occurrence of such close-packed structures in alloys at high pressure must be considered as a possibility.

There are further similarities among Ti, Zr, and Tl in that the bcc-hcp transition temperatures decrease with pressure, giving rise to the situation where transitions to a structure of lower coordination (bcc) from a nearly close-packed structure (hcp) may be obtained by iso-thermal compression. Whether these transformations involve a discontinuous change in the "atomic size" and are to be considered as "electronic" transitions remains to be seen. The bcc-hcp transition[26] in beryllium, which normally occurs at 1254±5°C, also may be expected to decrease in temperature with increasing pressure and yet it is extremely unlikely that any localization of an electron could take place. It would seem more useful to attempt to take into account the covalent contributions

to the bonding in these elements. With the presence of appreciable covalent contributions, any approxima-tions for the atoms as rigid spheres become of dubious validity.

[26] V. M. Amonenko, V. Ye. Ivanov, G. F. Tikhinskii, V. A. Finkels, and I. I. Chaporava, Phys. Metals Metallog. **12**, 77 (1961).

Fundamental Optical Absorption, Electrical Conductivity, and Thermoelectric Power of Calcium Oxide*

Homer H. Glascock, Jr.,† and Eugene B. Hensley
Department of Physics, University of Missouri, Columbia, Missouri
(Received 26 December 1962).

The opacities of thin backed films of CaO were measured at room temperature over the energy range 5.5 to 11.3 eV. At energies below 6 eV the opacity was low. A sharp peak, attributed to the formation of exci-tons, was observed at about 7.0 eV. A second strong peak was observed at 8.3 eV. This peak appears to have a doublet splitting of about 0.2 eV and probably should also be ascribed to excitons. Other peaks were observed at higher energies but were less reproducible. The width of the forbidden band was estimated to be near 7.7 eV. The electrical conductivity and thermoelectric power of sprayed aggregates of CaO were measured, as a function of temperature, for several states of activation and were found to exhibit the char-acteristics of a pore conductor. Using these data and the theory for pore conduction, the electron affinity for CaO was estimated to be 0.7 eV.

I. INTRODUCTION

THE work on calcium oxide to be reported here is part of a larger program whose purpose is the investigation of the electronic structure of the alkaline earth chalcogenides.[1-3] Interest in this family of com-pounds stems not only from the practical applications of the heavier oxides in oxide coated cathodes, but also because this family represents a divalent counter-part to the alkali halide family. Fundamental optical

absorption studies have previously been reported for fourteen of the sixteen members of this family and, with the work being presented here, only magnesium sulfide remains unstudied.[2,3] The thermoelectric proper-ties of calcium oxide being reported here represents an extension of similar work carried out on the heavier oxides which was primarily concerned with the pore conduction properties of porous aggregates of these materials.[4-6]

Although much of the early work on oxide-coated cathodes involved the use of calcium oxide, not until very recently has anything relating to the electronic structure of this material appeared in the modern

[1] J. R. Stevenson and E. B. Hensley, J. Appl. Phys. **32**, 166 (1961).
[2] G. H. Reiling and E. B. Hensley, Phys. Rev. **112**, 1106 (1958).
[3] G. A. Saum and E. B. Hensley, Phys. Rev. **113**, 1019 (1959).

[4] J. R. Young, J. Appl. Phys. **23**, 1129 (1952).
[5] E. B. Hensley, J. Appl. Phys. **23**, 1122 (1952).
[6] E. B. Hensley, J. Appl. Phys. **27**, 286 (1956).

literature. Janin and Cotton[7] observed a threshold for photoconductivity in a thin disk of powered calcium oxide at about 6.2 eV. Relatively large photocurrents were observed when the sample was irradiated by 6.7-eV light. Hopkins and Vick[8] made measurements of the thermionic emission and electrical conductivity of sprayed coatings of calcium oxide. From measurements of the ratio of the thermionic emission density to the electrical conductivity they estimated an average value for the electron affinity of calcium oxide to be 0.7 eV. Using essentially the same geometry as used in the present investigation, Mee[9] measured the electrical conductivity and Seebeck coefficient of a thin layer of calcium oxide contained between two nickel electrodes. He obtained a value for the Seebeck coefficient of about 2.4 mV/°K at 800°K, however, his measurements were not sufficiently extensive to establish its temperature dependence. Mee and Vick[10] made measurements of the electrical conductivity and photoconductivity using a probe diode similar to that used by Hopkins and Vick. They presented evidence to show that both the electrical conductivity at high temperatures and the photoconductivity were pore conduction phenomena.

