PHYSICAL REVIEW B VOLUME 60, NUMBER 19 15 NOVEMBER 1999-I

Elastic behavior near the metal-insulator transition of VO_2

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(Received 21 April 1999)

We report on temperature-dependent sound velocity measurements of surface acoustic waves performed on small VO_2 single crystals by means of ultrasonic microscopy. The elastic behavior of this compound has been studied ultrasonically through its metal-insulator transition. The investigations reveal a strong elastic anisotropy in the metallic phase which is reminiscent of the insulator TiO_2. Surprisingly, the anisotropy disappears almost completely, when the insulating phase is developed. The accompanying changes in lattice entropy are large and suggest that there is less reason to favor electron-electron correlations as a driving force of the metal-insulator transition in VO_2. [S0163-1829(99)08243-0]

Vanadium dioxide is one of the transition-metal compounds that has been attracting much attention for almost half a century due to its metal-insulator transition taking place near ambient temperature.[1] However, the microscopic origin of the experimentally observed conductivity jumps up to 5 orders in magnitude at $T_{\mathrm{MI}} \approx 339$ K and the mechanism stabilizing the low-temperature structural order is still not fully understood. Whether the ground state of VO_2 should be classified as a Mott-Hubbard insulator or may be explained within the conventional single-particle itinerant electron picture is still a matter of debate.[2] In the past, most activities were devoted to the role of electron-electron correlations in VO_2. Their importance for $T > T_{\mathrm{MI}}$ is particularly suggested from the large Pauli-like magnetic susceptibility of the metallic phase which is unusually high for a paramagnetic metal. Within the free-electron model the roughly estimated density of states at the Fermi level exceeds 20 states/(eV molecule) (Ref. 3) whereas recent band-structure calculations yield a density of states of only 3.36 (Ref. 4) and 4.18 states/(eV molecule) (Ref. 5), respectively.

The metal-insulator transition in VO_2 is of first order and the transformation entropy derived from latent heat data vary between 12.6 $\mathrm{J\,mol^{-1}\,K^{-1}}$ (Ref. 6) and 13.8 $\mathrm{J\,mol^{-1}\,K^{-1}}$.[7] Assuming electron localization as the main source, the entropy jump is about five times larger than that what is expected from band-structure calculations. Thus, in order to fit the experimental data of both the latent heat and the magnetic susceptibility, nearly the same enhancement factor is needed. Although strong electron correlations might explain this coincidence, it is nevertheless important to take into consideration mechanisms other than or in addition to purely electronic interactions that may be responsible for the metal-insulator transition and the simultaneously occuring structural instabilities.[8] As is well known, at T_{MI} the tetragonal structure of the metallic phase adopts a monoclinic symmetry with the nearest-neighbor cation distance dimerized in the insulating phase.[9,10] Hence, a realistic description must take into account changes in lattice entropy, too.

Studies of diffuse x-ray scattering[11] give hints that the lattice transformation is accompanied by a soft phonon mode at the *R* point of the Brillouin zone. Beyond that, however, the role of the lattice remains rather unclear insofar as details about the lattice dynamics of VO_2 are hard to obtain by common experimental methods. For instance, coherent inelastic neutron scattering, well established to study the phonon dispersion in crystals, is not feasible here due to the extremely large incoherent scattering cross section of vanadium.[12] Investigations by means of Raman spectroscopy suffer from the absence of a significant narrow-line phonon spectrum of the metallic phase.[13,14] As a consequence, neither neutron nor Raman experiments allow any definite conclusions about the phonon dispersion and the lattice force constants in this system. Hence, there is an urgent need for experimental data on this subject.

Bonding properties of crystal lattices are reflected in their elastic behavior. Especially in the long-wavelength limit, the stiffness coefficients can be determined quite accurately from sound velocity measurements usually performed by ultrasound in the MHz range. In spite of the fact that sufficiently large single crystals of VO_2 can be produced for quite some time, to our knowledge only one attempt is reported in the literature on this topic.[15] Unfortunately, the authors were not able to determine any of the elastic constants. An unpleasant peculiarity of larger single crystals is their notorious tendency to crack formation, triggered by the structural changes accompanying the metal-insulator transition. In addition, it is annoying that the insulating monoclinic phase supports the formation of domains typically some 10 μm in length. By means of optical microscopy the domain structure can be easily identified under polarized light. Sound waves, however, are typically excited over cross sections of several mm in diameter and both domains and cracks strongly influence the sound propagation. Hence, the obtained data are obscured by interference and scattering effects which question the reliability of conventional sound velocity measurements in this case.

