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High elastic modulus in *b*-axis-oriented single crystal V_2O_5

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Abstract

The elastic moduli of V_2O_5 are of great importance for the assessment of the buildup of strain during thin-film growth as well as for the analysis of defect generation and propagation. The usually rather small crystal dimensions make a precise experimental determination of the elastic constants highly challenging and only very little is known about the temperature dependent strain evolution. Here large V_2O_5 single crystals grown with different parameter sets are investigated by ultrasonic pulse experiments and by sampled continuous wave ultrasound spectroscopy. The elastic modulus C_{22} is determined to be 220 GPa at room temperature. Temperature dependent investigations of the elastic behavior show that ultrasonic experiments are suitable for highly sensitive detection of oxygen-deficient phases in rapidly grown samples. In addition they indicate the presence of temperature dependent elastic instabilities in inhomogeneous samples.

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1. Introduction

The Magneli-series V_nO_{2n-1} is known for its sharp temperature- and magnetic-field-dependent metal–insulator transitions, which are absent in the fully oxygenized parent compound V_2O_5. While V_2O_5 is generally studied as a model of this material system without exhibiting a phase transition [1], there is currently an intense research activity because of this compound's catalytic properties. It has been established that the undisturbed structure appears to be catalytically rather inactive. However, as yet unknown surface defects seem to increase the conversion rate, and therefore defect structures are now investigated for their role in enhancing the catalytic activity. A precise knowledge of the elastic properties is of great importance to understand the mechanisms of defect-generation and -migration in this material. Only few experiments aiming at determining the elastic constants directly have been reported. This lack of information is mainly due to the difficulty to obtain single crystals of V_2O_5 with satisfactory size dimensions. Consequently, sound velocity measurements were performed with unconventional techniques [2,3]. Since V_2O_5 crystals with dimensions of several millimetre along all principal axes can now be grown using floating zone melting, we have performed conventional ultrasound pulse experiments in order to determine the sound velocity. Subsequently a sampled continuous wave technique is employed to measure the temperature dependence of the ultrasonic attenuation in crystals of different quality. The results demonstrate that ultrasound attenuation is a powerful tool to detect growth related inhomogeneities.

2. Experimental

2.1. Crystal growth

Single crystals of V_2O_5 are commonly produced by

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means of chemical vapor transport (CVT) [4–6]. Even though this technique is widely and successfully used, there are some well-known drawbacks. The growth time is of the order of several days to weeks, the crystal size is very limited, the growth direction for the crystal cannot be controlled and, above all, contaminations from the transport reagent can be found in the crystals. Crystals of much higher purity can be produced by melt-techniques. Very thin, lamellar crystals of V_2O_5 can be obtained rather easily from the melt [7,8]. The dimensions along the *a*- and *b*-axis reach several millimetre (with special purification techniques up to several cm [8]), while the thickness along *c* is usually only a fraction of 1 mm. In order to reliably determine the elastic constant in at least one orientation by conventional ultrasound techniques, crystals with *c*-axis dimensions of several millimetre are needed.

Large single crystals of V_2O_5 were produced here via floating zone melting (FZM). The FZM furnace consists of two symmetrically mounted ellipsoidal mirrors. The construction of the mirrors is similar to those described in [9]. The axis of sample transport is perpendicular to the symmetry axis of the mirrors running through the common second focus of both mirrors. V_2O_5 powder (Chempur 99.9%) was pressed into rectangular bars of $6\times6\times70$ mm^3 and then sintered in air at 650 °C for 15 h. This sintered bar was mounted on the sample feed of the furnace, and a smaller sintered bar holding a seed crystal was fixed on the lower support. Crystals were grown at 5 and 30 mm/h. While the crystal-size parallel to the rod-axis is in principle only limited by the growth time and the physical restrictions of the furnace, homogeneous growth over the whole rod-width was only achieved after introducing a well-defined horizontal temperature gradient in the melting zone. By using this technique a significant increase in crystal thickness (along *c*) was achieved. Single crystals of typically $12\times5\times2$ mm^3 of high purity were routinely obtained and characterized. The structural quality and the dominant growth direction of the crystal were determined by Laue-X-ray back-reflection perpendicular to the easily cleaved (*a*,*b*)-surface of the single crystal. The direction along the cylinder axis was identified as the crystallographic *b*-axis.

