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Pressure dependences of the elastic constants of single-crystal Ti_2O_3 at 296 K

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We have measured the transit times of ultrasonic waves in Ti_2O_3 at 296 K using hydrostatic pressures up to 4 kbar. From them we deduce the pressure dependences of the elastic constants. Most modes stiffen with increasing pressure. However, the quasishear mode propagating in the mirror plane 45° from the [001] axis is found to soften with increasing pressure. The softening is explained in terms of an intrinsic instability of a cation sublattice. Comparisons are made with elastic constants of Al_2O_3 and V_2O_3 at 1 bar and with the pressure dependences of the elastic constants of Al_2O_3. It is inferred that electrons in 3*d* states contribute significantly to the elastic behavior of Ti_2O_3.

I. INTRODUCTION

Ti_2O_3 has the α-corundum structure of Al_2O_3 with space group $R\bar{3}c$. In the temperature range from approximately 400 to 500 K, Ti_2O_3 undergoes a gradual semiconductor to semimetal transition.[1-3] Although there are no magnetic[4] or structural[5] transitions accompanying the electrical transition, the c axis expands and the a axis contracts,[6] and there are anomalies in some of the elastic constants.[7]

Moreover, the cation sublattice of Ti_2O_3 (shown in Fig. 1) has an edge-shared parallelepiped structure. The interactions between the spins or cations on such a sublattice give rise to the antiferromagnetic ordering in V_2O_3. Similar arrangements of edge-shared octahedral anion sublattices have been shown to be intrinsically unstable.[8-12] in compounds having other crystal structures.

The pressure dependences of the elastic stiffness constants have been useful for understanding phase transitions[8,13] and temperature dependences of elastic constants.[14,15] They have also led to an appreciation of the role that the edge-shared polyhedral lattice structure plays in determining lattice stability.[13] Therefore it seemed appropriate to investigate how the elastic constants of Ti_2O_3 depend on pressure. We report on this investigation herein.

II. EXPERIMENTAL

The transit times of appropriate ultrasonic waves[16,17] were measured using the pulse-echo-overlap technique of Papadakis.[18] The samples were single crystals of Ti_2O_3 which have been used in previous ultrasonic investigations.[7,19,20]

Commercial, quartz and lithium niobate transducers plated coaxially with chrome gold and having a fundamental frequency of 30 MHz were used to generate the appropriate shear and longitudinal waves. Dow Corning 276-V9 resin was used as the bonding agent.

Hydrostatic pressures up to 4 kbar were generated with an Aminco motor-driven hydraulic pump and pressure intensifier. Connected to this system was a Harwood pressure vessel which contained the sample, with attached transducer, mounted in a spring-loaded holder. Harwood conical high-pressure electrical feed-throughs were used to conduct rf pulses to and from the transducer. Light-weight motor oil was used as the pressure fluid. The pressure was measured using a commerical (Harwood) calibrated manganin coil and a Bourdon gauge.

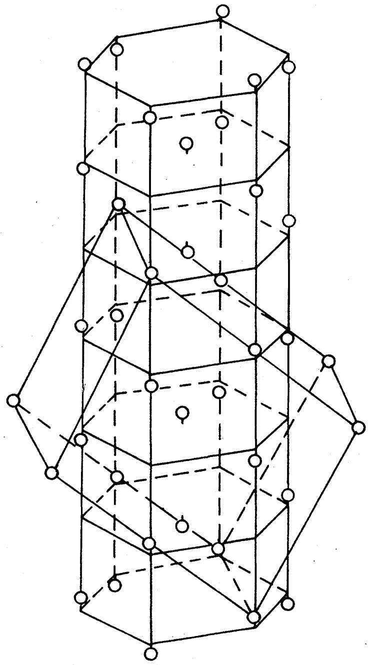

FIG. 1. Cation array showing hexagonal unit cell and edge-shared monoclinic sublattice. The sublattice structure is similar to that giving rise to the antiferromagnetic ordering in V_2O_3.

TABLE I. Sample length, wave propagation and polarization directions, and elastic constant determined.

