

EVIDENCE FROM PRESSURE EXPERIMENTS FOR ELECTRON SCATTERING
BY THE FERROELECTRIC LATTICE MODE IN ABO_3 SEMICONDUCTORS

S. H. Wemple, A. Jayaraman, and M. DiDomenico, Jr.

Bell Telephone Laboratories, Murray Hill, New Jersey

(Received 11 May 1966)

Electron transport in the ABO_3 perovskite-type oxides $SrTiO_3$ and $KTaO_3$ appears to occur in d bands derived primarily from B -cation t_{2g} orbitals.^{1,2} Although the energy band structure of these materials is not known in detail, there is evidence for a many-valley model based on the results of magnetoresistance³ and cyclotron resonance⁴ experiments, tight-binding calculations,⁵ and the occurrence of superconductivity in $SrTiO_3$.⁶ The electron-scattering mechanism in these compounds, which results in a $T^{-2.7}$ mobility temperature dependence over a wide temperature range,^{1,2} has not been explained heretofore. In this Letter we present results of hydrostatic pressure measurements as well as a physical model which support the conclusion that electron scattering in ABO_3 -type semiconductors is by the long-wavelength transverse-optical (TO) ferroelectric lattice mode.⁷ Since it is this lattice mode which gives rise to the unusual dielectric and ferroelectric properties of these materials, we establish a direct relationship between the dielectric and transport properties of ABO_3 perovskite-type oxides. Further, we believe that the observed effect of hydrostatic pressure on conductivity is consistent with a many-valley conduction-band model. This interpretation differs from that recently given by Tufte and Stelzer⁸ who concluded on the basis of their low-pressure piezoresistance results that the conduction-band minimum

in $SrTiO_3$ lies at $k = 0$. These authors also attributed the large hydrostatic-pressure coefficient to repopulation effects in a two-band model; we attribute it rather to a pressure-dependent scattering mechanism.

It is well known⁹ that the resistivity of a semiconductor can be affected by isotropic stress (or strain) by any of several processes; i.e., repopulation effects between bands, effective-mass changes, or changes in the carrier relaxation time. In order to distinguish which of these processes is operative in ABO_3 semiconductors, we have measured the variation of both electrical conductivity and dielectric constant with hydrostatic pressure to about 35 kbar in the cubic phases of $SrTiO_3$, $KTaO_3$, and the mixed crystal $KTa_{0.65}Nb_{0.35}O_3$ (hereafter abbreviated KTN). Some transport and dielectric properties of these materials are summarized in Table I.

The conductivity measurements were made using a van der Pauw sample shape,¹⁰ and the dielectric measurements were made at 100 kc/sec using a standard capacitance bridge. Hydrostatic pressure was generated in a piston-cylinder device containing a fluid-filled Teflon sample cell.¹¹ The pressure-transmitting fluid was usually a 50/50 mixture of n -pentane and isoamyl alcohol. All measurements were carried out at room temperature. The results of the conductivity measurements are shown in Fig. 1 where the conductivity has been

Table I. Some transport and dielectric properties of $SrTiO_3$, $KTaO_3$, and KTN.

Material	Optical band gap (eV)	Electron mobility at 295°K (cm ² /V-sec)	Donor energy (eV)	Curie-Weiss temperature (°K)	Dielectric constant at 295°K
$SrTiO_3$	3.2 ^a	6 ^b	0 ^b	32 ^c	310 ^c
$KTaO_3$ ^d	3.5	30	0	4	242
KTN	3.1 ^e	3 ^f	0.24 ^f	280 ^e	8300 ^e

^aJ. A. Noland, Phys. Rev. 94, 724 (1954).

^bSee Ref. 1.

^cSee Ref. 16.

^dAll data from Ref. 2.

^eF. S. Chen, J. E. Geusic, S. K. Kurtz, J. G. Skinner, and S. H. Wemple, J. Appl. Phys. 37, 388 (1966).

^fS. H. Wemple and S. K. Kurtz, Bull. Am. Phys. Soc. 11, 401 (1966).

