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TEM Observation of the High-Temperature Metal–Insulator Transition in Cr-Doped V_2O_3

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The high-temperature metal–insulator transition in Cr-doped V_2O_3, $(V_{1-x}Cr_x)_2O_3$, was investigated by TEM at a composition $x = 0.006$. Boundaries between the metallic phase and the insulator phase were observed between room temperature and 150°C by both heating and cooling and their crystallographic features were investigated. Boundaries are low-index planes and their orientations are such that the change of dimension by the transition in the direction parallel to the specimen surface is zero. This indicates that the orientation of the boundary is determined by the condition of minimum strain energy. Misfit dislocations parallel to the specimen surface were found to exist under this condition. The motion of the boundaries is fast, but the boundaries can be trapped by defects or at those places where the area of boundaries becomes minimum. The observation is consistent with the existence of the temperature hysteresis of the transition and the discontinuous change of the resistivity–temperature curve of this transition.

Introduction

In Cr-doped V_2O_3, $(V_{1-x}Cr_x)_2O_3$, with $0.005 < x < 0.018$, a paramagnetic metallic phase (M) is encountered between an antiferromagnetic insulating phase (AFI) at low temperatures and a paramagnetic insulating phase (PI). At still higher temperatures the system reverts back to another metallic phase M′. The system thus undergoes two sharp and one gradual metal–insualtor transitions at a fixed composition as the temperature is raised (*1–3*). The problem with which we are concerned here is the first-order metal–insulator transition at intermediate temperatures (M–PI transition). The nature of this transition is far less understood than AFI–M transition at low temperatures. The transition is known to occur in stepwise fashion and is accompanied by a large temperature hysteresis (*1*), indicating that the characteristics of the transformation are similar to those in martensitic transformations. Both phases exhibit the corundum structure, but the transformation is accompanied by changes in lattice constants; there is an expansion in the *a* axis, but a contraction in the *c* axis as it transforms from M to PI (the indexing of the structure in this paper is based on the hexagonal lattice). The crystallographic features of the transformation have never been investigated in detail by transmission electron microscopy (TEM) because the symmetry of the structures of both phases is the same and thus the TEM investigation of their coexistence is very difficult.

So far, there are two reports on the direct observation of the transformation by TEM (*4, 5*). Only one (*4*) among these shows a

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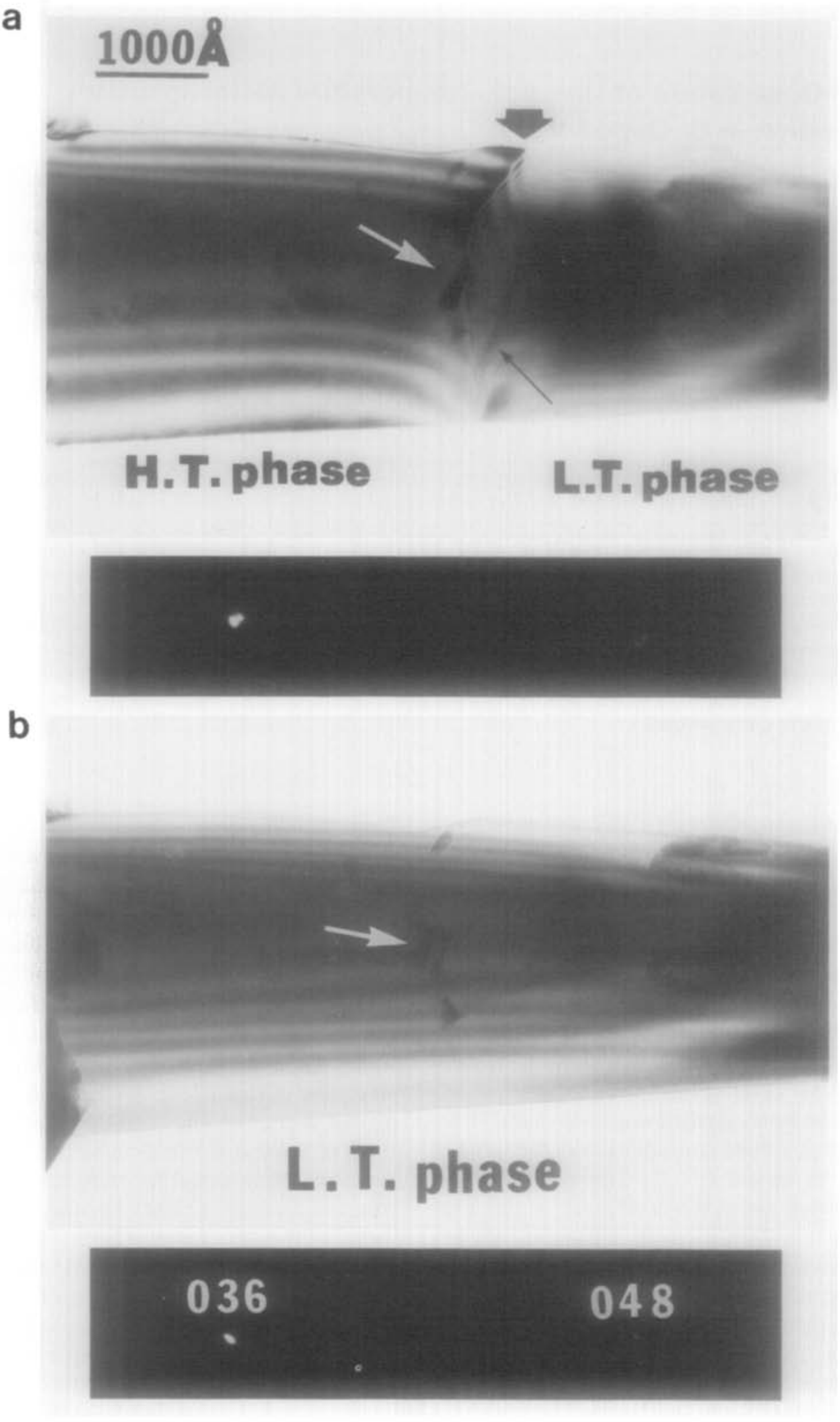
a
1000Å
H.T. phase
L.T. phase
b
L.T. phase
036
048

