

Investigation of the nature of a high-temperature phase transition in V_2O_3 by ultrasonic spectroscopy

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An investigation was made of the velocity of propagation of longitudinal acoustic waves in vanadium sesquioxide V_2O_3 at temperatures 250–550°K. The measurements were made in a wide range of ultrasonic frequencies from 70 to 1500 MHz. Dispersion of the velocity of sound was observed. The frequency dependence of the velocity was described well by the Mandel'shtam–Leontovich relaxation formula. The values and temperature dependences of τ , v_∞ , and $(v_\infty - v_0)/v_\infty$ were calculated. The acoustic anomalies observed in the investigated temperature range were explained qualitatively by the model of overlapping Goodenough–Zeiger bands. A deep minimum in the velocity of sound at $T = 520^\circ\text{K}$ was attributed to fluctuations in the vicinity of a magnetic phase transition.

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In the temperature range 350–570° K, pure (stoichiometric) V_2O_3 exhibits anomalies of some physical properties (magnetic susceptibility,¹ electrical conductivity,² and lattice constants³), which are attributed to a high-temperature phase transition. We carried out an investigation of the velocity of propagation of longitudinal ultrasonic waves in V_2O_3 in the region of this phase transition. This was done in a wide range of ultrasonic frequencies from 70 to 1500 MHz with the aim of finding the dynamic characteristics of the transition and, in combination with the numerous published experimental

data, to determine the nature of high-temperature anomalies of the properties of V_2O_3 .

EXPERIMENTAL RESULTS

Our measurements were carried out on five samples of V_2O_3 . Four of them were grown by the Verneuil method and the fifth by the gas-transport reaction method in which TeCl_4 acted as the carrier gas. Longitudinal acoustic waves were excited along the twofold and threefold crystallographic axes by lithium niobate transducers in the form of plates bonded to the ends of the samples. The standard method was used in determining the velocity of acoustic waves.⁴ The error in the determination of the relative velocity was $\sim 0.2\%$.

Figures 1 and 2 show the temperature (T) dependences

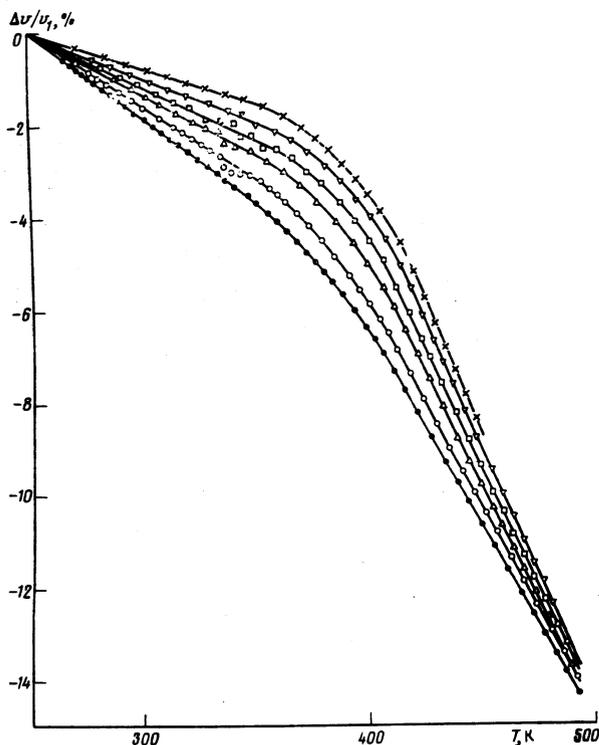


FIG. 1. Dependences of $\Delta v/v_1$ ($v_1 = 7.32 \times 10^5$ cm/sec) on the temperature T of a sample in which acoustic waves are traveling along the twofold crystallographic axis a at different frequencies f (MHz): ●) 150; ○) 570; △) 790; □) 900; ▽) 1120; ×) 1500.