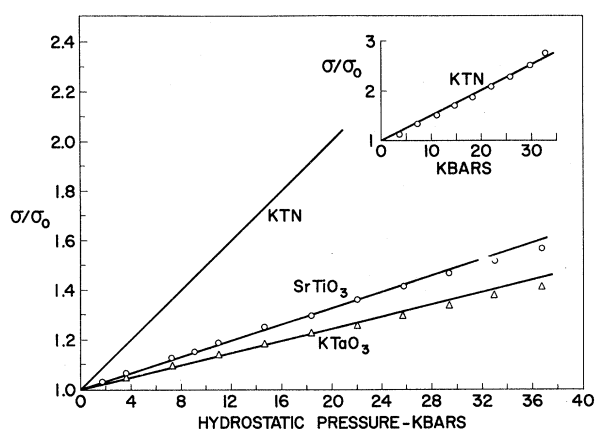


FIG. 1. Pressure dependence of electrical conductivity normalized to the value at zero pressure.

normalized with respect to the zero-pressure value. For each crystal the conductivity was found to increase nearly linearly with pressure over the pressure range investigated.¹² In every case, and most notably for KTN, the magnitude of the linear change in conductivity is too large to be explained by exponentially varying repopulation effects associated with energy-level shifts. The dimensionless elastoresistance coefficient $m_{11} + 2m_{12}$ relating the fractional change in conductivity to strain can be obtained from the slopes in Fig. 1 by using the equation

$$m_{11} + 2m_{12} = 3K \left(\frac{\sigma/\sigma_0 - 1}{p} \right), \quad (1)$$

in which $K = (c_{11} + 2c_{12})/3$ is the bulk modulus, c_{11} and c_{12} are the elastic stiffness constants,

and σ/σ_0 is the normalized conductivity at pressure p . The elastoresistance coefficients obtained in this way are listed in Table II. The result for SrTiO_3 is in substantial agreement with the data reported by Tufte and Stelzer.⁸

In the absence of repopulation effects, it is clear from the results shown in Fig. 1 that the electron mobility must be strongly stress dependent and must vary linearly with pressure. An explanation of the change in mobility ($\mu = e\tau/m^*$ where e is the electronic charge, τ the relaxation time, and m^* the effective mass) in terms only of changes in m^* would require that the approximately 1% lattice strains produced at the highest pressures decrease m^* by 30% in KTaO_3 , 50% in SrTiO_3 , and almost 300% in the mixed crystal KTN. These changes appear to be much too large. In addition, a linear relationship between $1/m^*$ and pressure is not expected⁹ at a conduction-band minimum. Because of these objections we have sought an explanation in terms of a stress-dependent scattering mechanism. In this connection it is important to recognize that lattice scattering is dominant in all the materials studied, as evidenced by the independence of mobility on carrier concentration.

The vibrational mode structure of the ABO_3 perovskite lattice has been investigated extensively.¹³⁻¹⁵ According to experimental evidence and current ferroelectric theories,⁷ the frequency ν_T of the long-wavelength TO mode is strongly temperature dependent, and can be described by

$$\nu_T^2 = \eta(T - T_c) = \eta C / \epsilon_0, \quad (2)$$

where η is an experimental constant, T is tem-

Table II. Effect of hydrostatic pressure on the electrical conductivity and static dielectric constant of SrTiO_3 , KTaO_3 , and KTN at 295°K.

Material	K (10^{12} dyne/cm ²)	Free-carrier concentration (cm ⁻³)	$m_{11} + 2m_{12}$	p_σ (kbar)	p_ϵ (kbar)	C^* (kbar)	$\bar{\nu}_T^a$ (cm ⁻¹)	$\bar{\nu}_\sigma$ (cm ⁻¹)	$\bar{\nu}_\sigma - \bar{\nu}_T$ (cm ⁻¹)
SrTiO_3	1.74 ^b	6×10^{18}	86	-61	-40	12 600	88 ^c	108	20
KTaO_3	2.05 ^d	$(0.5-2) \times 10^{18}$	79	-78	-51	12 300	85 ^e	105	20
KTN	1.57 ^f	5×10^{17}	248	-19	-4	33 200	20 ^g	44	24

^aBecause the Curie-Weiss temperature of KTN is not affected by the presence of free carriers, we have assumed that $\bar{\nu}_T$ is the same in both insulating and semiconducting samples.

^bR. O. Bell and G. Rupprecht, Phys. Rev. **129**, 90 (1963).

^cSee Ref. 12.

^dR. T. Denton, private communication.

^eSee Ref. 13.

^fT. Bateman, private communication.

^gEstimated from SrTiO_3 and KTaO_3 data.

perature, T_C is the Curie-Weiss temperature, C is the Curie constant, and ϵ_0 is the zero-pressure static dielectric constant. The frequency of the TO mode is also strongly stress dependent as revealed by the linear relationship between $1/\epsilon$ and pressure shown in Fig. 2.

For all three materials $1/\epsilon$ is linear in pressure over the pressure range investigated and follows the simple law¹⁶

$$\frac{1}{\epsilon} = \frac{p - p_\epsilon}{C^*}, \quad (3)$$

in which p_ϵ and C^* are constants. The experimentally determined values for these constants are listed in Table II together with the zero-conductivity pressure intercept $p_\sigma = -3K/(m_{11} + 2m_{12})$ obtained from Eq. (1).

