

Anisotropic Conduction in Nonstoichiometric Rutile (TiO_2)[†]

LEWIS E. HOLLANDER, JR., AND PATRICIA L. CASTRO
Lockheed Aircraft Corporation, Palo Alto, California

(Received May 2, 1960)

Measurements are reported for the anisotropic conductivity in rutile for different nonstoichiometric compositions. This anisotropy, ρ_a/ρ_c , has a peak in excess of 10 000 to 1 and is a maximum at the nonstoichiometric composition corresponding to $\rho_c = 10^8$ ohm cm. Based on these data, it is proposed that for very nonstoichiometric material, impurity band conduction predominates, and as the material is made more stoichiometric, a transition to conventional conduction via the conduction band occurs. This transition occurs at very different nonstoichiometric compositions for the two crystal directions. Thus, a large anisotropy is observed in the intermediate region.

INTRODUCTION

THE electrical properties of rutile have been under investigation for the past century, and the resulting literature contains considerable contradiction on the conduction scheme of rutile.¹⁻⁶ Correlated measurements of the resistivity in the "a" and "c" crystal directions in the same single crystal are almost nonexistent. In addition, most previous measurements have involved ceramics with admixtures. The measurements that have been performed on single crystals have been confined mostly to conducting (10^{-1} to 10^2 ohm cm) and to insulating samples (10^{13} ohm cm).

The authors have made measurements of ρ_a , resistivity in the "a" crystal direction, and ρ_c , resistivity in the "c" crystal direction, on the same crystal specimen for a number of crystals. Each specimen was of a different nonstoichiometric composition, with their resistivities ranging from $\rho_a = 10^8$ to $\rho_a = 1$ ohm cm. An anisotropy of conduction, ρ_a/ρ_c , in excess of 20 000 to 1 was observed. This anisotropy gives an insight into the mechanism for conduction in rutile and suggests a model which lends continuity to the conflicting results abundant in the literature.

EXPERIMENTAL PROCEDURE

Single-crystal rutile boules⁷ were x-ray oriented by the Laue back-reflection technique and then cut into samples $3 \times 8 \times 8$ mm, where the long dimensions are along the "c" and an "a" crystal axis. After cutting, some of the specimens were checked for possible misalignment of their orientation. The samples were cleaned and then placed in a quartz tube furnace and reduced in a mixture of hydrogen and argon at temperatures of

600° to 1000°C. The term reduced is used to mean the introduction in the crystal lattice of oxygen vacancies by heating the crystal in a reducing atmosphere and thereby creating a nonstoichiometric composition of titanium and oxygen. The desired resistivity can be controlled by the variation of the reaction temperature, hydrogen-argon mixture and the reduction time.⁸

The resistivity values reported were all two-contact measurements, since four-contact measurements introduced difficulties resulting from the large anisotropy of conduction. The electrodes were indium solder. Previous tests of this method of contacting rutile indicated negligible contact resistance. Each crystal was placed in a dark, dehumidified vial to eliminate photoconductive and hygroscopic effects. Each vial also contained a thermocouple employed for the resistivity versus temperature measurements. It was noted that the "a" axis resistivity increased during a period of approximately one week after removal from the furnace. This effect was more pronounced in the higher resistivity samples and may be attributable to the recombination of free titanium and oxygen in the lattice.

ACCURACY OF MEASUREMENT

With a 20 000 to 1 anisotropy ratio a slight misalignment of the crystal axis could result in considerable error. From the orientation data on the specimen checked before and after cutting, it is estimated that all samples were oriented to within $\pm 3^\circ$, and most were within $\pm 1^\circ$. Any misalignment would tend to decrease the anisotropy ratio, and therefore the peak of this ratio could be substantially larger than the values reported. Some twenty samples, cut from three different boules, were used in the experiment. The data obtained from these samples were well correlated. For the high resistivity measurements the surfaces were carefully cleaned and a 10^{13} ohm input impedance voltmeter used. Even so, there may be some error in low-temperature measurements of Figs. 2(J), (K), and (L), which may account for the observed change in slope.