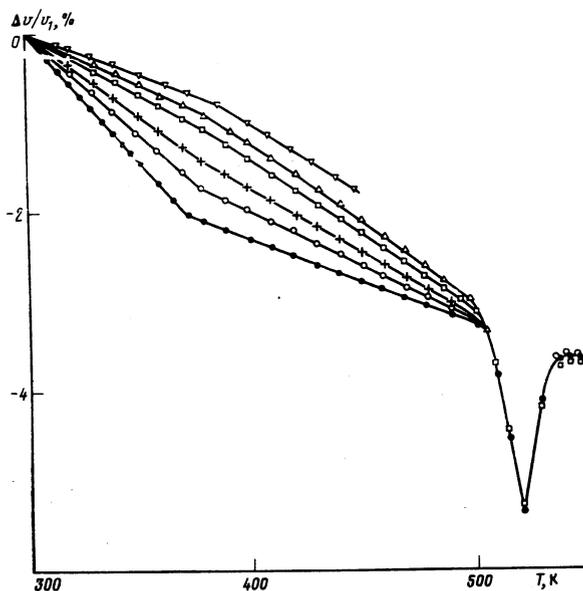


FIG. 2. Dependences of $\Delta v/v_1$ ($v_1 = 8.17 \times 10^5$ cm/sec) on the temperature T of a sample in which acoustic waves are traveling along the twofold crystallographic axis c at different frequencies f (MHz): ●) 150; ○) 470; +) 570; □) 780; △) 980; ▽) 1500.

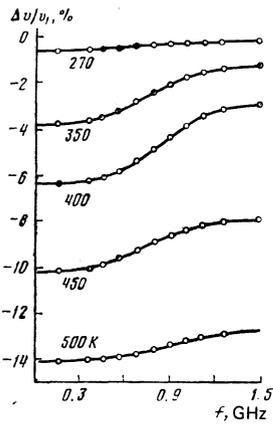


FIG. 3. Dependences of $\Delta v/v_1$ ($v_1 = 7.32 \times 10^5$ cm/sec) on the frequency of ultrasound f at various temperatures.

of the relative change in the velocity $\Delta v/v_1$ of the longitudinal acoustic waves traveling along the twofold (Fig. 1) and threefold (Fig. 2) crystallographic axes at various frequencies. It is clear from these figures that dispersion of the velocity of sound is observed above 250° K for the longitudinal waves traveling along the twofold axis and above 300° K for the waves traveling along the threefold axis.

The values of $\Delta v/v_1$ obtained for the five samples grown by different methods agreed within the limits of the experimental error and were easily reproduced during subsequent heating and cooling. No hysteresis was observed.

Figure 3 shows the dispersion dependences of $\Delta v/v_1$ on the frequency of the longitudinal ultrasonic waves traveling along the twofold axis, deduced from the curves in Fig. 1. Similar curves are also obtained from Fig. 2 for the longitudinal ultrasound traveling along the threefold axis.

The frequency dependence of v represented by all the dispersion curves is described well by the Mandel'shtam-Leontovich relaxation formula:⁵

$$v = v_\infty \left(1 - \frac{v_\infty - v_0}{v_\infty} \frac{1}{1 + \omega^2 \tau^2} \right), \quad (1)$$

where v_∞ is the velocity in the limit $\omega \rightarrow \infty$; v_0 is the velocity in the limit $\omega \rightarrow 0$; τ is the relaxation time.

In the limit $\omega \rightarrow \infty$, Eq. (1) assumes the form

$$v = v_\infty \left(1 - \frac{v_\infty - v_0}{v_\infty} \frac{1}{\omega^2 \tau^2} \right) \quad (2)$$

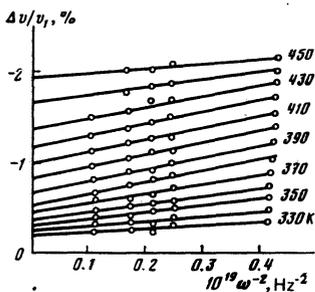


FIG. 4. Dependences of $\Delta v/v_1$ ($v_1 = 8.17 \times 10^5$ cm/sec) along the c axis on ω^{-2} at various temperatures; $\omega = 2\pi f$.