Equations (1) and (3) strongly suggest a relationship between electrical conductivity and static dielectric constant, of the form

$$\frac{\sigma}{\sigma_0} = -\frac{C^*}{p_\sigma} \left(\frac{1}{\epsilon} - \frac{p_\epsilon}{C^*} \right) + 1. \quad (4)$$

Substituting Eq. (2) for $1/\epsilon$ into this expression yields¹⁷

$$\frac{\sigma}{\sigma_0} = -\frac{1}{\eta p_\sigma} \frac{C^*}{C} \left\{ [\nu_T(p)]^2 + \eta \frac{C}{C^*} (p_\epsilon - p_\sigma) \right\}, \quad (5)$$

showing that the conductivity depends linearly on the square of the pressure-sensitive frequency of the TO ferroelectric mode. It can be shown that the form of Eq. (5) is consistent with a model which attributes electron scattering to the

TO ferroelectric mode. The effect of the TO mode is to produce local fluctuations in the size and shape of the unit cell. Normally, electron scattering from this mode is considered to be of negligible importance in polar semiconductors because these modes produce no net polarization charge. However, the conclusion that scattering by TO modes can be neglected is invalid if the surfaces of constant electron energy in k space are not spheres.^{18,19} In the ABO_3 semiconductors the conduction-band energy minima are believed to occur at the zone boundary. Thus the electron wavelength is comparable with the lattice constant and, as a consequence, electrons can be scattered by the local distortions of the unit cell produced by the TO mode. Based on these arguments we expect that the electron relaxation time τ will vary as

$$\tau \sim \langle a^2 \rangle^{-1}, \quad (6)$$

where $\langle a^2 \rangle$ is the mean square amplitude of the TO mode. Therefore, the conductivity should vary as $\sigma \sim \nu_0^{-2}$ since $\langle a^2 \rangle \sim \nu_0^{-2}$, where ν_0 is the mode frequency. The additional constant term in Eq. (5) can be qualitatively understood in terms of optical-mode dispersion. If we use Silverman's²⁰ optical-phonon dispersion relation for a polar linear chain near $q=0$, i.e.,

$$\nu_0^2 = \nu_T^2 + \alpha q^2, \quad (7)$$

where q is the phonon wave number, and α is a constant, we conclude after integrating over q that $\sigma \sim \nu_T^2 + \text{constant}$ as obtained above in Eq. (5).

The magnitude of the effective scattering frequency ν_σ at zero pressure, defined from Eq. (5) by

$$\nu_\sigma = \nu_T [1 + (\epsilon_0/C^*)(p_\epsilon - p_\sigma)]^{1/2}, \quad (8)$$

and the TO-mode frequency ν_T are listed for comparison in Table II. For each material the effect of dispersion ($\bar{\nu}_\sigma - \bar{\nu}_T$) is approximately 20 cm^{-1} ($0.6 \times 10^{12} \text{ cps}$) which, according to the neutron-spectroscopy data of Cowley²¹ on SrTiO_3 , corresponds to the dispersion within the first 10% of the Brillouin zone. We conclude that the magnitudes of $\nu_\sigma - \nu_T$ and $p_\epsilon - p_\sigma$ for KTaO_3 and SrTiO_3 are consistent with effects produced by TO-mode dispersion, provided that electrons are scattered primarily in the vicinity of $q=0$. For KTN, however, where

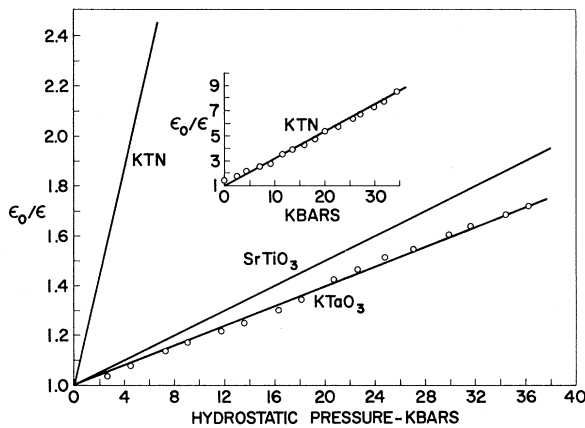


FIG. 2. Pressure dependence of reciprocal dielectric constant normalized to the value at zero pressure. The data for SrTiO_3 are taken from the paper by Samara and Giardini.¹⁶

$\bar{\nu}_O - \bar{\nu}_T = 24 \text{ cm}^{-1}$, we find that $\nu_O - \nu_T > \nu_T$, so that the phonon-dispersion argument given above relating σ to $\nu_T^2 + \text{constant}$ is not expected to hold. The fact that Eq. (5) holds experimentally for KTN suggests that either the above arguments are overly restrictive or perhaps there could be an additional contribution to the constant term arising from the broad linewidth of the TO mode (e.g., 40 cm^{-1} in KTaO_3).¹⁴ A more detailed analysis along these lines will be reported later.