TABLE I

THE LATTICE CONSTANTS OF $(V_{9.99}Cr_{0.01})_2O_3$ AT 23°C (Ref. (*6*))

Low-temperature metal phase

$a = 4.9540$ Å $c = 13.9906$ Å

High-temperature insulator phase

$a = 4.9974$ Å $c = 13.9260$ Å

The change of dimension for the M → PI transformation

$\Delta a/a = 0.0086$; $\Delta c/c = -0.0043$

micrograph which indicates the coexistence of the two phases. The boundary is reported to be "non crystallographic" (*4*), but no further details have been provided. The present paper is intended to study the detailed crystallographic features involved in the transformation under controlled conditions so that the phenomenological aspects of the transformation may be understood.

Experimental

Single-crystal specimens of the composition $(V_{0.994}Cr_{0.006})_2O_3$ (and some other chromium contents) were prepared by a triarc melting method at the Central Material Preparation Facility of Purdue University. At this composition, the M–PI transition occurs at 100–120°C by heating and at 30–40°C by cooling, as observed by electrical conductivity measurements. Grown crystals are crushed in an agate mortar, and fine, crushed pieces are mounted on carbon films for TEM observation. A JEM 200CX electron microscope with a side-entry goniometer was used for observation. For observation at high temperatures, a single tilting heating stage was utilized because a high-resolution, double-tilting heating stage was not available.

Results

The first task of the experiment was to observe the boundaries between the two phases by TEM on heating and cooling between room temperature and 150°C. As experienced by previous investigators (*4, 5*), the observation of boundaries between the two phases turned out to be very difficult. Indeed, the boundaries could be observed roughly in one out of twenty to thirty specimens, although the M–PI transition should definitely be occurring in each specimen. Two major reasons responsible for this fact are:

1. The boundaries move very fast (*5*) and, unless they are locked at some place in the viewing area of the microscope, it is not possible to observe them.
2. The difference in contrast between the two phases is so weak that, unless the orientation of the boundary is favorable, it is very difficult to observe the boundary.

The following are the accounts of the observation of boundaries in such rare cases.