Sample length (cm)	Propagation and polarization[a]	ρv^2
1.0610	$\vec{q}_L \| [001]$	C_{33}
1.0610	$\vec{q}_S \| [001]$ any $\hat{e}$	C_{44}
1.1336	$\vec{q}_L \| [100]$	C_{11}
1.1336	$\vec{q}_S \| [100]$ $\hat{e}_S$: 15° from basal plane[b]	$C_{FT} = \frac{1}{4}(C_{11} - C_{12} + 2C_{44}) + \frac{1}{4}[(C_{11} - C_{12} - 2C_{44})^2 + 16C_{14}^2]^{1/2}$
1.1336	$\vec{q}_S \| [100]$ $\hat{e}_S$:105° from basal plane[b]	$C_{ST} = \frac{1}{4}(C_{11} - C_{12} + 2C_{44}) - \frac{1}{4}[(C_{11} - C_{12} - 2C_{44})^2 + 16C_{14}^2]^{1/2}$
1.1750	$\vec{q}_{QL} \| 45° \, c(m)$[c]	$C_{QL} = \frac{1}{4}(C_{11} + C_{33} + 2C_{44} - 2C_{14}) + \frac{1}{2}[\frac{1}{4}(C_{11} - C_{33} - 2C_{14})^2 + (C_{13} + C_{44} - C_{14})^2]^{1/2}$
1.1750	$\vec{q}_{QS} \| 45° \, c(m)$[c] $\hat{e}_s \perp [100]$	$C_{QT} = \frac{1}{4}(C_{11} + C_{33} + 2C_{44} - 2C_{14}) - \frac{1}{2}[\frac{1}{4}(C_{11} - C_{33} - 2C_{14})^2 + (C_{13} + C_{44} - C_{14})^2]^{1/2}$
1.1750	$\vec{q}_S \| 45° \, c(m)$[c] $\hat{e}_s \| [100]$	$C_T = \frac{1}{4}(4C_{14} + 2C_{44} + C_{11} - C_{12})$

[a] Direction of polarization is omitted for longitudinal waves because $\hat{e}_L \| \vec{q}$.

[b] See Ref. 17 for the relation between the polarization angle and the elastic constants.

[c] Notation 45° $c(m)$ means a direction 45° from the c axis in the mirror plane.

The ultrasonic transit times were all determined at room temperature. Sufficient time was allowed after changing pressure to allow the system to reach thermal equilibrium. Temperature drift was negligible ($\Delta T < \pm 0.25$ K) throughout the course of the experiment. The sample length, the polarization and propagation directions of the ultrasonic waves, and the elastic constants determined are summarized in Table I.

III. DATA ANALYSIS

The elastic stiffness constants were obtained by using the frequency needed to superimpose two selected echoes (thus giving the reciprocal of the ultrasonic-pulse transit time) in relations like those given in Ref. 11. (These relations are applicable to the α-corundum structure as well as to the distorted rutile structure of semiconducting NbO_2 which is involved in Ref. 11.)

In obtaining values for the elastic stiffness constants we used a density[21] of 4.58 g/cm^3, a specific heat[22] at constant pressure of 26.5 cal/mol K, and a volumetric thermal expansion coefficient[23] of 17×10^{-6} K^{-1}. This resulted in a value of 1.0 for the thermodynamic Grüneisen γ.

The elastic constants at various applied pressures were deduced assuming the compressibilities to be independent of pressure. This approximation results in negligible error (less than 0.05% of $\partial C_{ij}/\partial P$) because the elastic moduli change very little over the entire pressure range involved.

IV. RESULTS

Shown in Figs. 2 and 3 are the pressure dependences at 296 K which were determined directly from the frequency needed to superimpose two selected echoes arising from pulses of approp-