2.2. Sound velocity

Due to the small crystal sizes of V_2O_5 usually available, no conventional ultrasound experiments have been reported in the literature. Nanai et al. reported sound velocity experiments along the crystallographic *c*-axis (labeled (010) in their paper) [2] as well as along all three principal axes [3]. Due to the restrictions in sample size the authors excited an acoustic wave package with a laser pulse which was focused on the crystal surface. The acoustic signal was detected by a conventional transducer after travelling through the sample and an 8 mm layer of water which served as an acoustic delay line. This sophisticated setup had to cope with several technical difficulties. Here we aim at determining the sound velocity more directly using different approaches. First we measure the transition time of a short ultrasound pulse generated and detected with quartz transducers. We compare this measurement of the group velocity with the result of exciting a long 5 MHz pulse and analyzing the response at a receiving transducer. Finally we measure the temperature dependent sound velocity changes by a 'quasi'-continuous wave technique, known as sampled continuous wave (SCW) experiment. In acoustic SCW experiments the resonances of a sample with known dimensions and plate-parallel end surfaces are determined. In these experiments ultrasound is excited and detected by one quartz transducer which is bonded to the sample surface. A radio frequency electromagnetic pulse with a width much longer than the acoustic travel time is applied to the transducer. After excitation of an acoustic pulse of the order of 50 μs, the frequency-dependent amplitude of the exponentially decaying acoustic response is recorded. The envelope of the received signal gives the attenuation and a fast Fourier transform (FFT) of the signal the acoustic resonance-frequency of the system. Clear amplitude maxima mark the acoustic resonances of the transducer-sample system. As a first approximation, the frequency difference between neighbouring resonances can be evaluated in a quite straight-forward manner. With sample length l and a separation of resonance frequencies Δf the sound velocity can be calculated by

$$v = 2l\Delta f \tag{1}$$

This expression only holds if the influence of the transducer on the acoustic sound path can be ignored. The modeling of a real system has been attempted by Bolef and Menes [10], taking advantage of the analogy between electromechanical and purely electrical problems, which are described as transmission lines. The assumption that the resonance frequencies of the sample and the transducer-sample composite differ by not more than 10^{-3} leads to considerable simplifications in the expression and finally to a correction which can be envisioned as modified sample length:

$$v = 2l(1+\delta)\Delta f \tag{2}$$

with

$$\delta = \frac{l_T\rho_T}{l_S\rho_S} \tag{3}$$

Here l_S and l_T are the length and ρ_S and ρ_T the mass density of the sample and transducer, respectively. This expression is valid as long as the influence of the transducer attenuation can be ignored. It was shown that detailed considerations of this influence lead to considerable improvements in the otherwise highly underestimated sound-velocity [11]. In the work presented here we use this approach to follow the temperature dependent relative velocity and attenuation changes.

3. Results and discussion

Large crystals of V_2O_5 were grown by FZM as described in Section 2.1. As-grown samples consisting of *b*-axis-oriented single crystals were used to measure the sound velocity. In order to study the influence of growth parameters on the defect-density and therefore the elastic behavior of V_2O_5 single crystals, a series of samples was grown at similar conditions with the growth speed varied. For the determination of the sound velocity, discs with a thickness between 2 and 10 mm were cut from the cylindrical crystalline sample. The parallel end faces of a,*b*-axis-oriented sample of 8.95 mm length and 6 mm in diameter were polished and covered with 5 nm CrNi and 150 nm Au to serve as ground-contact. An *x*-cut quartz transducer with base frequency of 5 MHz was mounted at both end faces to serve as excitation source and detector, respectively, for the acoustic pulse. A 200 V DC pulse was fed into the transducer at $t=0$ while the signal of the receiving transducer was recorded.