Figure 1a shows the transformation from the high-temperature insulating phase to the low-temperature metallic phase on cooling. The low-temperature phase (M) always starts from the thinner tip of the specimen on the right-hand side in the micrograph. At 40°C, a boundary is observed at the middle of the micrograph. This is indicated by a short black arrow. That this is the boundary of the two phases concerned is confirmed by the corresponding diffrac-

FIG. 1. Observation of a boundary between the metal phase and the insulator phase by cooling. (a) At 40°C. The boundary is observed at the center of the picture trapped by defects (indicated by a white arrow). A misfit dislocation (indicated by a thin arrow) parallel to the specimen surface is also observed. The corresponding diffraction pattern shows the coexistence of the two phases. (b) At room temperature (23°C). The boundary has swept the whole specimen. The corresponding diffraction pattern shows spots of the low-temperature phase. A defect which looks like a dislocation loop is indicated by white arrows, respectively, in both (a) and (b).

tion pattern which shows double 0 3 6 and 0 4 8 spots. The separations of these two spots agree well with the measurement of the lattice constants of these two phases by Robinson (*6*) (Table I). The elongation of these diffraction spots in one direction seems to be due to the specific shape (a thin rod) of the specimen. At the boundary, a defect (which looks like a dislocation loop) is detected (indicated by an arrow). The boundary seems to be locked by this defect in this case. In addition, a contrast which seems to be due to a misfit dislocation is found (indicated by a thin arrow). Since a single tilting stage was utilized, no further crystallographic information concerning the boundary could be obtained. That the contrast indicated by the thin arrow is due to a misfit dislocation is based on the fact that the imaging condition happened to be the "weak beam" condition (*7*). If the imaging condition deviates from the exact Bragg condition, the contrast in the matrix (such as the δ fringes observed at the boundary) decreases, whereas the contrast of dislocations can be increased by bringing the distorted part into the Bragg condition at the same time. Indeed, Yagi *et al.* (*8*) utilized this technique intentionally to observe misfit dislocations which arise in epitaxial films. Figure 1b shows the same part of the specimen at room temperature; the low-temperature phase has now swept through the entire specimen and the corresponding diffraction pattern below shows only single 0 3 6 and 0 4 8 spots.

In Fig. 2, the appearance and the motion of a boundary at 120°C on heating are shown. The high-temperature phase appears first at the tip of the specimen at the right-hand side and moves toward the left, while the temperature is kept constant. The boundary moves discontinuously, and the motion is found to be fast. In addition, the boundary location is affected by changes of the condition of the beam, such as tilting, converging, etc. The same specimen as shown here was repeatedly cooled and heated between room temperature and 150°C, and the boundary appeared at almost the same temperature in each case. Also, the boundary is found to stop at the same places in each case, indicating that boundaries are trapped at defects or at such places where the energy of the boundary becomes minimum. Indeed, a defect is found at the boundary in Fig. 1a.

It has also been found that, whenever boundaries are observed, these boundaries are almost perpendicular to the specimen surface. This seems to be due to the requirement that the boundary area has to be as small as possible. If the boundary is to be a certain (low index) crystallographic plane at the same time, the visibility of boundaries then depends on the orientation of specimens. This seems to be another reason why boundaries are so seldom observed.

In some as-crushed specimens, small regions of the high-temperature (PI) phase are sometimes observed even at room temperature. In addition to referring to diffraction patterns, identification of phases can also be made because regions of the high-temperature phase are found to expand by the strong electron beam. Two such cases are shown in Fig. 3 and Fig. 4, respectively. This experiment was carried out at room temperature; hence a double-tilting stage could be utilized, and the orientation of the boundaries could thus be determined. For the specimen shown in Fig. 3, the orientation of the boundary is (104), while for that in Fig. 4, it was found to be $(1\bar{1}2)$ and (012). These orientations do not change by the motion of the boundaries. These boundaries are found to be almost perpendicular to the image plane and the latter is essentially parallel to the specimen surface.

It is to be noted that these boundaries run along (low index) crystallographic planes, but the orientations are not unique. However, the boundaries are found to have cer-