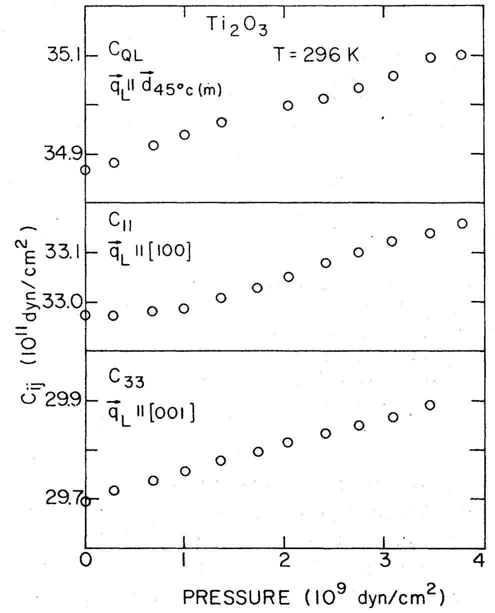

FIG. 2. Compressional elastic constants of Ti_2O_3 obtained directly from the appropriate 30-MHz longitudinal wave velocities. Propagation directions are given by $\vec{q}_L$.

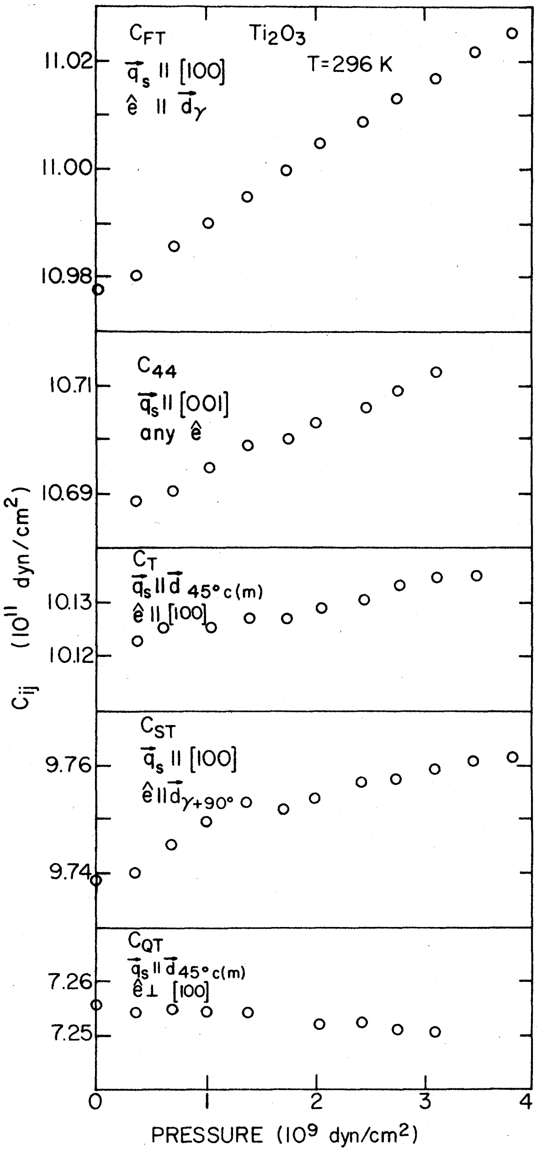

FIG. 3. Shear elastic constants of Ti_2O_3 obtained directly from the appropriate 30-MHz transverse wave velocities. Propagation and polarization directions are given by $\vec{q}_S$ and $\hat{e}$, respectively. The angle γ depends on elastic constants as indicated in Ref. 17. It has a value of 15° in Ti_2O_3.

riate longitudinal or transverse waves. The values we find for the C_{ij}'s at 1 bar are in good agreement with those reported by others.[7,24,25] The scatter observed in Figs. 2 and 3 are due to the finite width and shape of the rf wave comprising the echo packet.

All the elastic constants, with the exceptions of C_{QT} and C_{14}, stiffen with increasing temperature. C_{QT} shows a slight tendency to soften with increasing pressure while C_{14}, which is negative at 1 bar, becomes more negative with increasing pressure. The results are summarized in Table II.

V. DISCUSSION

A. Soft mode C_{QT}

The softening with pressure of the quasitransverse mode having elastic constant C_{QT} can be understood in terms of the cation sublattice in Ti_2O_3 shown in Fig. 1, which has an edge-shared polyhedral structure. The mode associated with C_{QT} propagates in the mirror plane 45° from the [001] axis and is polarized in the mirror plane. As such it can serve to tilt the sublattice in a manner similar to that which occurs in edge-shared octahedral lattices.[8-12] The interaction of the spins on such a polyhedral structure with those on the rest of the cation sublattice leads to a monoclinic distortion at the antiferromagnetic phase transition in V_2O_3.[26] We suggest that in Ti_2O_3 there is a weaker deformation-potential interaction between Ti ions on the polyhedral structure and the remainder of the cation sublattice. This causes C_{QT} to soften with pressure in such a way as to produce a monoclinic distortion at very high pressure.

