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Dielectric Relaxation of Hopping Electrons in Reduced Rutile, TiO_2†

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A sharp dielectric relaxation in rutile is observed at liquid-He^4 temperatures in the audio-frequency range in reduced specimens. A relatively narrow distribution of relaxation times is involved, distributed about $\tau^*=\tau_0^*e^{-Q/kT}$, with $Q=1.0\pm0.5\times10^{-3}$ eV and $\tau_0^*=10^{-6}$ sec. It is proposed that the relaxation is due to the hopping of an electron between normal cation sites around a complex ionic core. The change in dielectric behavior of specimens with increased trivalent impurity content suggest that the complex ionic core is an oxygen vacancy associated with an extrinsic trivalent substitional impurity.

IN the compound semiconductor reduced rutile (TiO_2) a large dielectric relaxation with a narrow distribution of relaxation times has been observed under impurity conduction conditions,[1] i.e., low temperatures and low impurity concentrations, and is the subject of this communication. This is the first time that a dielectric relaxation has been observed in rutile at low temperatures[2]; the relaxation does not occur in nominally "stoichiometric," unreduced rutile. Unlike other transition metal oxides,[3] this relaxation may be unequivocably ascribed to the electronic behavior of defect centers in the bulk material. The observed value of the activation energy rules out the possibility that ionic motion is involved. The active center proposed is that of an electron hopping between two otherwise equivalent normal Ti^{+4} lattice sites, the sites involved being nearest neighbor sites to a complex ion "core." This hopping is formally equivalent to dipolar reorientation. Although not the main concern of this letter, the complex ion core involved in this case is most likely to be an oxygen vacancy associated with a substitutional trivalent impurity.

The experimental results were obtained with a General Radio 1615 A capacitance bridge using a guard ring. The single-crystal disk-shaped specimens approximately 0.5 cm^2 and 0.1 cm thick were sectioned from an oriented Verneuil-grown boule obtained from the Linde Division of the Union Carbide Company.

The trivalent-impurity content is indicated to lie between 10^{15} and 10^{18} cm^{-3}. Measurements were performed with the specimens in liquid helium and in the dark. Since ESR spectra are sensitive to the method of reduction,[4-6] details of the reduction technique are given: An enclosing Vycor capsule of 47 cm^3 was partially evacuated at room temperature to a desired oxygen pressure of 25 μ Hg, heated for 114 h at 900°C, and then furnace cooled at a rate of 300°C/h.

The resulting degree of reduction was independently, and more reliably, determined from room-temperature conductivity measurements obtained by the van der Pauw method.[7] Carrier concentrations (electrons) of about 10^{18} cm^{-3} were found.

The bulk origin of the relaxation depicted in Fig. 1 is asserted since it was found to be independent of specimen dimensions, electrode material (gold, silver, or nickel), measuring field (in c direction) and dc bias up to a field of 670 V cm^{-1}. At higher temperatures, above 30°K, the specimen shows the expected field dependence[8] of the electrode capacitance. The decrease of the electrode capacitance with increasing temperature will be reported elsewhere. The relaxation was also found to be independent of magnetic field up to 21 kOe.

The experimental results were fitted to a Debye expression[9] for the complex dielectric constant $K+iK'$ appropriate to a homogeneous distribution of relaxation times τ in the range

$$\tau_0\leq\tau\leq\tau_1=\tau_0e^{-v_0/kT},$$

$$\tan\delta\approx A\{\tan^{-1}(\beta\omega/\omega_m)-\tan^{-1}(\omega/\beta\omega_m)\}/f(\beta), \quad (1)$$

where $\beta=(\tau_1/\tau_0)^{1/2}$, $f(\beta)=\tan^{-1}(\beta)-\tan^{-1}(1/\beta)$, ω is the angular frequency, and ω_m is that value at which $\tan\delta$ is a maximum. The best agreement between Eq. (1) and the experimental dispersion is obtained with $\beta=5$ at 2.3°K.

Although the dispersion is described by an homogeneous distribution of relaxation times, a single electron-hopping process is believed to be involved. Correlation between a center and other centers[10] will lead to a distribution of relaxation times.