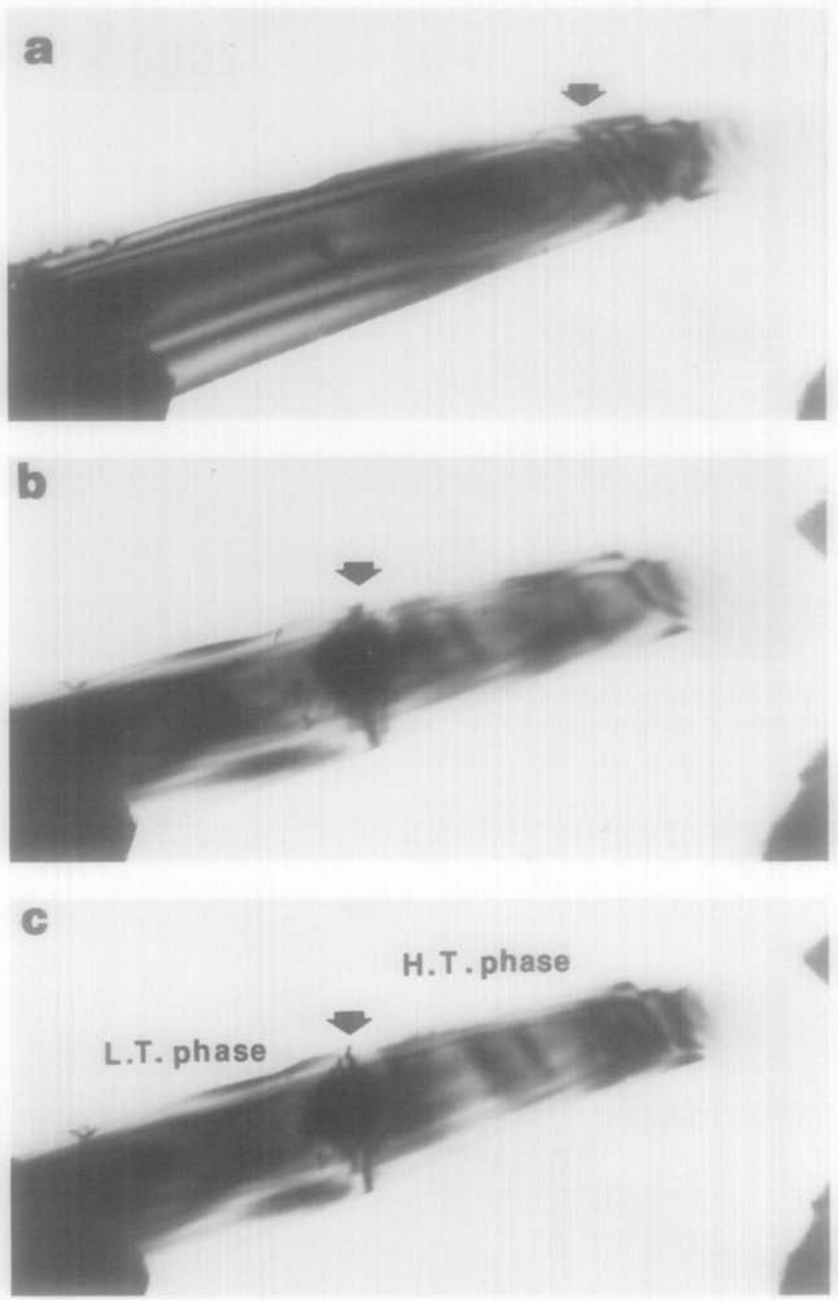

FIG. 2. Observations of a boundary by heating. The figure shows different stages of the motion of the boundary at 120°C. The location of the boundary is indicated by an arrow in each picture.

tain common characteristics. First, they are neither the basal plane nor the planes which include the *c* axis. Further, the direction which is included in the boundary and is perpendicular to the surface of the specimen is almost parallel to the basal plane

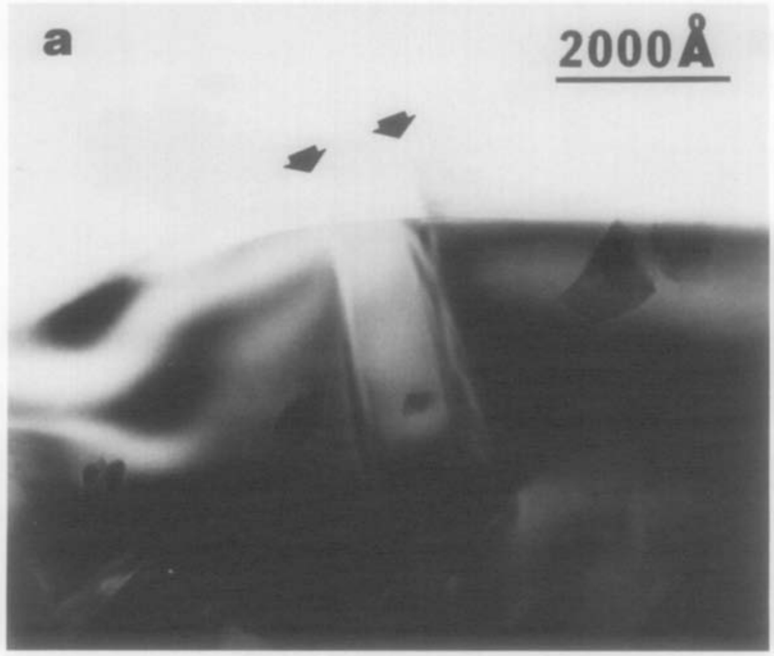

FIG. 3a. Observation of a retained high-temperature PI phase with the boundary in the (104) orientation. Boundaries are indicated by black arrows.