B. Interpretation of other C_{ij} and $(\partial C_{ij}/\partial P)_T$—comparison with Al_2O_3

Oxides of titanium are known to exhibit electronically related transitions of either a real or an incipient nature, as is evidenced by the semiconductor-semimetal transitions in Ti_2O_3 and V_2O_3 above room temperature[27] and the incipient ferroelectric transition in TiO_2.[28-30] In contrast, Al_2O_3, which is isomorphic to Ti_2O_3, does not exhibit any such instabilities. Furthermore, Al_2O_3 is the only sesquioxide for which both the elastic constants[31,32] and the pressure dependences of the elastic constants have been reported.[32] For these reasons we now compare the elastic behavior of Ti_2O_3 to that of Al_2O_3.

Table III shows the ratios of the elastic constants of Ti_2O_3 to those of Al_2O_3 and also the ratios of the fractional changes in C_{ij} per unit pressure. Most of the C_{ij} ratios have values to be expected in view of the density-to-molecular weight ratios[33] of Ti_2O_3 and Al_2O_3. However, there are some anomalies: C_{13} is larger in Ti_2O_3 than in Al_2O_3. This anomaly also occurs[34] in V_2O_3 which, like Ti_2O_3, has electrons in $3d$ states. Furthermore, in Ti_2O_3, C_{14} has a very small magnitude compared to the other elastic constants (see Table II) and is only about $\frac{1}{10}$ as large as it is in Al_2O_3. The

TABLE II. Summary of the elastic properties of Ti_2O_3.

	C_{11}	C_{12}	C_{13}	C_{14}	C_{33}	C_{44}	C_T	C_{QT}	C_{ST}	C_{FT}	C_{QL}
$C_{ij}(0)$ (10^{11} dyn/cm^2)	32.97 ± 0.3	13.16 ± 0.2	16.23 ± 0.2	−0.24 ±0.03	29.69 ± 0.2	10.69 ± 0.1	10.12 ± 0.1	7.26 ±0.07	9.74 ±0.09	10.98 ± 0.1	34.87 ± 0.3
$\left(\frac{\partial C_{ij}}{\partial P}\right)_T$	5.7 ±0.6	5.0 ±0.5	2.5 ±0.3	−0.4 ±0.1	5.7 ±0.6	0.9 ±0.1	0.4 ±0.1	−0.2 ±0.05	0.6 ±0.1	1.3 ±0.1	6.0 ±0.6
$\frac{1}{C_{ij}(0)}\left(\frac{\partial C_{ij}}{\partial P}\right)_T$ (10^{-12} cm^2/dyn)	1.7	3.8	1.5	16.7	1.9	0.8	0.4	−0.3	0.6	1.2	1.7

other elastic constants of Ti_2O_3 are within a factor of 2 of their counterparts in Al_2O_3 (see Table III). This indicates that Ti_2O_3 deviates even less from elastic hexagonality (in which case C_{14} would be zero) than does Al_2O_3 in which the deviation is already small.

The ratios of the fractional changes per unit pressure of all the elastic constants except C_{14} have ordinary values. In the case of C_{14} the ratio is anomalous in sign because pressure causes C_{14} to become more negative in Ti_2O_3 but to become less negative in Al_2O_3. The large fractional decrease of C_{14} with pressure in Ti_2O_3 does indicate that the deviation from elastic hexagonality increases rapidly with pressure. This is consistent with the fact that pressure causes the c/a ratio of Ti_2O_3 to increase[35] from its anomalously small value of 2.65 at 1 bar toward the c/a ratio of Al_2O_3.[32]