Thus, we use Rayleigh-type surface acoustic waves (SAW), which can be locally excited on a crystal surface by means of a high-resolution ultrasonic microscope. It is a great advantage of such a microscope that it typically operates at a sound frequency of 1 GHz. The corresponding wavelengths of the excited SAW amount to little more than a few μm and are much smaller than the single-domain crystallites usually obtained. Ultrasonic microscopy is therefore a powerful method for investigating the elastic behavior of small VO_2 crystals.[16]

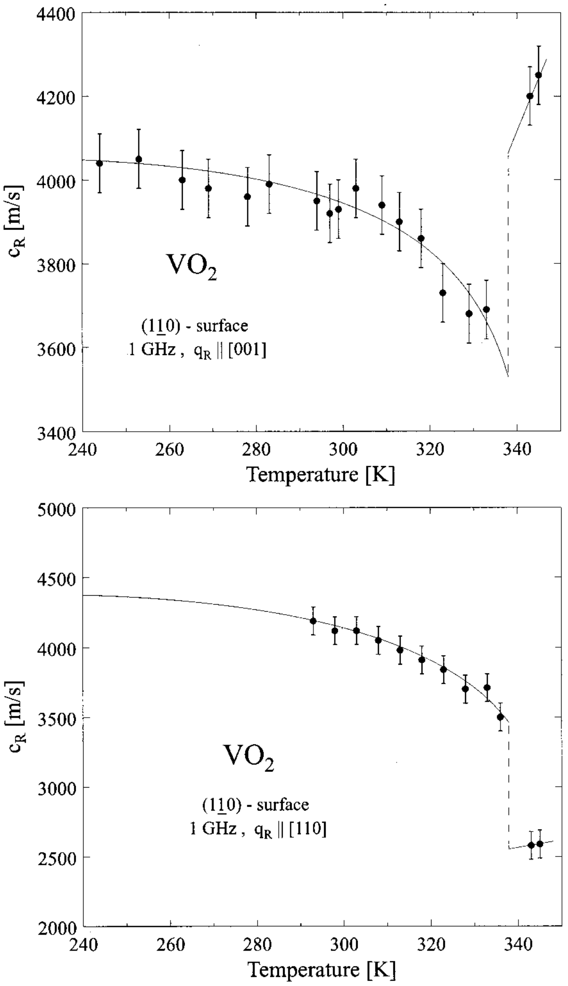

FIG. 1. Temperature dependence of the Rayleigh sound velocity c_R of 1 GHz surface acoustic waves propagating in the (1-1 0) plane along [001] and [110]. The lines are guides to the eye and the notation of the crystal axis refer to the tetragonal lattice of the VO$_2$ rutile phase.

The ultrasonic investigations are performed on single crystalline VO$_2$ grown by means of chemical transport reactions using a TeCl$_4$ carrier. A selection of crystals, suitable for ultrasonic microscopy, was first analyzed by the Laue technique of x-ray diffraction. The dispersion of high-frequency SAW may be strongly influenced by small surface defects and also by a weak unevenness of the crystalline surface. Therefore sound velocity measurements require samples with very smooth and even surfaces. It turns out that this prerequisite is fulfilled for our crystals predominantly in tetragonal (110) orientation. In order to avoid multiple scattering of the excited SAW, single-domain samples are first selected from the batch by optical inspection.

We neglect the monoclinic angle and all details concerning crystal orientation will refer to the tetragonal parent phase in the following. For surface waves propagating along the [110] and [001] directions in the (1-1 0) plane of VO$_2$ the experimentally obtained temperature-dependent sound velocity is shown in Fig. 1. Each data point in the diagram represents the mean value of a number of single measurements. The energy loss of the leaking SAW becomes considerably large for sound frequencies approaching 1 GHz. Particularly at lower temperatures, where high-pure methanol serves as an acoustic coupling medium, the radiation damping of surface waves becomes a severe problem. On the other hand, towards higher temperatures investigations by use of distilled water suffer more and more from boiling effects and it is therefore impossible to obtain reliable data above about 345 K.