In the present investigation, measurements were made of the fundamental optical absorption of thin films of CaO backed by LiF or fused quartz plates in the energy range 5.5 to 11.3 eV. Thermoelectric power and electrical conductivity measurements were made upon porous aggregates of CaO in the temperature range from 500 to 1250°K.

II. EXPERIMENTAL PROCEDURE

The vacuum ultraviolet spectrophotometer employed for measurements of the optical absorption has been described elsewhere.[2] Thin films of CaO were prepared by vacuum deposition of calcium metal on a single crystal of LiF or fused quartz plate which was subsequently heated in a low-pressure (less than 1 Torr) oxygen atmosphere. The absorption of the substrate limited the measurements to photon energies below 11.5 eV for samples supported by LiF and to below 7.5 eV for samples supported by fused quartz. Parlodion, which begins to transmit below 5.5 eV, was utilized as a filter for making white-light corrections. Measurements were made at room temperature with the spectrophotometer slits adjusted for a band pass of 4.25 Å.

The tube used for measurements of the temperature dependence of the electrical conductivity and thermoelectric power of porous aggregates of CaO was similar to that employed by Young.[4] The samples, prepared by vacuum reduction of sprayed calcium carbonate, consisted of porous disks 2.6 mm in diameter and 0.13

[7] J. Janin and L. Cotton, Compt. Rend. 246, 1536 (1958).
[8] B. J. Hopkins and F. A. Vick, Brit. J. Appl. Phys. 9, 257 (1958).
[9] C. H. B. Mee, Nature 190, 1093 (1961).
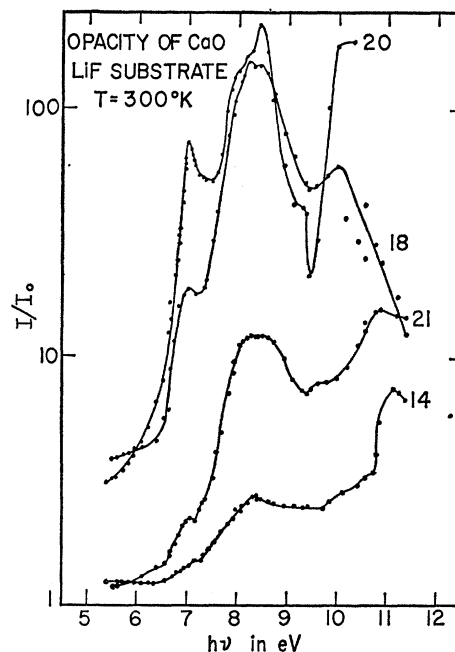[10] C. H. B. Mee and F. A. Vick, Brit. J. Appl. Phys. 12, 698 (1961).

FIG. 1. Opacity of thin films of CaO of various thicknesses on LiF substrate measured at room temperature. Films 14 and 18 were oxidized and annealed at temperatures of about 450°C for 20 min and films 20 and 21 were oxidized and annealed at 130°C for 1.25 and 0.5 h, respectively.

mm in thickness mounted between indirectly heated planar nickel electrodes 3.6 mm in diameter. Nickel-molybdenum thermocouples mounted on these electrodes permitted measurements of their temperatures.

III. EXPERIMENTAL RESULTS

Figure 1 shows four typical plots of the opacities versus quantum energy for LiF-backed CaO films. Opacity here is defined as the ratio of the light intensity transmitted by the substrate alone to the light intensity transmitted by the substrate plus the sample. The positions of the observed peaks in Fig. 1 plus those of two addition films are given in Table I. Films 13, 14,

TABLE I. Positions of fundamental optical absorption peaks in electron volts.

Sample No.	Position of peak in eV				
13	7.0				
14	7.1	8.3	(9.3)	(10.1)	11.0
18	7.0	8.3		10.0	
20	7.0	8.4	(9.2)	10.2	
21	7.0	8.3	(9.6)		10.9
28	6.9				

and 18 were heated to between 400 and 500°C for 10 min in oxygen and for another 10 min in vacuum. Films 20 and 21 were oxidized and annealed at 130°C for 1.25 and 0.5 h, respectively. The curve for film 13
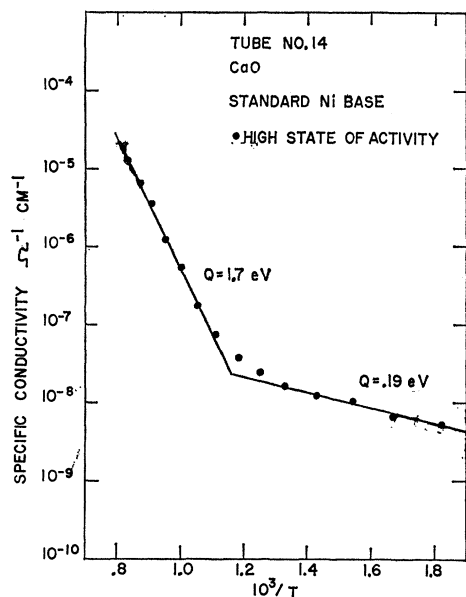
FIG. 2. Electrical conductivity of a porous aggregate of CaO versus reciprocal temperature (in °K) for a sample activated to a state of high conductivity.