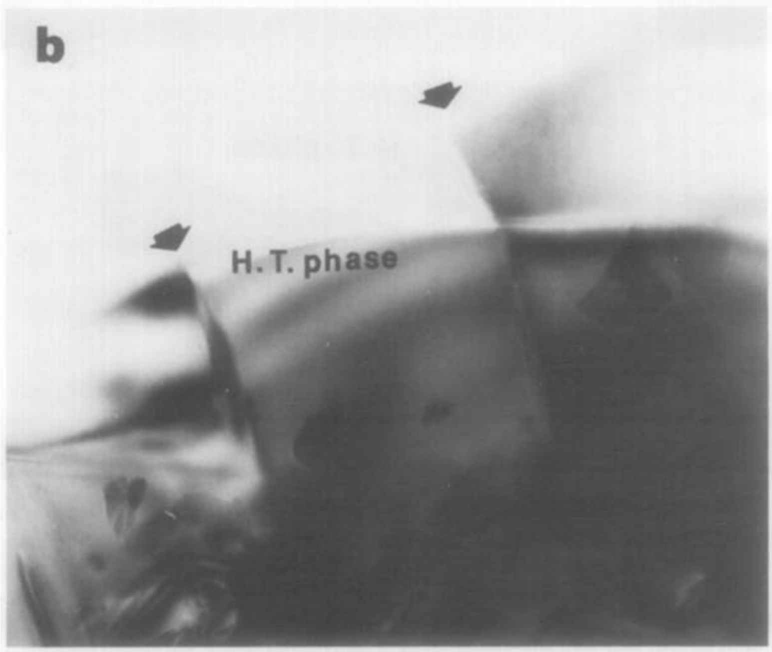

FIG. 3b. The same high-temperature PI phase expanded by irradiation.

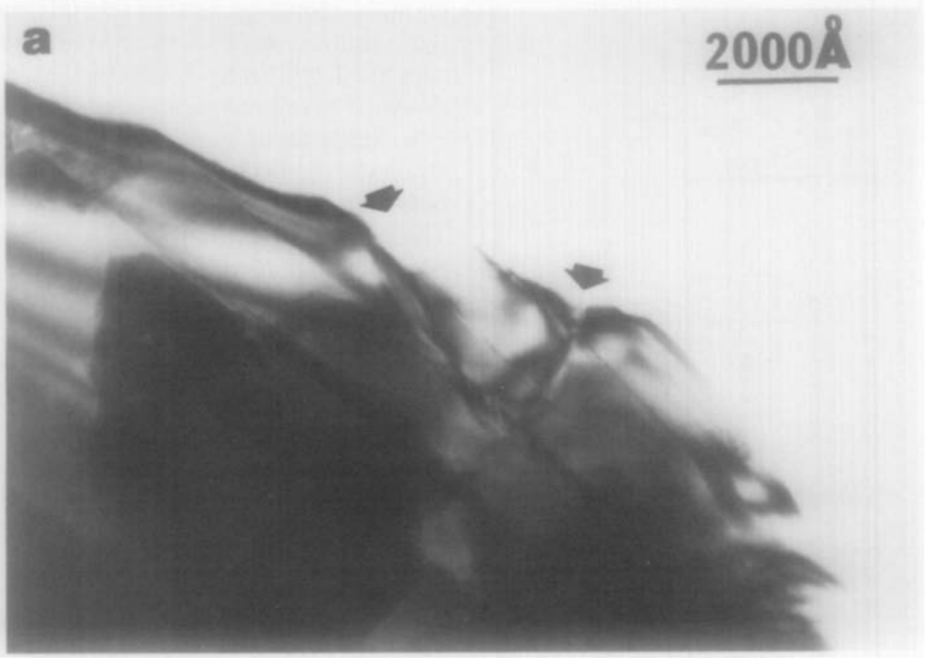

FIG. 4a. Observation of a retained high-temperature phase with boundaries in the (012) (left) and the $(1\bar{1}2)$ orientation (right).

