

Measurement of Electron Energy-Loss Function in Bulk Strontium Titanate

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(Received 30 April 1970)

The electron energy-loss function for SrTiO_3 has been measured for losses in the range 4–40 eV. The results below 20 eV agree qualitatively with results derived from optical measurements. Above 20 eV, where optical data are lacking, an absorption near the plasma resonance at 23 eV is observed, and another strong absorption at 31 eV may possibly be attributed to the $\text{O}^{2-}(2p)$ to $\text{Ti}^{+3}(5s)$ or $(5p)$ interband transitions.

INTRODUCTION

Electron energy-loss measurements have been made on bulk strontium titanate using the energy-analyzing electron microscope developed by Cundy, Metherell, and Whelan.¹ The measurements cover the range 4–40 eV and supplement the uv reflectance-spectra measurements of Cardona² which stop at 20 eV. The electron plasma resonance at approximately 23 eV is clearly shown, and another strong absorption peak at 31 eV is found which may be due to $\text{O}^{2-}(2p)$ - $\text{Ti}^{+3}(5s)$ or $(5p)$ interband transitions. In the region where the two measurements overlap, the measured energy-loss function agrees qualitatively with the energy-loss function derived by Cardona from the reflectance measurements.

Optical reflectance methods³ are commonly used to determine the complex dielectric constant. At energies in the band-gap region, the reflectance measurements are quite sensitive and help in understanding details of the band structure. At energies well above the band-gap energy, uv measurement becomes more difficult. In this latter region electron energy-loss measurements, which yield the imaginary part of the negative-reciprocal complex dielectric constant, become increasingly attractive.

THEORY

The energy lost when a high-energy electron transits a crystal is proportional to the energy-loss function⁴ $\text{Im}(-1/\epsilon) = \epsilon_2/(\epsilon_1^2 + \epsilon_2^2)$. ϵ is the complex dielectric constant. ϵ_1 is the real $[\text{Re}(\epsilon)]$ and ϵ_2 is the imaginary $[\text{Im}(\epsilon)]$ part of ϵ . If $\text{Im}(1/\epsilon)$ is measured, $\text{Re}(1/\epsilon)$ may be found from the Kramers-Kronig relation.⁵ Thus, if the energy-loss function is measured, both ϵ_1 and ϵ_2 may be derived showing the equivalence of the information obtained by energy-loss measurements to the information obtained by optical methods. For the purpose of directly interpreting the energy-loss function, it should be noted that the energy at which the absorption peaks are found will be the energy at which the peaks of ϵ_2 are found, shifted by $1/|\epsilon|^2$. At high

energies the shift will be rather small, and here the energy-loss function may be used to directly identify the absorption energy.

The band structure of SrTiO_3 has been calculated by Kahn and Leyendecker⁶ for energies close to the band gap. They find it necessary to use an effective oxygen charge of -1.7 to obtain the correct band gap. They also give a plot of the sum of Madelung plus ionization potentials for some ionic states. Using this plot and Moore's tables of atomic energy levels,⁷ a list of some interband transition energies for an effective oxygen charge $-1.7|e|$ is compiled and given in Table I.

For large band-gap insulators such as SrTiO_3 , the fundamental plasma frequency is close to the free-electron plasma frequency of the valence electrons⁴ and is given by $\omega_{p0}^2 = ne^2/\epsilon_0 m_0$. Here, n is the number density of the valence electrons, e the electronic charge, ϵ_0 the permittivity of space, and m_0 the electron rest mass. Using 24 electrons per unit cell and unit cell edge of 3.9 \AA , the value for ω_{p0} is found to be $3.59 \times 10^{16}/\text{sec}$ which is equivalent to a plasmon energy of 23.2 eV.

EXPERIMENTAL METHOD

The energy-analyzing electron microscope used in these measurements has been described in detail by Cundy, Metherell, and Whelan.¹ A Siemens Elmiskap 1 electron microscope is modified to receive a Mollenstedt velocity analyzer below the

TABLE I. Some interband transition energies of SrTiO_3 based on the sum of ionization and Madelung energies for effective oxygen charge of -1.7 .

O^{2-}	to Ti^{+3}	Energy/eV	O^{2-}	to Sr^{+1}	Energy/eV
$2p$	$3d$	3	$2p$	$5s$	18
$2p$	$4s$	14	$2p$	$4d$	20
$2p$	$4p$	19
$2p$	$4d$	24
$2p$	$5s$	29
$2p$	$5p$	32	$2p$	Term	26
				Limit	

final image plane. The microscope can be used in a conventional way to view the image or diffraction pattern of a sample. In addition, however, a particular image feature (or diffraction spot) can be positioned over the slit of the velocity analyzer, and velocity analysis performed. This feature is a great advantage in that it allows good sample areas to be selected with confidence. The measurements reported here use a beam energy of 80 keV under conditions where the energy resolution is on the order of 2 eV.

Since the thinning of SrTiO_3 for transmission electron microscopy has not been described in the literature, the method is now outlined. Strontium titanate samples sliced from flame-fusion-grown boules supplied by National Lead are mechanically polished to a thickness of approximately 50 μm . The polished slices are then cut into 2.4-mm discs and placed in the holder shown in Fig. 1. The holder and sample are placed in orthophosphoric acid held at 175 $^\circ\text{C}$. The sample is monitored using reflected light and a microscope. When small holes form in the central region of the sample, the holder is removed and rinsed. The sample is floated onto a 200-mesh microscope grid and mounted in the microscope sample holder, sandwiched between two grids to reduce charging effects. This method has produced very good electron-microscope samples.