The frequency at which the loss is a maximum shifts, as expected, to lower values with decreasing temperature. Assuming that τ follows the expression $\tau_0=\tau^*e^{Q/kT}$,

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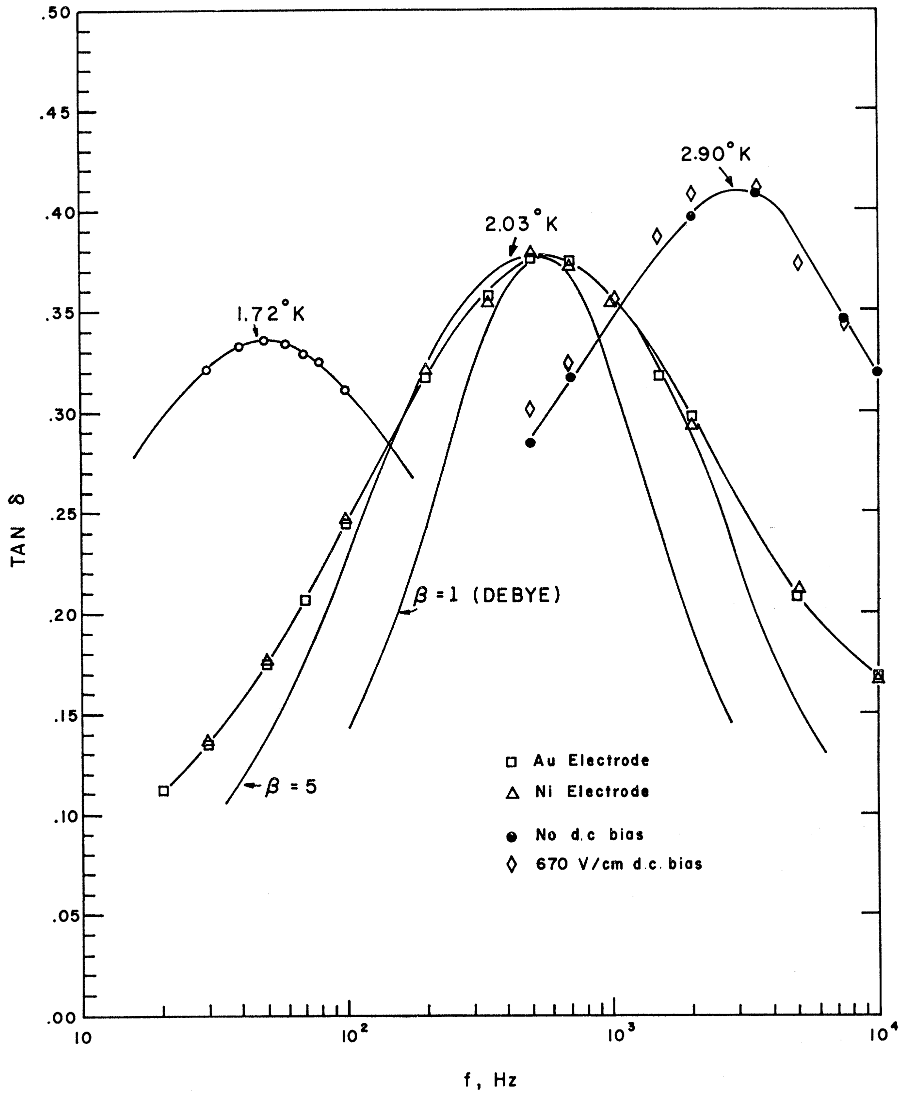

FIG. 1. Low-temperature dielectric-loss tangent of reduced rutile versus log (frequency).

and neglecting the relatively slow temperature variation of the dielectric constants, Q is found from the change with temperature of ω_m to be $(1.6\pm0.5)\times10^{-3}$ eV. The error introduced by using the values of ω at which tanδ is a maximum rather than those at which K' is a maximum is negligible in view of the relatively large inherent experimental error.

The height of the dispersion maximum A is given[9] by

$$A=\frac{K_0^2-K_\infty^2}{2K_0K_\infty}\frac{f(\beta)}{\ln\beta},$$

where K_0 and K_∞ are, respectively, the dielectric constants at frequencies small and large compared to $\omega_m/2\pi$. The Clausius-Mossotti expression with K_0, $K_\infty \gg 1$, gives

$$(K_0-K_\infty)/K_0=(4\pi ne^2d^2/9kT)K_\infty,$$

where n is the number of active electric dipoles per unit volume of moment $\mu_{el}=2ed$, and hence