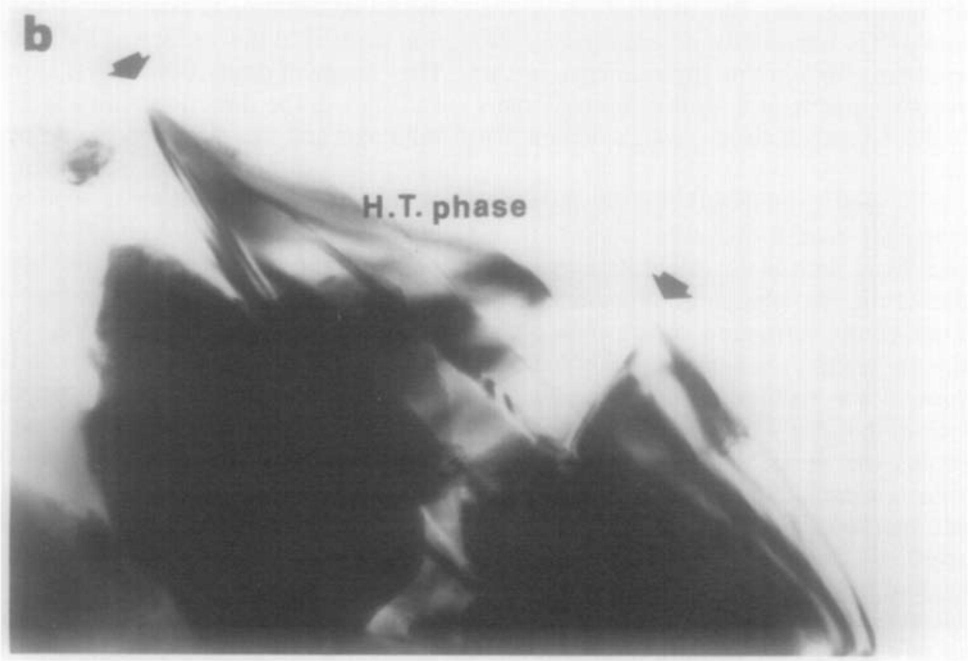

FIG. 4b. The same high-temperature phase expanded by irradiation.

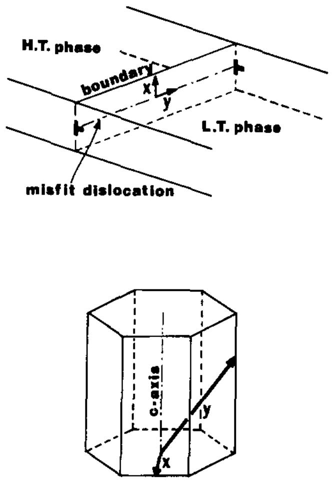

FIG. 5. Crystallographic relations of the boundary with respect to the surface of the specimen and the *c* axis of the crystal. The *x* direction is perpendicular to the surface of the specimen, while the *y* direction is parallel to the surface. Both directions are in the boundary.

(the direction *x* in Fig. 5). For the case in Fig. 3, this direction is [010], while for Fig. 4, it is [42$\bar{1}$]. The existence of this relationship indicates that the orientation of the boundary is essentially determined by the condition of minimum strain energy in the boundary, just as it is in the common martensitic transformations, as explained below.

As is well established for the common martensitic transformations, important relationships, such as the orientation relationships of the two phases involved and habit planes of the formation of the new phase from the matrix, are determined by the condition of the minimum strain energy (9). Since in this study the symmetry of phases remains the same, and the change in the lattice constants is relatively small, no distinct morphological relationships are expected. In the first place, there exists no invariant plane. Because of the lack of such distinct crystallographic features, it is difficult to visualize the general orientation relationships between the two phases in bulk crystals. However, in thin crystals, such as those utilized in TEM, the condition can be simplified and unique conclusions can be drawn. These are summarized as follows:

1. Since there is no plane in which the strain energy becomes zero, the area of the boundary should be as small as possible. This generally occurs when the boundary is perpendicular to the surface of the specimen. In addition, the boundary can stop at the location where the boundary energy becomes minimum: i.e., at the location where the cross section becomes a minimum or at a location where some defects are included. In other words, boundaries are visible by TEM when the orientation of the specimens is favorable to create boundaries perpendicular to the specimen surface.
2. Because specimens are thin, the cross section of the boundary is longest in the direction parallel to the surface (the direction *y* in Fig. 5) and shortest in the direction perpendicular to the surface. Under this condition, the orientation of the boundary is such that the change of the dimension by the transformation is minimum in the direction parallel to the surface of the specimen. The change of dimension by transformation vanishes in the direction which is 27° from the *c* axis and this direction should be parallel to the surface of the specimen in the boundary. This condition is well satisfied by the boundaries observed in Figs. 3 and 4.

