Optical Absorption Edge of $SrTiO_3$ Around the 105-K Phase Transition

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The wavelength-modulated absorption and reflection spectra of $SrTiO_3$ have been measured as functions of temperature. Over a 60-K temperature range around the structural phase transition the band gaps of both high- and low-temperature phases are observed simultaneously. This effect and an associated band-gap shift are attributed to the fluctuations at the second-order phase transition.

The optical properties of $SrTiO_3$ in the region of the absorption edge have recently been studied in great detail.[1,2] Both of these groups of workers find that the absorption edge is described by Urbach's rule over most of the temperature range between room temperature and that of liquid helium. Capizzi and Frova[1] found, however, deviations from Urbach's rule over a range of temperatures around 100 K. The observed structure in the absorption edge at these temperatures was attributed to phonon-assisted indirect transitions. Here we report the wavelength-modulated spectra of $SrTiO_3$, where two of these indirect edges are seen in modulated absorption and a third direct edge is seen in modulated reflectivity. We believe the two indirect edges correspond to each of the phases on either side of the 105-K cubic-to-tetragonal structural phase transition. Furthermore, contrary to the classical models of second-order phase transitions, it is found that because of the fluctuations the two phases appear to coexist over an appreciable temperature range, ~60 K in the case of $SrTiO_3$.

The absorption measurements were made on thin slabs, 0.1–0.2 mm thick, of pure $SrTiO_3$; and the reflectivity measurements were made on thick polished slabs, ~3 mm, of Fe-doped material. Both crystals were obtained from the National Lead Company and prior to being measured were annealed at 1550°C for 6 h and cooled to 200°C at 25°C/h. The damaged surface layer due to polishing was etched away with a mixture of nitric, hydrofluoric, and acetic acids before annealing. The apparatus used to measure the wavelength-modulated spectra is essentially the same as that described by Thompson, Rowe, and Rubenstein.[3]

The wavelength-modulated reflection spectrum between 3 and 5 eV is shown in Fig. 1 at 83 K. The peaks and minima in such modulation spectra occur close to critical points in the joint density of states,[4] and only direct optical transitions have been found to give a measurable contribution. Thus the structure at 3.34 eV, nearest the absorption edge, is attributed to the lowest-energy direct band gap. Structure has been observed in the normal reflectivity at this energy by Cohen and Blunt[2] and by Cardona.[5] Near the first direct band gap the optical properties are dominated by the real part of the dielectric constant, and the line shape for the various types of critical points may be calculated.[4] The line shape observed is very similar to that given by an M_0 critical point, as would be expected at the zone center. The structure seen at higher energies agrees with that seen in the normal reflectivity by Cardona[5] who observed peaks at 4.0 and 4.85 eV. These peaks correspond to the peak at 4.0 eV and the minimum at 4.86 eV although the peak at 4.0 eV shows some extra structure.

The wavelength-modulated reflection spectrum of a thin slab with parallel faces contains not only the reflection spectrum of Fig. 1 but also superimposed on this is the modulated absorption spectrum due to the light beam reflected from the back surface of the crystal. This is present only up to a certain level of the optical absorption coefficient beyond which the beam is totally absorbed. The wavelength-modulated absorption spectrum obtained in this way is shown in Fig. 2 for various temperatures around the structural

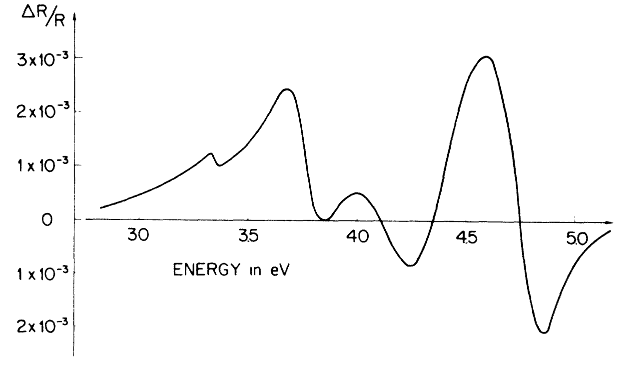

FIG. 1. The wavelength-modulated reflection spectrum of $SrTiO_3$ at 83 K.

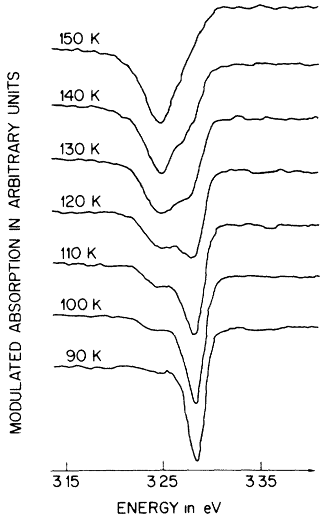

FIG. 2. The wavelength-modulated absorption spectrum of $SrTiO_3$ in the region of the band gap at various temperatures around the phase transition.