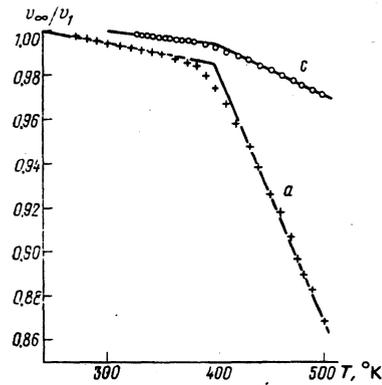


FIG. 5. Dependences of v_∞/v_1 on the temperature T for two directions of propagation of ultrasound along the a axis ($v_1 = 7.32 \times 10^5$ cm/sec) and c axis ($v_1 = 8.17 \times 10^5$ cm/sec).

and the velocity v becomes a linear function of the parameter ω^{-2} .

We determined v_∞ by plotting the experimental velocities $\Delta v/v_1$ as a function of ω^{-2} . Figure 4 gives the dependences of $\Delta v/v_1$ on ω^{-2} for the waves traveling along the c axis. It is clear from Fig. 4 that in the frequency range $f > 600$ MHz ($1/\omega^2 < 0.4 \times 10^{-19}$ Hz⁻²) the velocity varies linearly with ω^{-2} . The value of v_∞/v_1 is found from the point of intersection of the straight line $\Delta v/v_1(\omega^2)$ with the ordinate, i.e., at $\omega^{-2} = 0$.

The values of v_∞/v_1 obtained in this way are plotted as a function of temperature in Fig. 5. The quantities $(v_\infty - v_0)/v_\infty$ and τ are found by approximating the experimental curves with Eq. (1) using the least-squares method and an MIR-1 computer. The temperature dependences of τ and $(v_\infty - v_0)/v_\infty$ obtained from an analysis of the experimental curves are given in Fig. 6.

The results obtained in our study were compared with those given in the literature by measuring the electrical conductivity of one of the samples. The dependence of σ on $1/T$ is given in Fig. 7. The absolute values and the temperature dependence of σ for this sample are in agreement with the measurements of Feinleib and Paul² and Austin and Turner⁶ up to 500° K. Above 500° K, the resistivity ρ of pure V₂O₃ measured by Foex⁷ and by McWhan *et al.*⁸ decreases exponentially, whereas ρ mea-

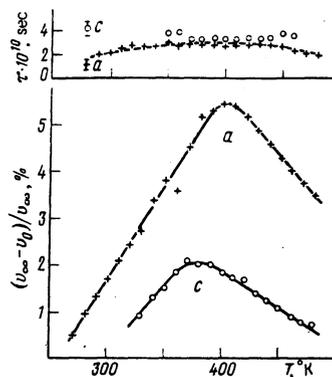


FIG. 6. Dependences of τ and $(v_\infty - v_0)/v_\infty$ on the temperature T for two directions of propagation of ultrasound.

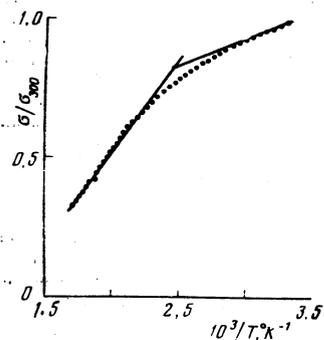


FIG. 7. Dependence of σ/σ_{300} on $10^3/T$.

sured at $T > 500^\circ$ K and reported in Refs. 2 and 6 either attains saturation or rises slowly on increase of T . This discrepancy between the published results can be explained by the existence of levels with an activation energy corresponding to 500° K, whose number is governed by the quality of a sample.

DISCUSSION OF EXPERIMENTAL RESULTS

There is as yet no agreed view on the nature of the high-temperature anomalies exhibited by V_2O_3 . A fuller picture is obtained if the properties of V_2O_3 are considered together with the properties of the compounds given by the formula $(V_{1-x}Cr_x)_2O_3$, where $x \leq 0.04$. It has been established that the addition of Cr is equivalent to the application of a negative pressure to the V_2O_3 lattice (3.6 kbar corresponds to 0.01 Cr). McWhan and Remeika³ investigated the electrical properties of chromium-doped V_2O_3 and concluded that a metal-insulator Mott transition takes place without a change in the lattice symmetry. This view is based on the large discontinuity of the electrical conductivity at this transition. The P - T phase diagram plotted by Rice and McWhan⁹ shows that the metal-insulator phase equilibrium curve terminates at a critical point which corresponds to a chromium concentration of less than 0.01 but still finite. It follows that the high-temperature anomalies of pure V_2O_3 lie in the transcritical region.