The direction which lies in the boundary and is perpendicular to the surface of the specimen (the direction *x* in Fig. 5) is almost parallel to the basal plane. In this direction, the change in the dimension by transformation is maximum. In thin specimens, the strain relief occurs most readily in this direction. Therefore, the boundary determined by conditions 1 and 2 becomes more favorable as the thickness of the specimen decreases, as in the case of specimens utilized in TEM observation. The orientation relationships discussed with respect to the boundaries are shown in Fig. 5.

If the conditions discussed above are correct, there is a possibility that misfit dislocations parallel to the surface of the specimen can be observed. According to Table I, the change in dimension perpendicular to the specimen surface (*a* direction in the basal plane; $\Delta a/a$) is ~1%, and since the thickness of the specimen is ~1000 Å, there should be one or two misfit dislocations. In Fig., 1a, such a misfit dislocation is observed under the weak beam condition (*7*). That this image is due to a misfit dislocation is corroborated by the observation of the boundary in a specimen including 1.2% Cr shown in Fig. 6. In Fig. 6a, the image of the boundary observed under the exact Bragg conndition is shown. Here, the 110 reflection is utilized. In Fig. 6b, the image of a misfit dislocation parallel to the surface of the speciman is observed, taken under the weak beam condition by tilting the specimen by ~1° from the exact Bragg condition. The boundary is observed to move by the change in the intensity of the electron beam. In such a case, the misfit dislocation is also found to move along with the boundary and to reappear at the same position with respect to the boundary at its new location. This confirms that the dislocation shown here is a misfit dislocation and not one by which the boundary is accidentally pinned.

Summary and Discussion

The metal–insulator transition at high temperatures in Cr-doped V_2O_3 was investigated by transmission electron microscopy for a composition $(V_{0.994}Cr_{0.006})_2O_3$. Boundaries between the metal phase (M) and the insulator phase (PI) were observed under certain conditions and were confirmed to have the following characteristics:

1. The boundaries are perpendicular to the surface of thin specimens. The boundaries can easily be trapped at places where the energy of the boundaries become minimum.
2. The boundary planes are neither the basal plane nor planes including the *c* axis, but make an angle of ~27° with the *c* axis. This angle is found to satisfy the condition that the change of dimension by transformation in the direction parallel to the surface of the specimen vanishes. The boundaries are parallel to low-index planes but these are not a unique plane.

These characteristics indicate that the orientation of the boundaries is essentially determiend by the condition of minimum strain energy at the boundary, but, at the same time, it is directly related to the crystal lattice. Van Landuyt *et al.* (*4*) earlier reported that the boundary plane was "non crystallographic." Although it is not clear what they mean by "non crystallographic," it gives the impression that the boundary is similar to that of soap bubbles and hence is not adequate in view of our findings.

Under the above conditions, the direction which is included in the boundary and is perpendicular to the specimen surface is parallel to the basal plane and, hence, the change in the dimension by transformation is maximum. Therefore, the existence of misfit dislocations parallel to the surface of the specimen is expected. The observation of misfit dislocations which satisfy the above condition (Figs. 1a and 6) thus supports the above conclusion with respect to the orientation of the boundaries. A more detailed investigation of misfit dislocations is under way in order to clarify the mechanism of boundary motion.

It should be remembered that the above conclusions with respect to the characteristics of the boundary are drawn based on extremely thin crystals suitable for TEM observation. The coexistence of the M phase and the PI phase could be far more complicated in bulk specimens because of far more complicated boundary conditions in the latter, although the principles in-