The analysis of the recorded signal as shown in Fig. 1 is straightforward. The crosstalk of the DC excitation-pulse is visible after a delay of about 110 ns, which is attributed to delays in cables, amplifiers and receiver. The arrival of the strain-pulse is easily determined as $\tau=1.1$ μs (onset of pulse). Furthermore, an additional sound pulse is detected after another round-trip of 2.2 μs-consequently about 3.3 μs after the start of the strain-pulse. The precision can be estimated to be about 5%. Taking into account the sample length of $l=8.95$ mm and the simple relation $v_s=l/\tau$ yields a sound-velocity of (8100 ± 200) m/s. Since this velocity is considerably higher than the velocities published in [2,3] we decided to check the velocity measurement with an additional approach. We applied a 10 μs rf electromagnetic pulse of 5 MHz to the excitation transducer. If this pulse-length is considerably longer than the travel time of an acoustic pulse in this material, an exponential increase of the received signal is expected after a delay corresponding to the time needed for the sound to traverse the sample (τ). The inverse is expected at the end of the excitation: the signal should start to decay exponentially at a time τ after the end of the excitation. Exactly this behavior is observed (Fig. 2) with $\tau=1.1$ μs as in the preceding experiment, leading, again, to 8100 m/s. It has to be noted that the resolution of this approach is limited by the rf oscillations of the signal. Deviation from constant amplitude can only be determined within about half an oscillation-corresponding to 0.1 μs at 5 MHz. The data from Fig. 2 should only be seen as a verification of the results obtained from Fig. 1. With a mass density of $\rho=3.357\times103$ kg/m^3 the corresponding elastic modulus C_{22} is (220 ± 6) GPa, using the relation $C=\rho v_s^2$.

In the experiments described above we have observed that the ultrasonic attenuation is extremely high in this material. We speculate that this is a result of the sound propagating along the only weakly (von-der-Waals-)bonded (*a*,*b*)-planes, most likely reflecting the expected pronounced anisotropy in sound-velocity which should result from the highly two dimensional structure of the system. A reliable

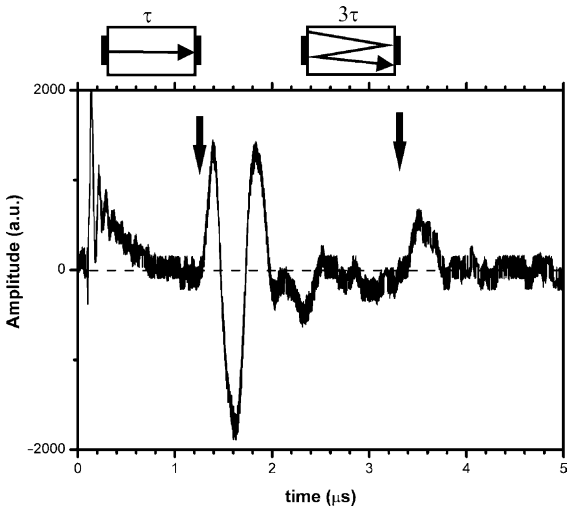

Fig. 1. Signal recorded at the receiving transducer. The crosstalk of the DC excitation-pulse, which was switched on at $t=0$, is visible after a delay of about 110 ns, which is attributed to cables and amplifiers. The arrival of the strain-pulse and the first echo is clearly visible at $\tau=1.1$ μs and 3τ, respectively.