[†] This work was supported by Lockheed Missile and Space Division General Research Program and the Microsystems Electronics Program.

¹ F. A. Grant, *Revs. Modern Phys.* **31**, 646-74 (1959).

² R. G. Breckenridge and W. R. Hosler, *Phys. Rev.* **91**, 793-802 (1953).

³ D. Cronmeyer, *Phys. Rev.* **113**, 1222-1228 (1959).

⁴ M. Earle, *Phys. Rev.* **61**, 56-62 (1942).

⁵ S. Zerfoss, R. Stokes, and C. Moore, *J. Chem. Phys.* **16**, 1166 (1948).

⁶ For historical interest see U. S. Patent No. 879,062.

⁷ Obtained from Linde Air Products Company.

⁸ L. E. Hollander, T. J. Diesel, and G. L. Vick, Lockheed Missile and Space Division Report No. 288112, August, 1959 (unpublished).

RESULTS

An extremely large anisotropy in conduction was observed. This effect is small where the oxygen vacancy density is high, corresponding to a $\rho_c = 10^{-1}$ ohm cm. The effect increases dramatically as the density of vacancy sites is decreased, and it is maximized at an oxygen deficiency corresponding to a resistivity of $\rho_c = 10^3$ ohm cm. Above this vacancy site density the anisotropy ratio diminishes. These results are illustrated in Fig. 1(a) where the anisotropy ratio, ρ_a/ρ_c , is plotted versus the resistivity in the "c" direction, ρ_c , for five different temperatures. Although the magnitude of the anisotropy increases with decreasing temperature, the occurrence of the peak in each case corresponds to approximately the same oxygen vacancy density since ρ_c at the peak is reasonably constant over the temperature range examined. However, the ρ_a/ρ_c versus ρ_a plot, shown in Fig. 1(b), shows a shift in the peak with temperature which may be a result of the temperature dependence of resistivity in the "a" direction. Each datum point on a particular temperature curve of Fig. 1 represents the anisotropy ratio for an individual specimen, and therefore also represents the ratio for that particular state of reduction. Considering the misalignment in orientation and other experimental errors, the curves described by these data are amazingly consistent.

In Fig. 2 the resistivity versus reciprocal temperature is plotted for both "a" and "c" directions for twelve different states of reduction and the curves are arranged in ascending order of resistivity. The temperature data of Figs. 2(A) and (B) indicate approximately the same slope for both the "a" and "c" directions. To obtain an indication of the activation energies, the temperature dependence of the carrier mobility will be neglected. From the temperature data of Figs. 2(A) and (B) an activation energy in the order of 0.02 eV can be computed based on the Boltzmann equation $\rho = \rho_0 e^{E/kT}$, where E is energy, k is Boltzmann's constant and T is absolute temperature. Figure 2(D) shows the first distinct difference in slope in the "a" and "c" directions. The activation energy in the "c" direction is still very small, but the "a" direction shows approximately a quarter of an electron volt. This trend continues for the crystals shown in Figs. 2(E), (F), and (G). These states of reduction, Figs. 2(D), (E), (F), and (G), embrace the peak of the anisotropy curve of Fig. 1. As the oxygen vacancy sites are further separated, the slope in the "c" direction also changes and in Fig. 2(I) both the "a" and "c" directions have slopes corresponding to activation energies of 0.3 eV. For the more stoichiometric crystals of Figs. 2(J), (K), and (L) the "a" axis slope remains fairly constant at 0.3 eV, as does also the "c" axis slope at low temperatures. But at temperatures above 0°C the "c" axis slope increases with a corresponding increase in activation energy up to 0.6 eV.