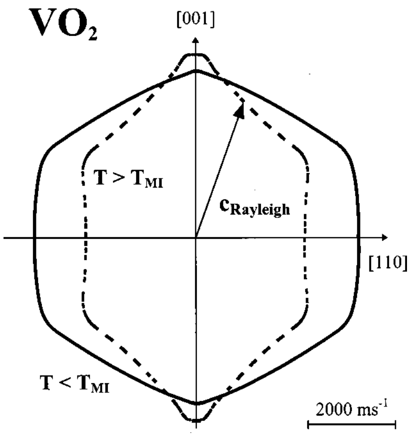

FIG. 2. Ray contours of the surface wave velocity in the (1-1 0) plane of metallic VO$_2$ at about 345 K and of insulating VO$_2$ at about 330 K. All specifications concerning crystal orientation refer to the tetragonal system.

As shown in Fig. 1, the sound velocity of the metallic phase gives some evidence for an anomalous elastic behavior above $T_{\rm MI}$. The velocity changes discontinuously at the transition temperature but in the opposite sense for the two modes shown. The [001] mode, propagating along the tetragonal *c* axis, shows a decrease of at least 10%. In contrast the [110] mode reveals a strong lattice stiffening in the basal plane. This corresponds to an increase in the elastic modulus of nearly 20%, which is exceptionally large.

From the sound velocity data it becomes obvious that the metal-insulator transition in VO$_2$ is accompanied by highly anisotropic changes in lattice bonding. In order to study the behavior near $T_{\rm MI}$ in more detail, we investigated the angular dependence of the SAW velocity. The angular-dependent sound velocity shown in Fig. 2 reveals a striking elastic anisotropy of metallic VO$_2$. As shown in Ref. 17, for a system of tetragonal symmetry the velocity $c^{[001]}$ of a Rayleigh mode propagating in the [001] direction is predominantly related to the stiffness coefficient C_{44} whereas the elastic modulus belonging to $c^{[110]}$ is essentially proportional to $1/2(C_{11}-C_{12})$. The anisotropy parameter of metallic VO$_2$ related to the ray contour in Fig. 2 is approximately[18]

$$A=\frac{2C_{44}}{C_{11}-C_{12}}\approx\left(\frac{c^{[001]}}{c^{[110]}}\right)^2=2.7. \qquad (1)$$

Noteworthy, it differs markedly from the isotropic case $A=1$ but is almost equal to the anisotropy parameter of TiO$_2$ (see, e.g., Ref. 19). In detail, our investigations reveal a ray contour of metallic VO$_2$ which is reminiscent of TiO$_2$. Metallic VO$_2$ is isostructural to TiO$_2$ which, however, is an insulator with a band gap of about 3 eV.[20] The fact that the mean sound velocity is much lower in VO$_2$ than in TiO$_2$ points to screening of the interatomic bonds by conduction electrons. On the other hand, the anisotropy differs only marginally and suggests isotropic screening. This idea fits in with results obtained from transport measurements,[21] where it is found that the electronic conductivity of metallic VO_2 is almost isotropic as well.

When the insulating state develops, the elastic anisotropy of VO_2 disappears almost completely and the mean stiffness increases drastically. These features strongly support the idea that the lattice is not passive in the initiation of the phase change. In particular, the stiffness increase is indicative of a decreasing phonon density of states and points to a considerable loss of lattice entropy at T_{MI}. Provided that the investigated crystal plane is representative of the whole system, the entropy loss can be estimated from our sound data.