RESULTS

Electron energy-absorption spectra are taken with pure SrTiO_3 , SrTiO_3 doped with 0.25% Co, and SrTiO_3 doped with 0.7% Co. The doped material exhibits photochromic effects,⁸ but in the energy range of this investigation (4–40 eV) no change attributable to the doping is observed. Data are gen-

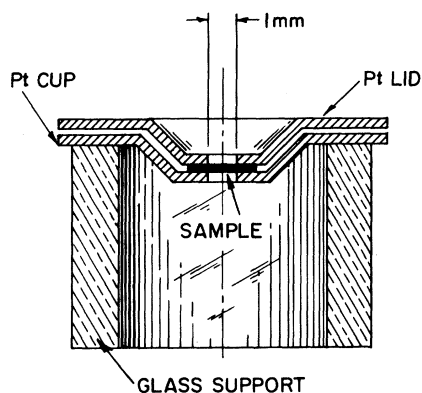


FIG. 1. Chemical polishing holder. The platinum cup and lid protect the sample edge so that small holes form in the central sample region before the sample disintegrates.

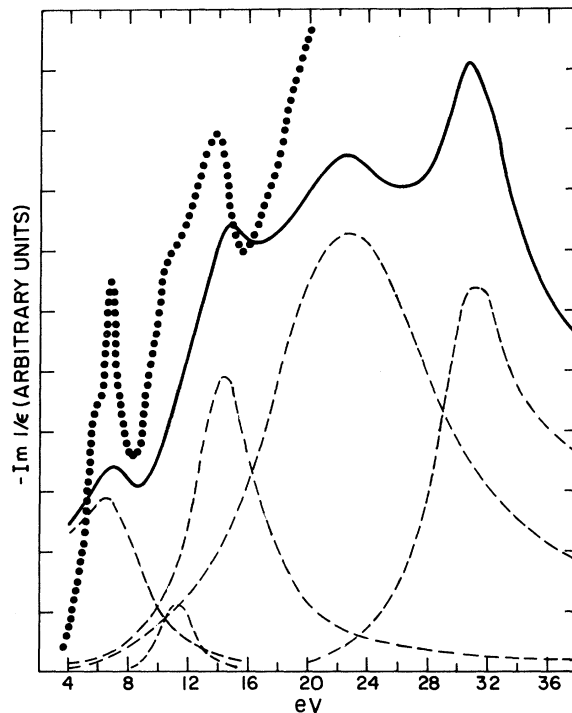


FIG. 2. Measured electron energy-loss function (solid line). Approximate fit by Lorentzian lines (dashed line). Energy-loss function derived by Cardona from optical measurements (dotted line). Cardona's results are normalized to these measurements at 15 eV.

erally taken on featureless portions of the image so that effects due to contrast-producing crystal imperfections are not included. It is not possible to identify crystal orientation and at the same time obtain the energy spectrum in these experiments. This is due to the deposition of what is probably polymerized pump oil on crystal regions subject to electron bombardment. If sufficient time is taken to obtain an orientation pattern, the crystal is then too dark to obtain an energy spectrum free of the strong carbon-plasma line. As a result, five random orientations for each sample are selected. Finally, since no distinction can be drawn between the results for different samples, all the (15) spectra are normalized to a common value at 32 eV and averaged. The resulting electron energy-loss function, in arbitrary units, is shown in Fig. 2. An approximate fit to the measured loss function by five Lorentzian lines and Cardona's results are also shown.

DISCUSSION

In the energy range where the electron-loss data overlap the optical results there is fair qualitative agreement. Using the peak locations of the Lo-

rentzian decomposition of the energy-loss functions the two methods agree to within about 1 eV. The lack of definition in the measured loss function as compared to the optical data is due to the 2-V energy resolution of the velocity selector and slit employed. The region below 4 eV, where effects due to the photochromic doping might be observed, is inaccessible because of the large zero-loss line spread.

In the region above 20 eV, the peak at 23 eV is probably the "free"-electron plasma resonance. The 31-eV peak is difficult to identify. Scanning Table I, it is attractive to attribute this latter peak to $O^{-2}(2p)$ - $Ti^{+3}(5s)$ or $(5p)$ interband transitions at 29 or 32 eV, respectively. A detailed high-energy-band calculation which includes the overlap integrals, however, would be required to make a more positive identification.

CONCLUSION

The electron energy-loss function for $SrTiO_3$ has been measured for losses in the range 4–40 eV. The results below 20 eV agree qualitatively with results derived from optical measurements. Above 20 eV where optical data are absent, an absorption near the plasma resonance at 23 eV is observed, and another strong absorption at 31 eV may possibly be attributed to the $O^{-2}(2p)$ to $Ti^{+3}(5s)$ or $(5p)$ interband transitions.

ACKNOWLEDGMENTS

I am grateful to Professor Sir N. F. Mott, Dr. A. Howie, and Dr. A. J. F. Metherell for the privilege of using the facilities of the Metal Physics Group of the Cavendish Laboratory. I wish also to thank Dr. D. Spalding for his instruction in the use of the energy-analyzing electron microscope.

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