In ABO_3 semiconductors the strong electron-TO-mode interaction which relates σ to ϵ is further evidence for a many-valley conduction-band model in these crystals. Detailed calculations of the interaction would require a knowledge of the charge distributions associated with the TO mode which are not presently available. The mobility temperature dependence expected for such an interaction is at present unknown. There are theoretical indications that the observed mobility temperature dependence may be associated with multiple-phonon processes.

The authors thank H. Scher for several helpful discussions. We also thank R. G. Maines and I. Camlibel for their technical assistance; W. A. Bonner and L. G. Van Uitert for providing the KTaO_3 and KTN crystals; and W. S. Baer for hydrogen reduction of the SrTiO_3 crystals.

¹H. P. R. Frederikse, W. R. Thurber, and W. R. Holser, Phys. Rev. **134**, A442 (1964).

²S. H. Wemple, Phys. Rev. **137**, A1575 (1965).

³H. P. R. Frederikse, W. R. Holser, and W. R. Thurber, Phys. Rev. **143**, 648 (1966).

⁴L. S. Senhouse, G. E. Smith, and M. V. DePaolis, Phys. Rev. Letters **15**, 776 (1965).

⁵A. H. Kahn and A. J. Leyendecker, Phys. Rev. **135**, A1321 (1964).

⁶J. F. Schooley, W. R. Holser, and M. L. Cohen, Phys. Rev. Letters **12**, 474 (1964); J. F. Schooley, W. R. Holser, E. Ambler, J. H. Becker, M. L. Cohen, and C. S. Koonce, Phys. Rev. Letters **14**, 305 (1965).

⁷W. Cochran, in *Advances in Physics*, edited by N. F. Mott (Taylor and Frances, Ltd., London, 1960), Vol. 9, p. 387.

⁸O. N. Tufte and E. L. Stelzer, Phys. Rev. **141**, 675 (1966).

⁹R. W. Keyes, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1960), Vol. 11, p. 149.

¹⁰L. J. van der Pauw, Philips Res. Rept. **13**, 1 (1958).

¹¹A. Jayaraman, A. R. Hutson, J. H. McFee, A. S. Coriell, and R. G. Maines, to be published.

¹²At higher pressures the data for KTaO_3 and SrTiO_3 show a small change in slope, but remain linear. This effect might be caused by a shift in the relative position of a higher conduction band with respect to the lowest conduction band. Investigations of the temperature dependence of this effect are currently in progress.

¹³A. S. Barker, Jr., and M. Tinkham, Phys. Rev. **125**, 1527 (1962).

¹⁴R. C. Miller and W. G. Spitzer, Phys. Rev. **129**, 94 (1963).

¹⁵A. S. Barker, Jr., and J. J. Hopfield, Phys. Rev. **135**, A1732 (1964).

¹⁶G. A. Samara and A. A. Giardini, Phys. Rev. **140**, A954 (1965).

¹⁷Samara and Giardini (Ref. 16) have given evidence that Eq. (2) holds even in the more general case when ϵ_0 is replaced by ϵ , the value at pressure p .

¹⁸F. J. Blatt, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 4, p. 199.

¹⁹H. Ehrenreich and A. W. Overhauser, Phys. Rev. **104**, 331 (1956).

²⁰B. D. Silverman, Phys. Rev. **135**, A1596 (1964).

²¹R. A. Cowley, Phys. Rev. **134**, A981 (1964).

SELF-CONSISTENT CURIE-LAW CALCULATION FOR ANDERSON'S DILUTE-ALLOY MODEL

D. R. Hamann

Bell Telephone Laboratories, Murray Hill, New Jersey

(Received 19 May 1966)

The effects of correlations on the behavior of Anderson's single-orbital model of an impurity in a dilute alloy¹ have been studied extensively recently.² The model is most amenable to study using double-time Green's functions,³ since taking exact account of the strong repulsion of opposite-spin electrons in the impurity "d" state precludes the use of diagrammatic expansions. When the chain of equations

of motion is decoupled and solved, the d -state susceptibility, χ_d , is usually found to be temperature independent at reasonable temperatures. A Curie law has only been found in a treatment which uses the temperature-dependent occupation numbers for the uncoupled d state throughout, thus seeming to force this result,⁴ and an unpublished calculation.⁵ We shall show that a careful and systematic decoupling of the equa-