was similar to film 20 out to about 8.2 eV beyond which the opacity was too large to measure. Film 28 was formed on a fused quartz plate. It was held at 325°C for 0.5 h in an oxygen atmosphere and annealed in vacuum for 1 h at 425°C. The curve for film 28 was also similar to film 20 out to 7.1 eV, at which point, the absorption of the quartz prevented further measurements.

Observations were made of the stability of the films to changes produced by atmospheric moisture. Film 28 was exposed to dry room air for several hours, but no appreciable change was observed in the first absorption peak. However, heating the film for several hours at 400°C in a wet atmosphere wiped out the first peak and greatly increased the opacity below 6 eV.

Measurements of the electrical conductivity were made on seven samples for from one to three states of activation. Where measurements were made over a sufficient range of voltages, it was found that the current-voltage plots at high temperatures were curved toward the voltage axis, whereas at low temperatures the plots were curved toward the current axis. This behavior has also been observed for other alkaline earth oxide coatings.[4] Plots of the logarithm of the electrical conductivity versus the reciprocal of the temperature exhibited either one or two linear regions in the temperature range 500 to 1250°K. The break between the linear regions occurred near 900°K. A typical plot is shown in Fig. 2. For all the different activations obtained, the slopes of the high-temperature region varied between 1.6 and 2.6 eV.

Figure 3 shows a plot of the thermoelectric power versus the reciprocal of the temperature. Going from

high to lower values of temperature, all samples exhibited maximum values of thermoelectric power from 2 to 6 mV/°K with a sharp drop in the region of the break in the corresponding electrical conductivity curve. In most cases, measurements could not be extended to lower temperatures because of the high resistivities of the samples.

IV. DISCUSSION

The optical absorption spectrum of CaO exhibits several peaks between 5.5 and 11.5 eV. The first peak, at 7.0 eV, is by far the sharpest and by analogy with the spectra of the other alkaline earth chalcogenides is almost certainly due to the formation of excitons.[11] A second prominent peak occurs at 8.3 eV which is relatively strong and broad and shows some evidence of being a doublet with a splitting of about 0.2 eV. This peak should also probably be ascribed to exciton formation since structure of this type is seldom associated with the threshold of direct band to band transitions. Other peaks are observed at higher energies as may be observed in Fig. 1, however, the details of their structure are not sufficiently reproducible to justify stating any conclusions.

Although there is no direct evidence concerning the width of the band gap in CaO from the present investigation, it is useful to attempt to infer its value from the position of the first exciton peak. From published
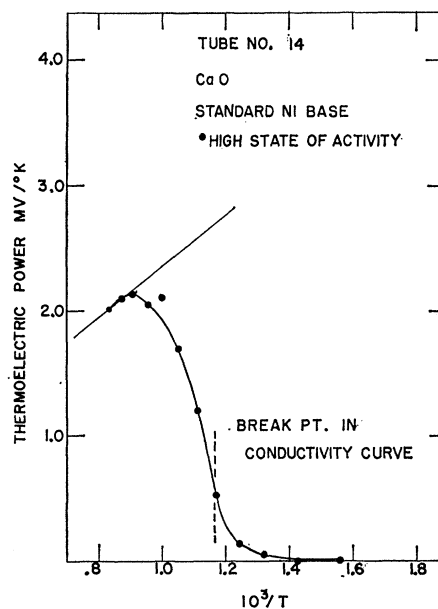

FIG. 3. Thermoelectric power of a porous aggregate of CaO versus reciprocal temperature (in °K) for the same sample as in Fig. 2.