Two other circumstances to be noted are as follows: First, the quasishear mode C_{QT} softens slightly with increasing pressure in Ti_2O_3 while it stiffens with increasing pressure[32] in Al_2O_3. Second, although the Cauchy relations $C_{12}=C_{66} \equiv \frac{1}{2}(C_{11}-C_{12})$ and $C_{13}=C_{44}$ are obeyed approximately in Al_2O_3,[32] there are large deviations from these relations in Ti_2O_3. The deviations are even increased somewhat by pressure (as can be verified by using results in Table II). Thus a central force model is not appropriate for Ti_2O_3, whereas it was found to be adequate for Al_2O_3.[32] From a structural point of view this is perhaps not surprising since the rhombohedral angle in Ti_2O_3 (56.7°) (Ref. 36) is larger than in Al_2O_3 (55.3°),[37] and thus deviates more from the 53.5° value possessed by a lattice comprised of hexagonal-close-packed anions interacting via central forces. However, reference to data on V_2O_3, which has a rhombohedral angle[36] of 53.5°, indicates that while one of the Cauchy relations ($C_{12}=C_{66}$) is almost satisfied, the other Cauchy relation ($C_{13}=C_{44}$) is even further from being fulfilled than it is in Ti_2O_3. The latter circumstance, coupled with the already noted fact that C_{13} has larger values in both Ti_2O_3 and V_2O_3 than in Al_2O_3, indicates that electrons in 3*d* states are responsible.

From the foregoing discussion it should be apparent that one must go beyond rigid-ion models in order to understand the elastic properties of Ti_2O_3. We suggest that what is necessary is an inclusion of the influence of electrons in Ti 3*d* orbitals. The effect on the elastic constants which we have in mind here is not that arising from strain-induced transfer of electrons between different 3*d* subbands which causes elastic constant anomalies at the semiconductor-semimetal tran-

TABLE III. Elastic constants and pressure derivatives of the elastic constants of Ti_2O_3 relative to those of Al_2O_3 [a].

C_{ij}	C_{11}	C_{12}	C_{13}	C_{14}	C_{33}	C_{44}
$\frac{C_{ij}(Ti_2O_3)}{C_{ij}(Al_2O_3)}$	0.66	0.81	1.39	0.10	0.59	0.75
$\frac{\frac{1}{C_{ij}}\left(\frac{\partial C_{ij}}{\partial P}\right)_T (Ti_2O_3)}{\frac{1}{C_{ij}}\left(\frac{\partial C_{ij}}{\partial P}\right)_T (Al_2O_3)}$	1.4	1.9	0.5	−30	1.9	1.8

[a] Values for Al_2O_3 are from Ref. 32.

sition[7] in Ti_2O_3. Rather, the effect is a consequence of the directionality and polarizability of occupied bonding 3*d* states. These features of *d* electrons have been found to be important for the ir-active optical-phonon modes[38] in Ti_2O_3.

C. Use of $(\partial C_{ij}/\partial P)_T$ data for analyzing $(\partial C_{ij}/\partial T)_P$

We now use the pressure dependences of the elastic constants of Ti_2O_3 to analyze the temperature dependences of the elastic constants. This will be done by using the relation

$$\left(\frac{\partial \ln C_{ij}}{\partial T}\right)_P = + \left(\frac{\partial \ln C_{ij}}{\partial T}\right)_V - \frac{\beta_V}{K_V}\left(\frac{\partial \ln C_{ij}}{\partial P}\right)_T + \Delta , \tag{1}$$

where β_V and K_V are the volumetric thermal expansion coefficient and compressibility, respectively, and Δ is a correction term needed for crystals with symmetry lower than cubic because for them the strain contribution to the temperature dependence of an elastic constant is not given simply by the volume contribution represented by the second term on the right-hand side of Eq. (1). For Ti_2O_3, as in most other axial crystals, it is not known how the C_{ij}'s depend on uniaxial strains so that we cannot determine an accurate value for Δ. However, if both axial strain derivatives of a given elastic constant have the same sign, it turns out that[39]

$$0 \leq \left| \frac{\Delta}{(\beta_V/K_V)(\partial \ln C_{ij}/\partial P)_T} \right| \leq \left| \frac{2\beta_a K_c - \beta_c K_a}{\beta_V K_V} \right| , \tag{2}$$