Honig *et al.*¹⁰ found that the electrical conductivity exhibited by $(V_{0.99}Cr_{0.01})_2O_3$ was smaller than that reported in Ref. 3 and that this discontinuity depended on the heat treatment and the rate of passage through the transition. For this reason, Honig *et al.*¹⁰ concluded that a metal-metal α - β corundum structural transition occurs in pure V_2O_3 . The same conclusion follows also from the x-ray data obtained by the same authors¹¹ and indicating the coexistence of the α and β phases in the region of the transition.

The x-ray structure data obtained by Robinson and Rice^{12,13} confirm those of McWhan and Remeika³ and they show that at room temperature the absolute values of the lattice constants of V_2O_3 and their temperature dependences resemble the corresponding results obtained for V_2O_3 with the α -corundum structure, whereas above 500° K they resemble those of V_2O_3 with the β -corundum structure. Between these temperatures the lattice constants vary continuously; regions of coexistence of the two phases are not observed although the measurements of Rice and Robinson¹³ were carried out

on the samples of Honig *et al.* Consequently, the x-ray structure analysis of pure V_2O_3 confirms the existence of a critical point in the P - T phase diagram given in Ref. 9.

It thus follows that one of the proposed models (Mott transition) postulates an instability of the electron states as the cause of the transition, whereas the other model (α - β corundum transition) postulates a lattice instability. However, in the case of a strong electron-phonon interaction, which occurs in V_2O_3 , it is hardly possible to distinguish these two mechanisms.

On the other hand, the two mechanisms are based mainly on the electrical conductivity and x-ray structure data. Another phase transition mechanism has been considered in the literature and in this case the actual energy band structure of V_2O_3 is taken into account. We have in mind here the Goodenough model¹⁴ discussed in detail by Zeiger.¹⁵ In this model the electron spectrum is represented by two narrow energy bands. In pure V_2O_3 the first (wider) band is almost empty above 150° K and it overlaps only slightly the second almost-filled band. The band overlap increases with temperature and this is responsible for the anomalies of the thermodynamic and transport properties in the range 250 - 500° K. As pointed out by Zeiger, this model can also explain the phase transition and critical point exhibited by the compounds $(V_{1-x}Cr_x)_2O_3$. We shall interpret the acoustic and electrical experiments on the basis of this model.¹⁶

At temperatures below $\sim 350^\circ$ K the electrical conductivity (Fig. 7) varies with temperature as T^{-1} , which is typical of metals. When the temperature is increased from 350 to 450° K, there is a change to a similar dependence but with a higher coefficient. Such a dependence is easily explained by an increase of the contribution made to the electrical conductivity by the wider band as the band overlap increases. The fact that the deviation from the T^{-1} law is observed at 350 - 450° K shows that a redistribution of electrons between the bands occurs mainly in this temperature range. This redistribution is completed above 480° K. It may occur for two reasons: either the wide band drops below the Fermi level and becomes completely filled or the anomalous relative shift of the bands ceases. The data available at present are insufficient to distinguish between these two cases.

Dispersion of the velocity of sound is observed at temperatures 270 - 500° K (Figs. 1 and 2). The dispersion maximum occurs at a temperature of the order of 400° K, which corresponds to the maximum band overlap according to Zeiger. From the phenomenological point of view, the state of V_2O_3 at this temperature is closest to the critical point of the phase diagram of $(V_{1-x}Cr_x)_2O_3$, which is also located at 400° K (Ref. 9).