[11] The ionization of F centers by excitons is probably the source of the photoconductivity observed by Janin and Cotton (Ref. 7) at 6.7 eV which is well into the shoulder of the first exciton peak. A similar effect has been observed in the case of BaO [W.W. Tyler and R. L. Sproull, Phys. Rev. 83, 548 (1951)].

values of the band gaps and exciton peaks for the alkali halides,[12] the ratios of the band gap energies to the energies of the first exciton peaks may be obtained. Almost all of these ratios lie between 1.07 and 1.15. The ratio of the band gap of 4.4 eV estimated for[13] BaO to its first strong exciton peak at 4.1 eV[14] is 1.07. Similarly, the corresponding values for MgO of 8.7 and[2] 7.6 eV result in a ratio of 1.15. Assuming that the ratio for CaO is similar to those above, the band gap for CaO should lie between 7.5 and 8.1. Since the lower values of the ratio dominate for the alkali halides and since it is felt that the estimate for the band gap for MgO may be slightly high, the most probable value for the band gap for CaO is estimated to be 7.7 eV.

Electrical conductivity and thermoelectric power measurements were made over a range of temperatures on porous aggregates of CaO crystals. In all cases, the thermoelectric emf at the hot junction between the Ni and CaO was found to be positive indicating that the charge carrier is negative. The conductivity and thermo-electric power curves such as shown in Figs. 2 and 3 are qualitatively quite similar to those predicted by Hensley for pore conductors.[12] These curves also show a strong resemblance to data obtained by Young[4] and others for BaO which has been established to be a pore conductor.[6,15] This is believed to be strong evidence that a porous aggregate CaO is also a pore conductor. This conclusion has received further support from Mee and Vick[10] who have shown that the magnetoresistivity of the conductivity in the high-temperature region is similar to that predicted for a pore conductor by Forman.[15]

Based on the conclusion that a porous aggregate of CaO is a pore conductor, it is possible to obtain an estimate of the electron affinity of calcium oxide. At the temperature of the break in the conductivity plot, the specific conductivity of the pores should be equal to the specific conductivity of the crystallites. Setting the expressions for these two conductivities equal to each other, it is possible to solve the resulting equation for the electron affinity.[16] Thus,

$$\chi = kT_b \ln(\mu_p/\mu_c),$$

where T_b is the temperature of the break in the conductivity plot and μ_p and μ_c are the mobilities of the electrons in the pores and crystallites, respectively. Estimates of the dimensions of the pores in sprayed oxide coated cathodes, which should correspond to the mean free paths of the electrons in the pores,[5] usually range around $(6\pm4)\times10^{-4}$ cm. Since the mean free paths of the electrons are independent of their energies, this corresponds to a mobility at 900°K of $(5\pm3)\times10^4$ cm^2 V^{-1} sec^{-1}.[17] No values for the mobility of electrons in CaO crystals are available. However, since the electron scattering in an ionic crystal should be primarily by polar mode vibrations, its value probably will not differ greatly from BaO. Pell[18] has obtained a value for the mobility of electrons in BaO of approximately (6 ± 3) cm^2 V^{-1} sec^{-1}. Using the median values for these mobilities we obtain a value for the electron affinity of CaO of 0.7 eV. If either of these mobilities are in error by as much as an order of magnitude, this value for the electron affinity will be changed by less than 0.2 eV.

The agreement between the value of the electron affinity obtained here with the value obtained by Hopkins and Vick[8] using a plot of $\ln(J/T\sigma)$ versus $1/T$ is probably somewhat fortuitous. The method used here suffers from the uncertainties in the mobilities used. Hopkins and Vick tacitly assumed that both the mean free path of the electrons and the electron affinity were independent of the temperature. Also, it has been shown[6] that the exposed surface of an oxide-coated cathode, which is involved in thermionic emission measurements, tends to have a higher work function than the interior of an oxide-coated cathode, which is involved in conductivity measurements. Nevertheless, the agreement between the two methods seems to indicate that the errors involved either tend to cancel each other or are of minor importance.

[12] J. Eby, K. Teegarden, and D. Dutton, Phys. Rev. 116, 1099 (1959).
[13] This estimate is based on the photoelectric emission from the valence band of BaO having a threshold of 5.0 eV [L. Apker, E. Taft, and J. Dickey, Phys. Rev. 84, 508 (1951)] and the electron affinity of BaO being 0.6 eV (see Ref. 16).
[14] R. Zollweg, Phys. Rev. 97, 288 (1955).
[15] R. Forman, Phys. Rev. 96, 1479 (1954).

[16] E. B. Hensley, Thermoelectricity, edited by P. H. Egli (John Wiley & Sons, Inc., New York, 1958), p. 193.
[17] W. Shockley, Electrons and Holes in Semiconductors (D. Van Nostrand, Inc., New York, 1950), p. 277, Eq. (28b).
[18] E. M. Pell, Phys. Rev. 87, 457 (1952).