where β_a, β_c, K_a, and K_c are, respectively, thermal expansion coefficients and compressibilities along the *a* axis or the *c* axis. Using values[35] of $K_a = -2.4 \times 10^{-13}$ cm^2/dyn and $K_c = -0.9 \times 10^{-13}$ cm^2/dyn we calculated the right-hand side of Eq. (2) to be between about 0.4 and 1.4, with the ambiguity arising because of the range of values for the thermal expansion coefficient along the *a* axis given or implied by various investigations (i.e., 5×10^{-6} K^{-1} in Ref. 40, about 0 in Ref. 41, and -2.6×10^{-6} K^{-1} in Ref. 42). We have calculated a value for the volumetric-term contribution to the temperature dependence of each elastic constant by using the pressure dependence we measured, a value of $K_V = 5.0 \times 10^{-13}$ cm^2/dyn deduced from the elastic constants, and the value of β_V mentioned in Sec. III.

Table IV shows values for the temperature dependence of each elastic constant deduced from Ref. 23, the volumetric contribution to the temperature dependence as discussed above, and what the pure thermal contribution would be if Δ were negligible (keeping in mind during our discussion the ambiguity in Δ as indicated above).

For most of the elastic constants the volumetric contribution and the $\Delta = 0$ pure thermal contribution to the temperature dependence each exhibits normal behavior, i.e., each is negative and has a magnitude like that usually observed. However, the variations of C_{13} and C_{14} show some unusual effects. The measured temperature dependence of C_{13} near room temperature[7,23,24] in combination with the volumetric contribution implies that the explicit thermal contribution increases with increasing temperature. This behavior is consistent with the occurrence of the maximum in C_{13} as the semiconductor-semimetal transition is traversed between 400 and 500 K. It also is consistent with $(\partial C_{13}/\partial T)_P$ being negative and large in magnitude in semimetallic V_2O_3 between 150 and 273 K.[43]

No value for $(\partial C_{14}/\partial T)_P$ is entered in Table IV since measurements on Ti_2O_3 near 296 K have failed to provide a reliable value for it. It can be seen that the volumetric component of the temperature dependence of C_{14} is unusually large in magnitude. The significance of this remains to be explained.

TABLE IV. Volumetric and explicit thermal contributions to the temperature dependence of the elastic constants of Ti_2O_3 (Units of 10^{-4} K^{-1}).

C_{ij}	$\left(\frac{\partial \ln C_{ij}}{\partial T}\right)_P^{a}$	$-\frac{\beta_V}{K_V}\left(\frac{\partial \ln C_{ij}}{\partial P}\right)_T$	$\left(\frac{\partial \ln C_{ij}}{\partial T}\right)_{V,\Delta\to 0}$
C_{11}	−1.49	−0.49	−1.00
C_{12}	−2.02	−1.33	−0.69
C_{13}	−0.06	−0.53	+0.47
C_{14}[b]	•••	−5.9	•••
C_{33}	−1.89	−0.66	−1.23
C_{44}	−2.01	−0.28	−1.73

[a] From Ref. 23.

[b] The small temperature dependence of C_{14} does not permit an accurate determination of $(\partial \ln C_{ij}/\partial T)_p$. In units of 10^{-4} K^{-1}, $-9 \leq \partial \ln C_{14}/\partial T \leq 17$ (from Ref. 23).

VI. CONCLUSION

Several anomalies were found in the pressure dependences of the elastic properties of Ti_2O_3. The observed softening in C_{QT} is believed to be due to an intrinsic instability in the edge-shared polyhedral structure of the cation sublattice. Large deviations from the Cauchy relations indicate that a central force model would be inadequate to explain the elastic properties of Ti_2O_3, although such a model is suitable for Al_2O_3. Furthermore, it is believed that the cause of the violation of the Cauchy relations in Ti_2O_3 is due to the directionality of the $3d$-electron orbitals on the titanium ions. The increase in the magnitude of C_{14} with increasing pressure indicates that the deviation from hexagonal elasticity, although small, increases with pressure. Finally, the explicit temperature and dilatation contributions to C_{13} suggests that $(\partial C_{13}/\partial T)_P$ serves as a precursor, even at room temperature, to the semimetal-semiconductor transition which occurs between 400 and 500 K.

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