$$A=\frac{2\pi ne^2d^2}{9kT}(K_0+K_\infty)f(\beta)/\ln(\beta).$$

This expression for the dispersion maximum predicts that

$$T(\tan\delta)_{\max}\ln(\beta)/f(\beta)$$

should be a constant. The experimentally determined values of this quantity: 1.43, 1.05, and 0.86 at $T=2.90$, 2.033, and 1.72°K, respectively, show a systematic decrease in contradiction to the theoretical expectation. The experimental behavior may be explained by assuming that the number of active dipoles is thermally activated from some lower-lying state, i.e.,

$$n=n_0\exp[-\Delta E/kT]$$

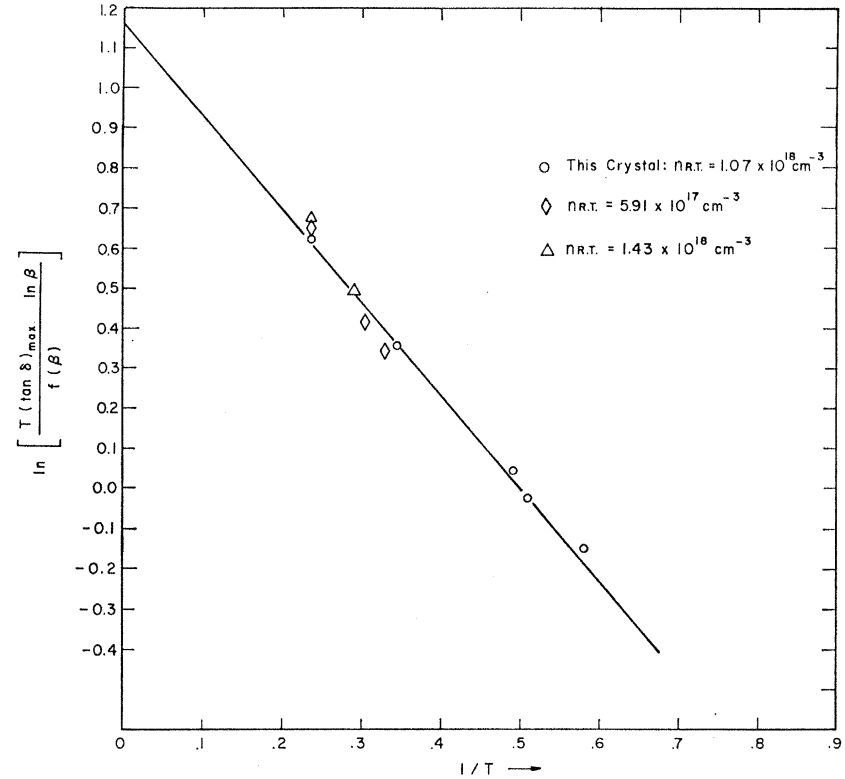

FIG. 2. $\ln\left[\frac{T(\tan\delta)_{\max}\ln(\beta)}{f(\beta)}\right]$ versus $\frac{1}{T}$.

(see Ref. 11). In this case

$$\ln\left[\frac{T(\tan\delta)_{\max}\ln(\beta)}{f(\beta)}\right]$$

should be a linear function of inverse temperature. This behavior is verified by the data plotted in Fig. 2, the best fit being obtained with

$$\Delta E = 1.95\times10^{-4}\ \text{eV} \quad \text{and} \quad n_0 = 1.5\times10^{16}\ \text{cm}^{-3}.$$

All specimens from the same boule were found to have the same value of $(\tan\delta)_{\max}$ at the same temperature, even though their respective reduction states corresponded to a sevenfold variation in room-temperature resistivity from 1.6 to 11.5 Ω cm. Thus the peak height is independent of N_d, the degree of reduction. The peak height was, however, considerably reduced by diffusing Fe into the specimen (effected by dusting high-purity iron powder onto the specimen surface before reduction). This behavior indicates that the ion core involved here cannot be simple, and probably consists of an intrinsic reduction defect, i.e., an oxygen vacancy or titanium interstitial, associated with a trivalent impurity. (The association of Ti^{+3} interstitials into pairs has been established by internal friction measurements.[2]) The oxygen vacancy associated with one substitutional impurity (with a net single positive charge and capable of trapping one electron on a nearest neighbor Ti^{+4} cation site to form a Ti^{+3} ion) is the most likely ion core in this case.