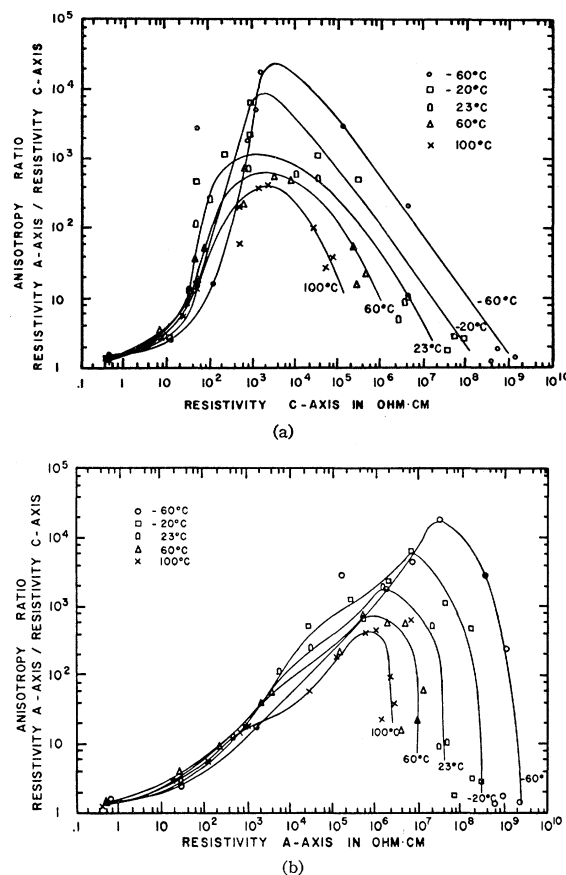


FIG. 1. Anisotropic conduction in nonstoichiometric rutile. (a) Anisotropy ratio ρ_a/ρ_c versus resistivity in the "c" direction, ρ_c . (b) Anisotropy ratio ρ_a/ρ_c versus resistivity in the "a" direction, ρ_a .

DISCUSSION

There appear to be two types of conduction in nonstoichiometric rutile. The contribution of each is determined by the density of oxygen vacancy sites in the lattice. At high vacancy densities, corresponding to low resistivities ($\rho_c < 10^3$ ohm cm), impurity banding is the principal means of conduction. Breckenridge and Hosler suggested impurity banding effects for samples they studied in this region.² Piezoresistive measurements by Hollander, Diesel, and Vick indicated the electron wave functions were strongly overlapped in the "c" direction in crystals with ρ_c less than 10^3 ohm cm. However, in the "a" direction this wave function overlap was appreciable only at lower resistivities corresponding to far higher oxygen vacancy densities.⁹

As the oxygen vacancy sites are decreased in number, and therefore spaced further apart, the electron wave functions no longer overlap. This occurs first in the "a" direction and is demonstrated clearly in Fig. 2(D). At this point conventional conduction via the conduction band becomes the predominant conduction mechanism.

⁹ L. E. Hollander, T. J. Diesel, and G. L. Vick, Phys. Rev. **117**, 1469-72 (1960); L. E. Hollander, Phys. Rev. Letters **370-1** (1958).

