Diffuse x-ray scattering due to the lattice instability near the metal-semiconductor transition in VO_2

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From studies of x-ray diffuse scattering it was found that a lattice instability near the metal-semiconductor transition in VO_2 occurs at the R point with wave vector parallel to ΓR and polarization vector parallel to the c axis. This result is in agreement with predictions by Gupta, Freeman, and Ellis.

Vanadium dioxide has been the subject of much experimental work and speculation in recent years because of its phase transition from semiconductor to metal at $T_c = 67.5$ °C. This transition is accompanied by a slight lattice distortion from a monoclinic structure in the low-temperature semiconducting phase to the tetragonal rutile structure in the metallic phase. The low-temperature phase is characterized by a pairing of the vanadium atoms along the c axis resulting in a doubling of the unit-cell dimension, and at the same time there is a doubling along the a axis.[1-3] The large thermal displacements found for the metallic phase[4] are compatible with a possible soft-mode transition. Although inelastic-neutron-scattering experiments are not available for VO_2, due to the large incoherent-scattering cross section of vanadium, a study of Raman scattering shows a broadening of the phonon spectrum, which suggests a large electron-phonon coupling.[5]

Recently, Gupta, Freeman, and Ellis[6] have examined the electronic structure of metallic VO_2. The dominant band exhibits strong nesting features corresponding to a vector $\vec{q}_0 = 2\vec{k}_F = \Gamma R$ and the generalized susceptibility $\chi(\vec{q})$ shows a maximum at the R point (see Fig. 1). It can be shown that the general susceptibility function $\chi(\vec{q})$ plays an important role in the expression of the renormalized phonon frequencies and that, with some simplifying assumptions, a divergence in $\chi(\vec{q})$ at the R point can lead to a softening of the corresponding vibrational mode.[7] Therefore, they suggested that the formation of a charge-density wave with wave vector $\vec{q}_0 = \Gamma R$ is possible and a soft phonon at the point R might be expected near T_c. As an important test of these ideas, x-ray diffuse scattering should be detected near the R point as T_c is approached, as the diffuse scattering intensity is proportional to the general susceptibility.[8]

The intensity of diffuse scattering due to a phonon mode[9] is given by

$$I_D = NI_e \sum_{\kappa,\kappa'} F_\kappa(\vec{K}) F^*_{\kappa'}(\vec{K}) \sum_s \frac{\langle U^2_{\vec{q}_s}\rangle (\vec{K}\cdot\vec{e}^{\kappa}_{\vec{q}_s})(\vec{K}\cdot\vec{e}^{\kappa'}_{\vec{q}_s})}{(m_\kappa m_{\kappa'})^{1/2}}, \tag{1}$$

where $\vec{K}$ and $\vec{e}^{\kappa}_{\vec{q}_s}$ are, respectively, the scattering vector and the polarization vector of the phonon with a wave vector $\vec{q}$ of the sth branch, and m_κ denotes the mass of the κth atom. The structure factor $F_\kappa(\vec{K})$ is determined by the coordinate of the κth atom in the unit cell. The factors N and I_e are the number of unit cells and the scattering intensity by one electron. Further, $\langle U^2_{\vec{q}_s}\rangle$ is the mean square amplitude of vibration in the sth branch with wave vector q, which can be written[10]

$$\langle U^2_{\vec{q}_s}\rangle = k_B T/\omega^2_{\vec{q}_s} \tag{2}$$

for $\hbar\omega_{\vec{q}_s} \ll k_B T$, where $\omega_{\vec{q}_s}$ is the angular frequency of the $\vec{q}_s$ phonon.

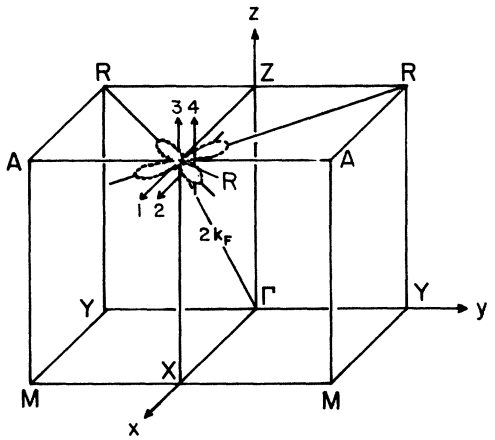

FIG. 1. Brillouin zone of the rutile phase of VO_2. Directions employed in measurements near the R point in Fig. 2 are shown by numbered arrows. Also shown is the diffuse cross of scattering at the R point expected from a "transverse" phonon polarized in the z direction.

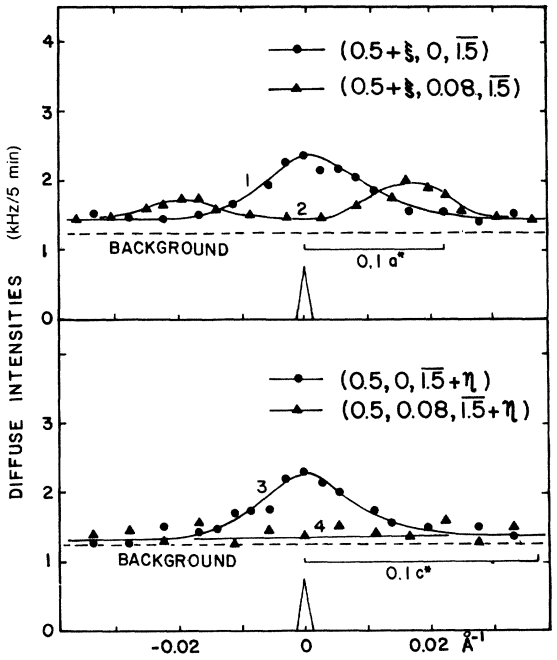

FIG. 2. Diffuse intensities vs position in reciprocal space for the four directions given in Fig. 1 near the R point at T_c+3 °C. Small triangles show the FWHM of the superlattice reflection (0.5, 0, −1.5) at T_c-5 °C. (Solid lines through the data are merely an aid to the eye.)

