ_{pol} which reduces ΔE somewhat. ψ_{pol} is very difficult to calculate, but something like 1 to 2 eV is typical. This gives a calculated ΔE of approximately 4 eV, which is as good an agreement as can be expected for this type of calculation. The Ga^{3+} free-ion energy levels are also shifted by the lattice potential, but the energy difference of the $3d^{10}$ and $3d^9 4s$ states should change very little. This energy difference amounts to some 20 eV, which indicates that the observed absorption cannot be attributed to internal excitation of the gallium.

It is interesting to compare the Ga$_2$O$_3$ band gap with that of Al$_2$O$_3$. No measurement of the Al$_2$O$_3$ band gap has been reported, but it probably exceeds 8 eV. On the basis of the model presented here for the Ga$_2$O$_3$ absorption-edge energy, we expect a much larger band gap for Al$_2$O$_3$ due to the absence of the tetrahedrally coordinated cations. The difference in absorption-edge energy due to the slightly different cation-oxygen spacing and cation ionization energy should be small compared to the difference caused by the different coordination numbers. It is therefore believed that this model affords a simple interpretation of the difference in band gap for these two oxides.

A completely satisfactory explanation for the shoulder observed on the absorption edge has not been formulated. Attempts to fit the shape of the curve to the current theories, e.g., indirect excitons, were unsuccessful. Except for the blue shift of the edge as the temperature is lowered, the curves are almost identical at room temperature and liquid-helium temperature. However, it should be noted that the temperature coefficient for the portion of the edge to the long-wavelength side of the shoulder is much larger than the portion to the short-wavelength side. One possible explanation for the shoulder is as follows: The distance of the nearest neighbor Ga$_I$ is slightly different for O$_I$ and O$_{II}$ (1.80 and 1.83Å, respectively). We therefore expect a slightly different transition energy of approximately $(e^2/r_0)(\Delta r/r_0)$ for the two cases. The energy difference computed in this way is within 10% of the energy difference obtained when the two portions of the curve are extrapolated to the energy axis. A similar effect would also be expected to accrue from a slight difference in the electrostatic lattice energy at the two oxygen sites.

It is interesting to note that on the basis of the proposed model the exciton state is either not degenerate or has much lower degeneracy than is usually the case, e.g., in the alkali halides.[10] This is due to the low symmetry of the Ga$_2$O$_3$ lattice. Thus, the O$_I$-to-Ga$_I$ transition involves only one pair of ions at the same distance, the O$_{II}$ to Ga$_I$ only two. This could lead to interesting consequences, e.g., in calculations of the polarization energies.

The relationship of the photoconductivity to the absorption edge is not clear from the data presently available. The long-wavelength response is presumably due to impurities. The short-wavelength cutoff is a surface-sensitive property typical of ionic photoconductors.

---

[10] R. S. Knox, *Theory of Excitons* (Academic Press Inc., New York, 1963), p. 64.

A study of the photoresponse as a function of temperature, applied voltage, illumination history, etc., of crystals prepared under a variety of conditions may be required before a complete understanding is obtained.

Although the good agreement between the observed position of the Ga$_2$O$_3$ absorption edge and the crude calculations based on the model presented here may be somewhat fortuitous, it is believed that this model forms a convenient basis for further work, both theoretical and experimental.

ACKNOWLEDGMENTS

Nuclear Magnetic Resonance of Solidified H$_2$-D$_2$ Mixtures. I. Steady-State Experiments*

J. R. GAINES,† E. M. DE CASTRO,‡ AND J. G. DAUNT

Department of Physics, The Ohio State University, Columbus, Ohio

(Received 9 April 1965)

Steady-state NMR measurements using a marginal oscillator technique at 10 Mc/sec have been made on solid mixtures of n-H$_2$-n-D$_2$ of n-H$_2$ concentration from 100% to 1% in the temperature range 1.1°K to about 12°K. Striking differences in the line shape were observed, particularly in the n-D$_2$-rich sample, with change in temperature, the line shape at the lowest temperatures revealing a composite structure. The question whether this line shape transition is due to isotopic phase separation is discussed, and this interpretation is considered unlikely. It is concluded that the transition is probably associated with a hindering of the rotation of the ortho-H$_2$ molecule. Narrowing of the resonance lines with increasing rf power was observed. It is shown that no satisfactory explanation of this effect is possible using the Bloch equations. This narrowing is in excellent agreement with a recent calculation by Provotorov, however, and his theory is used to obtain a value of the exchange interaction in solid H$_2$ of approximately 10^{-7} °K. The progressive-saturation technique is used to obtain values of the product T_1T_2 for several of the mixtures. The data showed that T_1T_2 has a value at 4.2°K of about 2×10^{-6} sec^2 for concentrations of n-H$_2$ from 10% to 100%.

I. INTRODUCTION

SOLID H$_2$ is a mixture of ortho ($J=1$) and para ($J=0$) molecules which might in a first approximation be considered a random array near the melting point (approximately 14°K). Because of the relatively large gyromagnetic ratio of the proton and the slow conversion rate from the ortho species to the ground-state para species, solid H$_2$ is a favorable solid to study in detail from the standpoint of NMR and has been the subject of several extensive investigations.[1-3] The

investigations revealed two linewidth transitions, one associated with a translational motional narrowing at about 10°K and the other, the so-called λ transition, at about 1.5°K due to lifting of the rotational degeneracy of the orthomolecule in the solid. On the other hand, D$_2$ has a relatively weak nuclear magnetic moment and this solid has not been so extensively studied. However, the same linewidth transitions as in solid H$_2$ have been observed in solid D$_2$.[4,5] No experiments have been done upon mixtures of H$_2$ and D$_2$

---

[1] J. Hatton and B. V. Rollin, Proc. Roy. Soc. (London) A199, 222 (1949).

[2] F. Reif and E. M. Purcell, Phys. Rev. 91, 631 (1953).

[3] T. Sugawara, Y. Masuda, T. Kanda, and E. Kanda, Sci. Rept. Res. Inst., Tohoku Univ. A7, 67 (1955).

[4] B. V. Rollin and E. Watson, *Proceedings of the Conference on Low Temperature Physics, Paris, 1955* (Centre Nationale de la Recherche Scientifique and UNESCO, Paris, 1956), Paper 63.

[5] J. R. Gaines, E. M. de Castro, and D. White, Phys. Rev. Letters 13, 425a (1964).