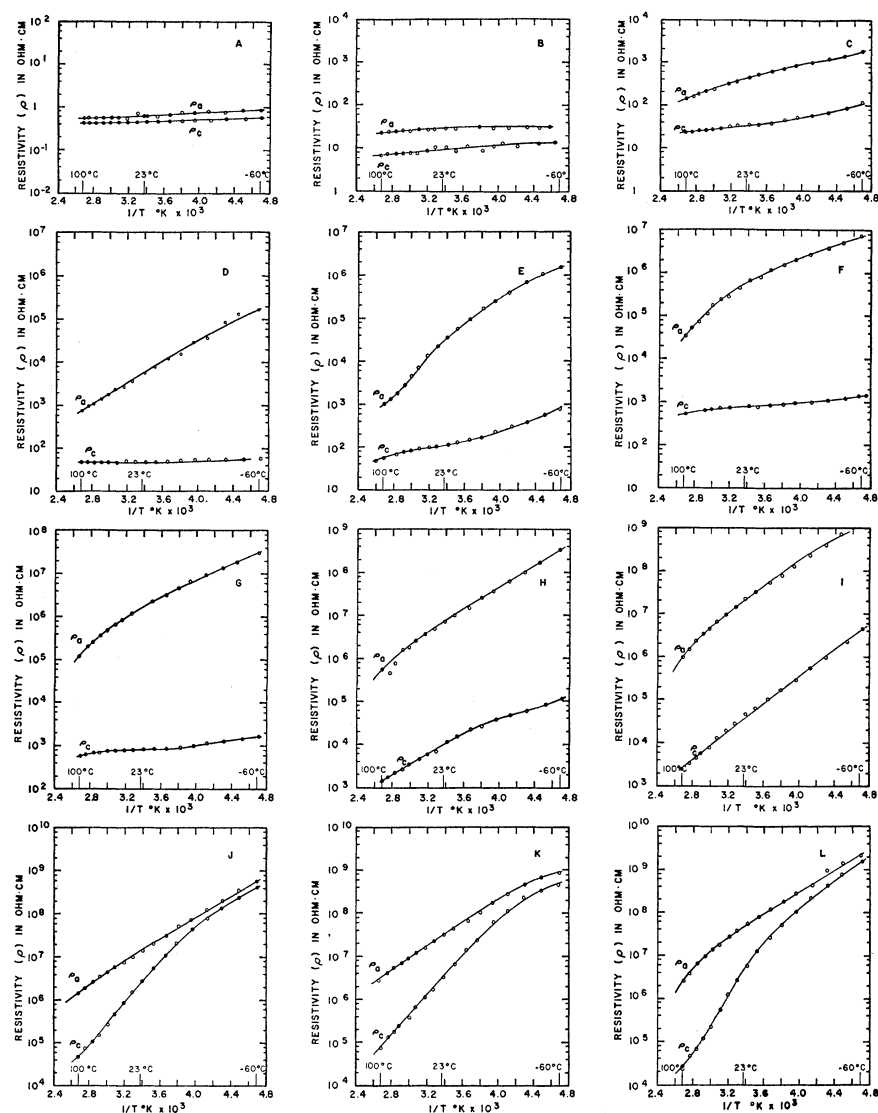


FIG. 2. Temperature dependence of resistivity in both "a" and "c" crystal directions for various non-stoichiometric compositions of rutile.

Applying this analysis to the "c" direction, it is seen that the electron wave functions cease to overlap somewhere between Fig. 2(G) and Fig. 2(H) at a ρ_c between 10^8 and 10^4 ohm cm. Beyond Fig. 2(H) conduction via the conduction band becomes the principal mechanism in both crystal directions. The anisotropy curves of Fig. 1 are in agreement with this theory. It is seen that the region of large anisotropy is that region which lies between the transition from impurity band conduction to conduction via the conduction band in the "a" and "c" directions. Because the "a" direction and the "c" direction undergo their transition at very different oxygen vacancy densities, this extraordinarily large anisotropy is possible.

The large anisotropy can also be examined on the basis of the separation of the Bohr orbits in the "a" and

"c" directions. A crude hydrogen atom approximation of the Bohr radius, a , can be obtained from the relation

$$a = K\hbar^2/m^*e^2 \text{ in angstrom units,}$$

where K is the dielectric constant of the material being examined, m^* is the effective electron mass, e is the electronic charge, and \hbar is Planck's constant divided by 2π . For rutile the dielectric constants are $K_a \cong 89$ and $K_c \cong 173$, and the lattice spacings are $a = 4.594$ Å and $c = 2.959$ Å with a c/a ratio of 0.6441.¹ Assuming an isotropic effective electron mass, there is three times the probability of overlap in the "c" direction as in the "a" direction. In the critical transition region where the electron wave functions just overlap in the "c" direction the three to one factor could account for the observed anisotropy.