Equations (1) and (2) show that the diffuse intensity is inversely proportional to the squared phonon frequency over a small region of reciprocal space. Thus, the intensity is enhanced at the wave vector q where the frequency of a particular phonon is low.

Near the 0.5, 0, −1.5 point (R point), the scattering vector is $\vec{K}=0.5\vec{a}^*-1.5\vec{c}^*$ ($|\vec{a}^*|=0.220$ Å^{-1}, $|\vec{c}^*|=0.347$ Å^{-1}). Therefore, x-ray diffuse scattering "sees" the motion of atoms which oscillate almost in the c direction. In Fig. 1, the Brillouin zone is given for the space group $Pmnm$. If a "transverse" phonon ($\delta\vec{q}=\vec{q}-\vec{q}_0$ parallel to RR) softens near the R point and near T_c, diffuse scattering is expected in the R-R direction, whereas softening of a "longitudinal" phonon would cause diffuse scattering in the z direction. The case of the "transverse" phonon is shown in Fig. 1.

Here we report the first observation of x-ray diffuse scattering compatible with such softening. Measurements near the point 0.5, 0, -1.5 were made with Cu $K\alpha$ radiation from a singly bent pyrolytic graphite monochromator. A Ni filter (which reduced the background by one third, while reducing a Bragg peak only 12%) was placed in front of the detector to reduce fluorescence. Measurements were made in a camera with a thin Be hemispherical cover, and with a rough vacuum.

The observed diffuse intensity near the R point at T_c+3 °C is shown in Fig. 2. Small triangles in the figure give the resolution function estimated from the FWHM (0.0031 Å^{-1}) of the superlattice reflection (0.5, 0, -1.5) at T_c-5 °C. The background level shown by a broken line is estimated to be 1240 cts in 5 min by measurement at the 0.5, 0, -1 point at T_c+3 °C. The fluorescent intensity from vanadium is the strongest component of the background, but is independent of position in reciprocal space. Other contributions to the background are air scattering and Compton scattering both of which are also independent of the scattering angle in the small region where the measurements were carried out. For the $\vec{a}^*$ direction through the R point (see scan 1 in Fig. 1), a diffuse intensity maximum is observed at the R point. However, double maxima are observed for the 0.5 + ξ, 0.08, -1.5 direction (scan 2). For the $\vec{c}^*$ direction there is a single maximum for scan 3, but diffuse scattering could not be detected for run 4. Therefore, the x-ray data is consistent with the softening of a transverse phonon near the R point, as shown in Fig. 1.

The temperature dependence of the diffuse scattering due to a soft phonon arises because $\omega_{\vec{q}_s} \propto (T-T_0)^{1/2}$.[11] From Eqs. (1) and (2), we have then

$$I_D \propto T/(T-T_0)\,, \tag{3}$$

where T_0 is the classical phase transition temperature. In Fig. 3 the observed temperature dependence of the diffuse scattering intensity at the R point is shown. The measurements were carried out by decreasing the temperature. (The transition temperature T_c is 67.5 °C.) The position of the 0.5, 0, -1.5 point was established from neighboring fundamental Bragg peaks above T_c and a larger

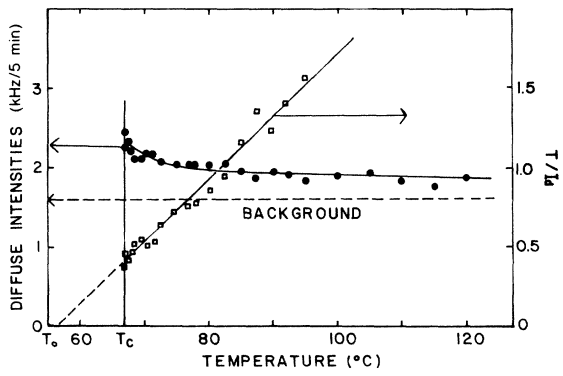

FIG. 3. Temperature dependence of the diffuse intensity at 0.5, 0, −1.5. The reciprocal net intensities are also shown as small squares.

resolution (0.0055 $Å^{-1}$) was used in the measurements in order to get adequate intensities. (The background level was 1610 cts (5 min) at the 0.5, 0, -1 point at 120 °C, which is higher than that in Fig. 2 due to the lower resolution.) It is found that the diffuse intensity increases with decreasing temperature. The inverse intensities are also plotted in the same figure. The straight line was placed with a slope of +1 following Eq. (3) and the classical second-order phase transition temperature T_0 was determined to be (56.6 ± 0.5) °C, some 11 °C below T_c. It is now well known that beyond a few degrees above T_c, many first-order transformations behave in a classical manner,[12-14] and that T_0 should be slightly below T_c.

The results are consistent with the calculation of the general susceptibility by Gupta, Freeman, and Ellis[6] who suggest that the formation of a charge-density wave with the wave vector $\vec{q}_0 = \Gamma R$ is accompanied by a lattice instability at the R point. Similar effects are found in[15] NbO_2 and[16] $V_{1-x}NbO_2$ which show some indications of a possible soft phonon lattice instability, accompanied by a semiconducting to metallic phase transition. The fact that the diffuse intensity reported here for VO_2 is probably due to a charge-density wave is supported not only by its classical behavior, but also that the intensities at other points such as 1.5, 0, −0.5 (relative to 0.5, 0, −1.5) are much weaker, as is true of the superstructure reflections below T_c.

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