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Report:

Vanadium dioxide undergoes a phase transition from monoclinic (M) to tetragonal (= r-utile, T) symmetry at 68°C. The main structural effect is the conversion of alternatingly shorter and longer V-V distances into a sequence of equal distances, thus halving the translational repetition length in the \vec{c} -direction[†] as well as the unit-cell volume. Because of that structural change, the phase transition has long been considered as a prototype of a Peierls transition. The absence of magnetic ordering in the low-temperature phase, the drop of electrical resistivity at the transition temperature, and the positive temperature coefficient of the resistivity in the high-temperature phase supported that picture (see, e.g., [1]).

Recently, RM. Wentzovitch et al. [2] have questioned that view by considering also a Mott-Hubbard transition and concluded from an LDA pseudopotential calculation that the low-temperature phase is a band insulator. However, they also point out that the relation to the Mott insulator $\mathbf{V}_2\mathbf{O}_3$ is obvious and ask whether the categories Mott versus band insulator can be rigorously distinguished.

The project utilises Compton-scattering measurements on single crystals of \mathbf{VO}_2 in order to obtain more experimental evidence to discriminate between the two categories. In the absence of correlation effects (but probably even then), the reciprocal form factor $B(\vec{s})$, which is the Fourier transform of the momentum density $\pi(\vec{p})$ as well as of directional Compton profiles $J(\vec{q})$, has nodes at the translational lattice points $\vec{s} = \vec{s}_{uvw}$ if all bands of a solid are filled [3-5]. It should also be true for a genuine Mott insulator [6]. A metallic solid, on the other hand, has no such symmetry restriction; as a matter of fact, the Fourier sum of the $B(\vec{s}_{uvw}) \neq 0$ is equal to the occupation density $n(\vec{k})$ in \vec{k} -space [3, 4]. Measuring

[†] While carrying out this project, the choice of the monoclinic basis-vector system taken from literature and used in the application has turned out to be very inconvenient. We now use $\vec{a}_1 \propto 2\vec{a}$, $\vec{a}_2 \propto \vec{b}$ and $\vec{a}_3 \propto -\vec{c}$

Compton spectra with the scattering vector \vec{K} parallel to various \vec{s}_{uvw} , particularly those of low u, v, w indices, therefore provides interesting pieces for the puzzle of the nature of the phase transition.

The single crystals were grown by a chemical transport reaction at high temperature and therefore true single crystals only in the rutile phase. When passing into the monoclinic phase, the symmetry can be broken in four different ways and thus the specimens contained domains with four different orientations. Yet, also the superimposed \vec{s}_{uvw} split into two sets: those with doubling of the periodicity under $T \rightarrow M$ ($uvw_T = 001, 110, \dots; \vec{s}_d$) and those without ($uvw_T = 111, \dots; \vec{s}_i$).

The possible outcomes for those two sets are for the high-temperature phase

- (T1) $B(\vec{s}_d) = B(\vec{s}_i) = 0$ (all bands are filled, there is only a small concentration of charge carriers),
- (T2) $B(\vec{s}_d) \neq 0$ and $B(\vec{s}_i) = 0$ (VO_2 is a short-range metal),
- (T3) $B(\vec{s}_d) \neq 0$ and $B(\vec{s}_i) \neq 0$ (VO_2 is a long-range metal),

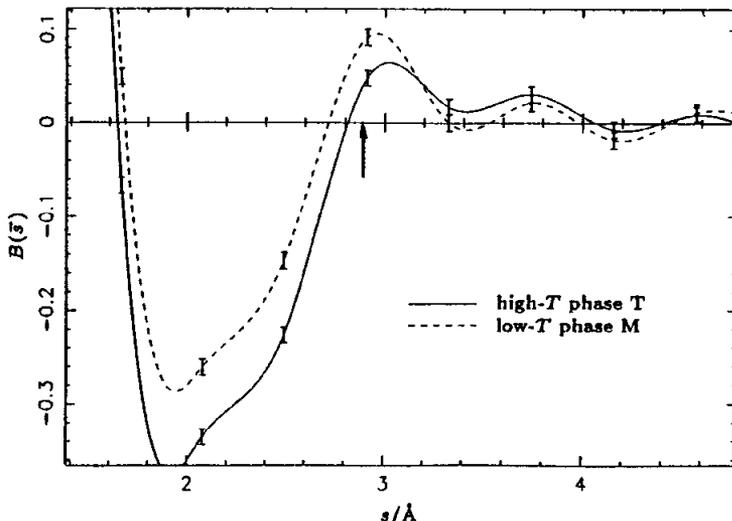
and for the low-temperature phase

- (M1) $B(\vec{s}_d) \simeq 0$ and $B(\vec{s}_i) = 0$ (VO_2 is a Mott insulator),
- (M2) $B(\vec{s}_d) \neq 0$ and $B(\vec{s}_i) = 0$ (VO_2 is a band insulator).

We have been able to collect data of sufficient statistical accuracy for two directions of the type \vec{s}_d : 001_T and 110_T . The figure shows the particularly relevant part of $B(\vec{s}), \vec{s} \parallel \vec{s}_{001_T}$, of both phases with $s_{001_T} = 2.87 \text{ \AA}$ marked by an arrow. The $B(\vec{s})$ of the two phases differ far outside the experimental uncertainties; the scale of the effect of about 0.1 electrons also proves how important it has been to invest the allotted amount of beamtime. None of the curves fulfils $B(\vec{s}_{001_T}) = 0$, and the low-temperature phase does it even less, i.e. the experiment supports the cases (T2) or (T3) (the high-temperature phase is a [because of the fast decay of B] medium-range metal) and (M2) (the low-temperature phase is a band insulator). This is in agreement with a Peierls-type phase transition.

- [1] P. B. Allen et al., Phys. Rev. B 48, 4359 (1993)
- [2] R. M. Wentzovitch, W. M. Schula, and P. B. Allen, Phys. Rev. Letters 72, 3389 (1994)
- [3] W. Schülke, phys. stat. sol. (b) 80, K67 (1977) and 82, 229 (1977)
- [4] W. Weyrich, Habilitationsschrift, Darmstadt 1978
- [5] P. Pattison and W. Weyrich, J. Phys. Chem. Solids 40, 213 (1979)
- [6] W. Weyrich, to be published.

Reciprocal form factor $B(\vec{s})$ of VO_2 , \vec{c} direction



‡ The oscillations on $B(\vec{s})$ are an artefact of the finite spectral range of the experiment and have to be minimised by further