If $\omega\tau \gg 1$, electrons can no longer be transferred from one band to the other during one acoustic wave period and, therefore, v_∞ no longer includes a contribution from the transfer of electrons between the bands in the course of propagation of sound. However, when the band overlap becomes considerable, there is a large contribution to v_∞ from the static redistribution of elec-

trons between the bands and the associated modification of the lattice (Fig. 5). This redistribution becomes important at $T \sim 380^\circ \text{K}$ since the absolute values and temperature dependence of v_∞ up to 380°K are identical with those found by extrapolation from the temperature range $150\text{--}250^\circ \text{K}$ (Ref. 4). The change in the temperature dependence of v_∞ in the 400°K range (Fig. 5) cannot be explained by a change in the density of a crystal because in the temperature range in question ($300\text{--}600^\circ \text{K}$) the volume of a unit cell changes by just $\sim 1\%$ (Ref. 12). Clearly, this change results from the redistribution of electrons between the bands.

When temperature is increased above 450°K , dispersion of the velocity of sound decreases (Figs. 1 and 2). This means that the relative positions of the bands become less affected by the formation and the process of redistribution of electrons in the bands is completed. Zeiger's calculations lead to the same conclusion. However, the linear temperature dependence of v_∞ at $T > 450^\circ \text{K}$ shows no tendency to change. Consequently, the change in the slope at $T > 450^\circ \text{K}$ is not an anomaly which exists only in the temperature range where the electron redistribution takes place. It is associated with a change in the anharmonicity constants which occurs as a result of this redistribution. In other words, the temperature dependence of v_∞ is an integral effect which is governed not by the possibility of electron transitions from one band to another (as in the dispersion of sound) but by the actual electron densities in each band. The bulk of electrons is transferred from the wide to the narrow band at temperatures from 350 to 450°K and it is in this range that there is a change in the temperature dependences $v_\infty(T)$ and $\sigma(T)$.

The anharmonicity governing the dependence $v_\infty(T)$ may be of the lattice or electron origin. The importance of the electron anharmonicity can be demonstrated simply by analyzing the data on the dispersion of the velocity of sound using the Goodenough-Zeiger model.

The total free energy $F(\varepsilon, n_2, T)$ (here, ε is the strain; n_1 and n_2 are the electron densities in the first and second bands; $n_1 + n_2 = n = \text{const}$) can be represented in this model by the sum of the free energy of the lattice $F_l(\varepsilon, T)$ and the free energy of electrons in the bands in question:

$$F(\varepsilon, n_2, T) = F_l(\varepsilon, T) + n_1 \mu_1 + n_2 \mu_2 + \Delta_0 - kT \int \rho_1(E) \ln \left[1 + \exp \left(\frac{\mu_1 - E - \Delta_1}{kT} \right) \right] dE - kT \int \rho_2(E) \ln \left[1 + \exp \left(\frac{\mu_2 - E - \Delta_2}{kT} \right) \right] dE \quad (3)$$

Here, $\rho_1(E)$, $\rho_2(E)$ and μ_1 , μ_2 are the densities of states and the chemical potentials of the first and second bands, respectively,

$$\Delta_1 = \frac{\partial H_{\text{int}}}{\partial n_1}, \quad \Delta_2 = \frac{\partial H_{\text{int}}}{\partial n_2}, \quad \Delta_0 = H_{\text{int}} - n_1 \Delta_1 - n_2 \Delta_2, \quad (4)$$

are the corrections to the energy originating—in the self-consistent field approximation—from the Hamiltonian H_{int} describing the interaction of electrons with the lattice and with one another.¹⁵

Using the relaxation equation

$$\frac{\partial n_2}{\partial t} = -\gamma \frac{\partial F}{\partial n_2}, \quad (5)$$

we can easily obtain the relationships

$$\left. \begin{aligned} c_\infty &= \frac{\partial^2 F}{\partial \varepsilon^2}, \quad c_\infty - c_0 = \left(\frac{\partial^2 F}{\partial \varepsilon \partial n_2} \right)^2 / \frac{\partial^2 F}{\partial n_2^2}, \\ \frac{1}{\tau} &= \gamma \frac{\partial^2 F}{\partial n_2^2}, \end{aligned} \right\} \quad (6)$$

where c_∞ and c_0 are the elastic moduli for $\omega\tau \gg 1$ and $\omega\tau \ll 1$, respectively.

Within the limits of the experimental error, the values of τ are independent of the direction of propagation of sound in a crystal (Fig. 6), in full agreement with the model.