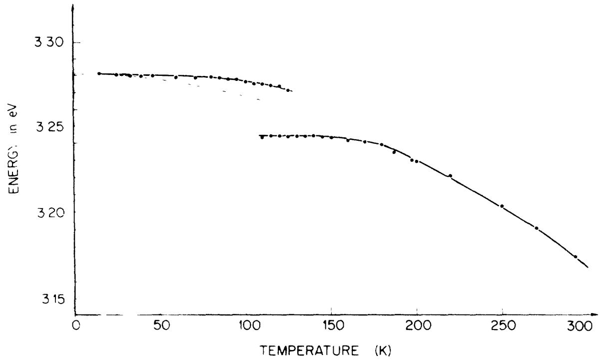

FIG. 3. Variation of the band gap of $SrTiO_3$ as a function of temperature. The broken line is $E_g = E_0 - \alpha\Gamma^2$, where $E_0 = 3.281$ eV and $\alpha = 1.26 \times 10^{-6}$ eV K^2.

phase transition. Both at temperatures well above and well below the phase transition only one minimum is observed, characteristic of the high- and low-temperature phases, respectively. Since neither of these edges is seen in the modulated reflection spectrum, they are thought to be due to indirect transitions, in agreement with the analysis of Capizzi and Frova.[1] On approaching the phase transition from either side, the spectrum characteristic of the other phase is seen long before the phase transition is reached. It should be pointed out that, within the resolution of the experiment, only the lowest-energy band gap shows this effect. None of the other transitions seen in the modulated reflectivity of Fig. 1 show any change on passing through the phase transition.

A change of the band gap on passing through the phase transition, as a result of halving the Brillouin zone, was proposed by Fleury, Scott, and Worlock.[6] It was not expected, however, that there would be a wide temperature range over which optical transitions characteristic of both phases are seen simultaneously. This type of behavior is not seen in EPR,[7] ultrasonic attenuation,[8] Raman scattering,[6] neutron scattering,[9] or thermal expansion.[10] Some of these experiments show a second-order phase transition defined to within $\frac{4}{100}$ K. The effect observed here cannot be explained by domain formation of the tetragonal phase since this is known[11] to produce a dichroism of only 3 meV which would not be resolved here and is an order of magnitude less than the energy separation of the band gaps of the two phases observed.

The temperature range over which the two optical transitions characteristic of each phase are simultaneously observed is the same as that over which the Fe^{3+}-V_0 EPR lines[12] are broadened as a result of critical fluctuations, and that where a central diffusive peak is observed in neutron scattering.[13] Since the characteristic measuring times of these three experiments differ by many orders of magnitude, this suggests that the fluctuations involved are of the same frequency range. However, whereas in the EPR and neutron-scattering experiments an averaging of the characteristic properties of the two phases is observed in the critical region, the optical absorption spectra show two distinct band gaps, one for each phase, due to the fluctuations. This doublet nature of the absorption spectrum can be interpreted as the coexistence of the two most probable structural configurations in the neighborhood of the phase transition. The difference in the indirect band gaps of these two configurations reflects a part of the combined changes in the electronic band structure and phonon spectrum induced by the phase transition.

The presence of fluctuations is further seen in the temperature variation of the band gap, taken in this case to be the energy of the modulated absorption minimum, as shown in Fig. 3. The data between 200 and 300 K show a quadratic temperature dependence[14]: $E_g = E_0 - \alpha T^2$, where $E_0 = 3.281$ eV and $\alpha = 1.26 \times 10^{-6}$ eV K^2. The linear term is not expected below the Debye temperature, ~450 K.[15] Below 180 K the results lie below this curve, the total deviation being 22 meV at the transition temperature. The results below the transition temperature extrapolate to the E_0 of the high-temperature–phase band-gap variation. A similar band-gap shift, albeit of the opposite sign, was recently observed by Wemple[16] in $BaTiO_3$ for temperatures above the first-order ferroelectric phase transition. In $SrTiO_3$ the fluctuations not only cause a band-gap shift but allow the simultaneous observation of both crystallographic phases over a wide temperature around the second-order phase transition.

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Observation of an Anomaly in the Thermal Resistivity and the Lorentz Number of the Metallic Antiferromagnet CeAl

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A 20% peak in the thermal resistivity w is observed in the temperature interval 7 to 12°K for CeAl, an antiferromagnet with a Néel temperature of 9.5°K. The maximum value of w occurs above T_N at about 9.8°K, while the slope dw/dT has a positive peak at T_N. This is the first experimental evidence for a divergent dw/dT in a metallic magnet. The Lorentz number has a monotonic temperature dependence with dL/dT maximum at T_N.

Although theoretical studies[1] of the thermal resistivity near the Néel temperature of a metallic antiferromagnet have predicted anomalies due to critical scattering, spin disorder, and energy gaps induced by superzone effects, experimental studies[2-4] have been of poor resolution and have resulted in unstriking, varied, and sometimes controversial findings. We report here measurements of the thermal resistivity w near T_N of the intermetallic antiferromagnet CeAl, $T_N = 9.5$°K, which give the first evidence that the temperature derivative of the thermal resistivity, dw/dT, is divergent at T_N. Although the ultimate aim of such a study is to determine the exponent [power of $\epsilon \equiv (T-T_N)/T_N$] which characterizes the divergence in dw/dT, and to determine which parameters of the metal affect this exponent if universal behavior is not observed, some preliminary matters should be settled first. In particular, does dw/dT diverge at T_N in any system, or is w itself maximum at T_N? If $|dw/dT|$ diverges at T_N, is dw/dT positive or negative above and below T_N? Although early workers presumed that a maximum in w occurred at T_N (a minimum in the thermal conductivity K) higher-resolution experiments[2] generally agree that the maximum in w does not occur at T_N and are consistent with the possibility that $|dw/dT|$ is maximum at T_N although they are not of sufficient resolution to suggest this behavior. Nellis and Legvold[3] have