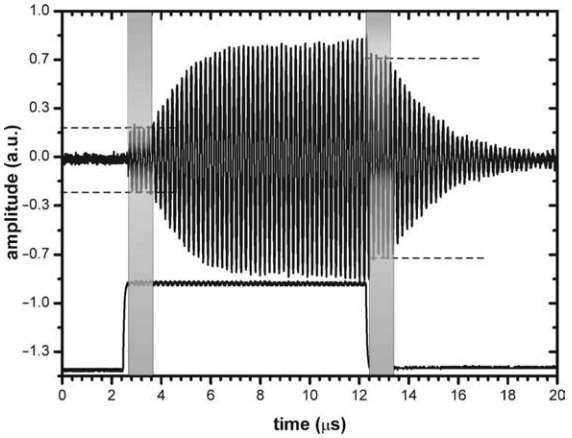

Fig. 2. Signal recorded at the receiving transducer while applying a 10 μs rf electromagnetic pulse of 5 MHz to the excitation transducer (upper curve). Pulse gate-signal (lower curve). The crosstalk of the excitation-pulse, which was switched on at $t=2.45$ μs, is visible with constant amplitude (shaded area at the beginning of the pulse) after a delay of about 200 ns, which is due to cables and amplifiers. The arrival of the strain pulse at the receiving transducer 1.1 μs after start of excitation leads to an amplitude increase until the signal saturates. The reverse effect is visible after switching off the pulse: at $t=12.2$ μs the signal drops by the value of the rf crosstalk amplitude, remains constant as long as the strain-pulse arrives at the receiving transducer (shaded area at the end of the signal) and starts to decay exponentially 1.1 μs after the excitation is switched off, reflecting the arrival of the end of the strainpulse.

analysis will require a detailed knowledge of the elastic modulus tensor-which is not available to date.

In the following, the temperature dependent relative attenuation changes are investigated by sampled continuous wave experiments which have a much higher resolution than pulse experiments. As a consequence of the high background attenuation, SCW experiments have to be performed on rather thin samples in order to be able to excite and detect clear acoustic resonances. Therefore, a slice of 2 mm thickness was cut from the cylindrical sample used above and from a rapidly grown sample. Both faces were plate-parallel and polished. One side was covered with CrNi and Au to serve as ground contact for the 5 MHz *x*-cut quartz transducer. Fig. 3 shows the temperature dependent attenuation at about 22 MHz for two different samples. While the attenuation appears to be rather featureless over the whole temperature range for the slowly (5 mm/h) grown crystal (curve *a*), a pronounced attenuation anomaly at about 250 K (curve *b*) for the rapidly grown sample (30 mm/h) is attributed to inhomogeneities in the less ordered sample. Further investigations are needed to unambiguously determine the source for this attenuation contribution in disordered samples. Frequency dependent measurements of the peak position, however, allow to rule out thermally activated processes (as for example defect excitation). The characteristic frequency of thermally activated processes is expected to increase with increasing temperature-and would therefore lead to an increase in attenuation-peak position with increasing excitation frequency. The anomaly observed here, however, shifts to lower temperatures. We therefore assume that this anomaly is directly related to intrinsic phase transitions. In this context it is worth mentioning that the metal–insulator transition of V_4O_7 occurs at 250 K-which is just the temperature of the attenuation anomaly observed here.

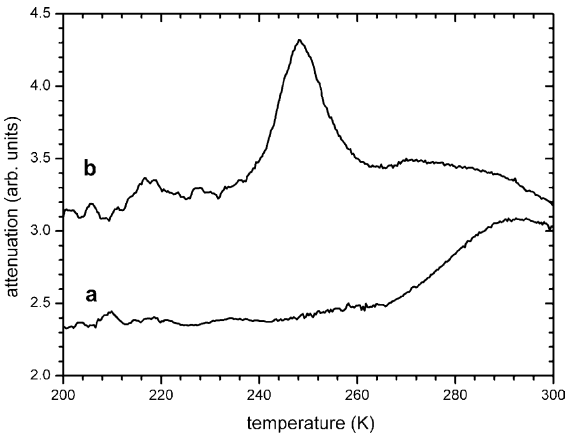

Fig. 3. Temperature dependence of the ultrasonic attenuation in two different samples of V_2O_5. While the attenuation is rather featureless for a slowly grown crystal, pronounced attenuation anomalies are clearly visible in the fast grown sample-indicative of spurious phases with reduced oxygen stoichiometry.

4. Conclusion

The elastic modulus C_{22} of V_2O_5 was determined by ultrasound pulse-transmission experiments. Using two different approaches lead to (220 ± 6) GPa, corresponding to a sound velocity along the *b*-axis of V_2O_5 of (8100 ± 200) m/s. While this value is surprisingly high, a pronounced anisotropy is expected in this layered, highly two-dimensional system. The temperature dependent ultrasonic attenuation of well-ordered, high-quality single crystals was found to be rather featureless in the temperature range investigated here. In contrast, rapidly grown, intentionally disordered crystals show a pronounced attenuation peak, which is ascribed to internal spurious phases, most probably oxygen deficient V_4O_7. It is suggested to use temperature dependent attenuation anomalies as a sensitive 'fingerprint' for the crystal-quality in this material system.

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