It follows from Eq. (3) that

$$\frac{\partial^2 F}{\partial \varepsilon \partial n_2} = \frac{\partial \Delta_2}{\partial \varepsilon} - \frac{\partial \Delta_1}{\partial \varepsilon} \quad (7)$$

If the interaction of electrons with the lattice could have been described by the deformation potential constants, the expression on the right-hand side of Eq. (7) would have depended only on the anisotropy of these constants and would have been independent of temperature.

Figure 8 shows the temperature dependence of the ratio of the differences $c_\infty - c_0$ for two crystallographic directions. The strong temperature dependence of this ratio shows that the approximation of the deformation potential constants is clearly insufficient for describing the electron-phonon interaction throughout the temperature range from 330 to 500°K . We can attempt to explain the temperature dependence $\partial^2 F / \partial \varepsilon \partial n_2$ by narrowing of the energy bands as a result of thermal expansion of the lattice. However, we can easily show that the change in the electron energy is, in the first approximation, proportional to the change in the band width. Therefore, the dependence in Fig. 8 cannot be explained by the linear dependence of the band width on the strain.

Considerable dispersion of the velocity of sound in the vicinity of the critical point is associated with the long relaxation time. An analysis of the results shows that the relaxation time varies only negligibly throughout the investigated temperature range and the dispersion maximum is associated with the maximum of the quantity $(v_\infty - v_0) / v_\infty \cong (c_\infty - c_0) / 2c_\infty$. Usually an increase in the relaxation time in the vicinity of the critical point is associated with a reduction in the rigidity of the system, which in our case is described by $\partial^2 F / \partial n_2^2$,

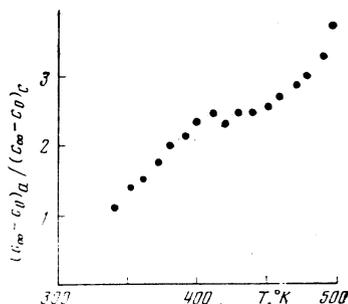


FIG. 8. Dependence of $(c_\infty - c_0)_a / (c_\infty - c_0)_c$ on the temperature T .

and the kinetic coefficient γ is assumed to be independent of temperature. In the present case we may expect a considerable temperature dependence of the kinetic coefficient γ . In fact, the following approximate formula can be written down for γ :

$$\gamma = 2\pi\hbar^{-1} |M_{12}|^2 \rho_1(\mu - \Delta_1) \rho_2(\mu - \Delta_2), \quad (8)$$

where M_{12} is the matrix element of the transition between the first and second bands. At low temperatures the band overlap is small and since the densities of states at the band edges are low, the product $\rho_1 \rho_2$ in Eq. (8) is small. The band overlap increases with rising temperature and so do the densities of states near the Fermi level. A further increase in the band overlap causes the density of states of the first band (the total number of states in this band is half that in the second) to pass through a maximum and then to fall. There is an associated fall in γ . Therefore, γ has a maximum in the region of the transition. The weak temperature dependence of τ can be explained by the fact that this maximum compensates the minimum of $\partial^2 F / \partial n_2^2$ in the region of the transition.

It follows from our results that the acoustic anomalies observed at temperatures 250–500° K are in qualitative agreement with the Goodenough–Zeiger model of overlapping bands.

There is no dispersion in the vicinity of the deep minimum of the velocity of sound at 520° K (Fig. 2). Hence, this minimum is not associated with the high-temperature phase transition described above. On the other hand, at 520° K there is a specific heat singularity¹⁷ and the small-angle scattering of cold neutrons has revealed the appearance of magnetic order.¹⁸ This may be associated with the localization of electrons in the second (narrower) band. The band is formed from the orbitals of the vanadium atoms lying in the basal plane.¹⁴ At 520° K the distance between the atoms is 2.90 Å (Ref. 12), which is close to 2.94 Å identified by Goodenough¹⁴ as the critical value for the total localization. The minimum of the velocity of sound at 520° K may thus be attributed to fluctuations in the vicinity of a magnetic phase transition.

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¹⁾The published measurements of the Hall effect^{6,16} revealed no anomalies in this temperature range. The absence of these anomalies is difficult to reconcile with the Goodenough–Zeiger model. The problem requires further experimental studies.

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