CONCLUSIONS

It has been experimentally demonstrated that there is a transition from impurity band conduction to conventional conduction via the conduction band in rutile as the oxygen vacancy density is decreased. Temperature versus resistivity measurements in the “*a*” and “*c*” crystal directions of rutile have been made over a wide variation in nonstoichiometric compositions of titanium and oxygen. An anisotropy of conduction greater than 1000 to 1 was observed at room temperature, increasing to more than 10 000 to 1 at -60°C . The results of this study indicate that associated with each crystal direction there is a continuous transition from impurity band conduction to conventional conduction via the conduction band, which is determined by the oxygen vacancy

density. However, the nature of this dependency on the oxygen vacancy density differs in the “*a*” and “*c*” crystal directions, allowing large anisotropies in the intermediate region of the transition. It is hoped that much of the published experimental data can now be reinterpreted with respect to the crystal directions and more unanimity of understanding achieved.

ACKNOWLEDGMENTS

The authors would like to express their appreciation to Gerald Vick and Dr. Kermit Cuff for assistance in interpreting our data and for very helpful discussions, and to J. R. Field for his craftsmanship and ingenuity in the preparation of our crystal samples.

PHYSICAL REVIEW

VOLUME 119, NUMBER 6

SEPTEMBER 15, 1960

Metallic Transitions in Ionic Crystals: Some Group Theoretical Results

M. FLOWER, N. H. MARCH, AND A. M. MURRAY
Department of Physics, The University, Sheffield, England
 (Received May 3, 1960)

In view of a discrepancy between results available in the literature, the problem of finding the different irreducible representations for points on the surface of the Brillouin zone in NaCl and CsCl type lattices is re-examined for particular points of high symmetry. The lattice harmonics to be included in cellular-type calculations are listed up to and including $l=10$ for two points on the surface of the Brillouin zone in each case. Our results confirm the earlier work of Bell up to $l=6$, and extend her tables somewhat. The present findings however are at variance with Behringer's work on LiH for one of the points (*W*) which he considers.

1. INTRODUCTION

BEHRINGER¹ has recently reported a theoretical investigation designed to predict the pressure at which a metallic transition might occur in the ionic crystal LiH. Independently, two of us (M. F. and N. H. M.) have been working on the general problem of metallic transitions in ionic crystals, but with two essential differences from Behringer's work. Firstly, we have been considering the CsCl structure, rather than the NaCl structure adopted by Behringer. Although Behringer comments in his paper that the CsCl structure may be an important feature in discussing the metallic transitions, he does not deal quantitatively with this case. Secondly, from the point of view of the methods used in the band structure calculation, Behringer uses expansions in symmetrized plane waves, whereas so far all our work has made use of the cellular method.

However, both methods utilize the symmetry of the wave functions; in Behringer's calculation the form of the appropriate symmetrized plane waves is thereby fixed, whereas in our cellular treatment we determine in this way the allowed spherical harmonics in the expan-

sion of the wave function for a given \mathbf{k} within each cell. It is this group theoretical aspect of the problem on which we focus attention in this note. The compelling reason for a re-examination of existing work resides in the discrepancy which we find between the results of Behringer for the point *W* (see Sec. 2) and those given by Bell² on which our work is based. Behringer states that for the representation W_1 (W_s in the notation of Howarth and Jones), the wave function is *s*-like around both the nuclei in the LiH crystal, assuming the NaCl structure. On the other hand, Bell's tables indicate that the function is *p*-like around the second nucleus for this point in the Brillouin zone, if *s*-like around the first. It is the main purpose of this note to resolve the discrepancy, and then to extend the available results in certain directions.

2. NaCl STRUCTURE

(a) Point *W*. $\mathbf{k} = (\pi/2a)(2,1,0)$

To avoid repetition, we shall refer the reader to Behringer's notation. However, it is convenient for the purposes of the present argument to reproduce the

¹ R. E. Behringer, Phys. Rev. **113**, 787 (1959).

² D. G. Bell, Revs. Modern Phys. **26**, 311 (1954).