As is well known, the Debye temperature Θ_D may be calculated in harmonic approximation and depends primarily on the mean sound velocity $\langle c_{\mathbf{q},j}\rangle$ averaged over all directions $\mathbf{q}$ and acoustic branches $j=1,2,3$. The Debye model then yields a relationship

$$\Theta_D \propto \langle c_{\mathbf{q},j}\rangle. \tag{2}$$

The lattice stiffening at T_{MI} leads to an increase of the mean sound velocity of about 15% and the Debye temperature should behave analogously according to Eq. (2). Since the phonon entropy S_{ph} at a given temperature depends mainly on Θ_D, a considerable change in entropy is therefore expected. The high-temperature expansion of $S_{\mathrm{ph}}(T)$ given by Thirring can be used as an adequate approximation for temperatures higher than $0.2\Theta_D$.[22] As a function of Θ_D, the phonon entropy in lowest order has the form

$$S_{\mathrm{ph}} \approx 3Nk_B\left(\frac{4}{3}+\ln\left\{\frac{T}{\Theta_D}\right\}\right), \tag{3}$$

where N is the number of atoms per mol VO_2 and k_B is the Boltzmann constant. Accordingly, for the entropy change ΔS_{ph} at T_{MI} and by use of the definitions

$$\Theta_D^{+,-}=\Theta_D(T>T_{\mathrm{MI}},T<T_{\mathrm{MI}}) \quad \text{and} \quad \Delta\Theta_D \equiv \Theta_D^- - \Theta_D^+, \tag{4}$$

one obtains

$$\Delta S_{\mathrm{ph}} \approx 3Nk_B \ln\left\{\frac{\Theta_D^-}{\Theta_D^+}\right\}\Bigg|_{T\to T_{\mathrm{MI}}} \approx 3Nk_B\left(\frac{\Delta\Theta_D}{\Theta_D^+}\right)\Bigg|_{T\to T_{\mathrm{MI}}}. \tag{5}$$

Replacing the respective quantities by their actual values yields

$$\Delta S_{\mathrm{ph}} \approx 11.2\ \mathrm{J\,mol^{-1}\,K^{-1}} \quad \text{for} \quad \left(\frac{\Delta\Theta_D}{\Theta_D^+}\right)\Bigg|_{T\to T_{\mathrm{MI}}}=0.15. \tag{6}$$

This result matches quite well with the experimental value $\Delta S \approx 13\ \mathrm{J\,mol^{-1}\,K^{-1}}$ obtained from latent heat measurements.[6,7] Hence, our result is quite suggestive of a phase transition, where the lattice plays the dominant role in the transition scenario.

Support to this idea is also given by x-ray diffraction studies,[23] where it is found that the atomic thermal displacement parameters of both phases differ strongly and indicate a 10–20 % increase of the Debye temperature at T_{MI}. This is in fair agreement with our results.

In the monoclinic phase the lattice parameter moderately decreases on further cooling.[24] On the other hand, the sound velocity shows a pronounced increase. The behavior of the two modes shown in Fig. 1 is exemplary for the whole crystal plane. The increase below T_{MI} exceeds 10% for a temperature range of 100 K and points to a progressive stiffening of the lattice which is indeed surprising. Temperature coefficients found in ordinary materials are considerably smaller and the velocity increase over 100 K is not much more than 1–2 %.

There is much evidence for the hypothesis that the anomalous stiffening is a basic feature of the insulating phase. In particular, the temperature-dependent sound velocity and the behavior of $\Theta_D(T)$ obtained from specific-heat measurements[23] exhibit a striking similarity. This unusual elastic behavior may be ascribed to lattice anharmonicities which, according to Fig. 1, become stronger on approaching T_{MI} from below. Even though the lattice parameter remains well behaved and lacks any anomalous behavior towards T_{MI}, the decreasing lattice stiffness points clearly to a weakening of the interatomic bonds. Unfortunately, it can hardly be gathered from the elastic properties whether this behavior is caused by thermal excitation of localized electron states or arises mainly from temperature-dependent band-structure effects. There is indeed some evidence from optical experiments that the peculiar elastic behavior of insulating VO_2 is closely connected with considerable changes in the electron band structure.[25–27] Since the overall change in stiffness is of percentage order, it can be expected, however, that lattice and electron degrees of freedom are strongly coupled. Whether such a strong electron-phonon interaction gives rise to excitations of polaronic type or is more related to the Jahn-Teller mechanism, as recently proposed,[28] has to be left for future investigations.

We thank K.-H. Höck and V. Eyert for stimulating discussions on this topic. The VO_2 single crystals were kindly provided by S. Horn and M. Klemm. This work was supported by the Deutsche Forschungsgemeinschaft (Forschergruppe HO 955/2-1).

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