Haul and Dümbgen[12] have shown, from oxygen self-diffusion coefficient measurements, that the oxygen-vacancy concentration in their specimens was constant and independent of the oxygen partial pressure at temperatures ≈1000°C, i.e., independent of the state of reduction, which occurred, presumably, by the formation of Ti^{+3} interstitials. Assuming that the oxygen vacancy concentration in the specimens here is also independent of the reduction state, the decrease in peak height with increasing impurity concentration may be explained. As the concentration of trivalent impurity is increased, the (fixed concentration of) oxygen vacancies will become progressively more and more associated with two trivalent impurities. An oxygen vacancy with two trivalent impurities has a net charge of zero, cannot trap an electron, and no longer contributes to the low-temperature relaxation. The observed quenching of the relaxation by increasing the substitutional impurity concentration cannot be explained if the ion core involved Ti^{+3} interstitials, since their concentration varies with reduction.

There is no difficulty in justifying the localization of electrons on normal cation sites at low temperatures.

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[11] The previously mentioned rapid increase of the surface capacitance with decreasing temperature below 40°K indicates that the Schottky exhaustion layer is decreasing in thickness. This means that the Fermi level ζ is decreasing rapidly, and that the Boltzman approximation $n = n_0\exp[-\Delta E/kT]$ used here is probably justified for states close to the conduction band.

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Experimentally, normal Ti^{+3} ions have been observed by paramagnetic resonance.[6] The cation sites closest to the positive ion "core" are in the region of lowest electrostatic energy, and these nearest-neighbor sites will be preferentially occupied at low temperatures. The large dielectric constant in rutile (≈ 150) does not favor the alternate hydrogenic state since the energy is reduced by the factor $1/K_\infty$ and the radial extent of the hydrogenic orbit, being longer than an estimate of the inter-center distance, would give rise to metallic impurity conduction, not observed in rutile.[13]

The observation of electrons hopping to and fro at low temperatures indicates the nature of some of the localized states in reduced rutile, namely polarons localized on cation sites, forming Ti^{+3} ions, in a region of low electrostatic potential adjacent to a positive ion core. Also, the results indicate that consecutive intercationic electron hopping in one direction will be involved at higher temperatures during dc impurity conduction in rutile, and in other similar transition-metal oxides. Dielectric measurements of this type will probably be fruitful in measuring the values of some of the parameters involved in a general treatment of the problem.

Note added in proof. A more extensive experimental and theoretical paper will be published [R. K. MacCrone and L. A. K. Dominik, Bull. Am. Phys. Soc. **12**, 42 (1967)].

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Optical Properties of Gallium Arsenide-Phosphide*

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The index of refraction of $Ga(As_{1-x}P_x)$ is measured as a function of photon energy by the minimum-angle-of-deviation prism method at 300 and 87°K. The dielectric constant in the optical region is found to vary linearly as a function of mole fraction of GaP between the values for GaAs and GaP. Curve-fit data are presented which allow calculation of index of refraction at 300 and 87°K for a given crystal composition x and photon energy. Transmission data on $Ga(As_{1-x}P_x)$ are obtained at 300 and 77°K. The reflectivity is calculated from the index of refraction and is used to calculate the absorption constant, assuming multiple internal reflections in the crystal. In the infrared, true free-carrier absorption is observed for degenerate GaAs-rich mixed crystals, whereas absorption due to transitions from donor levels to the conduction band is dominant in GaP-rich mixed crystals. The band-to-band absorption seen by Spitzer and Whelan in GaAs is observed in GaAs-rich alloys, and is thought to be due to transitions from the (0,0,0) minimum to minima in the ⟨111⟩ directions. Finally, the absorption edge is investigated, and the Burstein shift of the absorption edge to higher energies with increased doping is observed, as well as shifts to lower energies due to compensation. In all cases, the fundamental absorption edge is found to exhibit an exponential dependence on photon energy.

INTRODUCTION

Very little has been published previously on the optical properties of n-type $Ga(As_{1-x}P_x)$. A few papers[1–4] have given the forbidden energy gap as a function of mole percent GaP. Allen and Hodby[5] have discussed the absorption constant due to the transition from the X_{3v} to the X_{1c} conduction-band minima. Abagyan *et al.*[6] and Chen[7] have given far infrared absorption data for supposedly pure Ga(AsP). Absorption data for GaAs are plentiful,[8–10] as well as for GaP,[11,12] and index-of-refraction data for GaAs [13] and

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