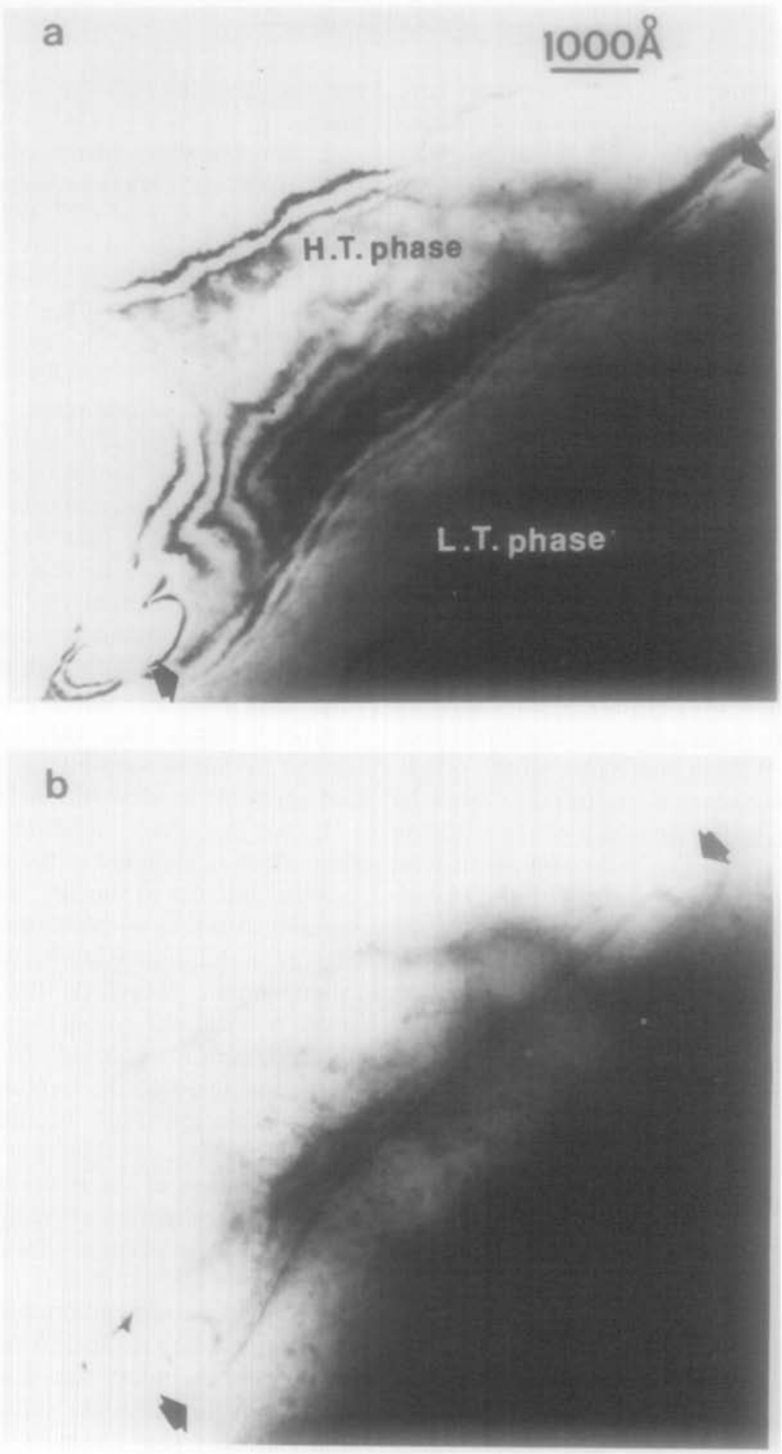

FIG. 6. Observation of a misfit dislocation in a $(V_{0.988}Cr_{0.012})_2O_3$ specimen. (a) Observation of a boundary under the exact Bragg condition. Fringes due to the boundary are indicated by arrows. (b) Observation of a misfit dislocation in the boundary under the weak beam condition. This misfit dislocation is indicated by arrows.

volved are the same. In particular, this complication contributes to a large temperature hysteresis of the transformations, especially in bulk specimens—a fact which is well known in the study of martensitic transformations (*9*).

The motion of boundaries is discontinuous because boundaries are found to be trapped by defects or at places where the boundary energy becomes minimum. Along with a large amount of temperature hysteresis in bulk specimens, this behavior explains well the hysteresis and the discontinuities in the resistivity–temperature curve of the transformation as observed by Kuwamoto *et al.* (*1*). This also explains the fact that a detailed behavior of the transformation varies with individual specimens.

It has been found that the high-temperature (PI) phase can be retained at temperatures as low as ambient or below. The retention of a high-temperature phase to low temperatures is also well known in martensitic transformations. Clearly such specimens with retained high-temperature PI phase in bulk form, remain in a nonequilibrium state. Not only is the absolute value of resistivity of such a specimen uncertain, but its temperature coefficient is also unpredictable. Therefore, the discrepancies among researchers with respect to such as on the temperature coefficient of resistivity of the M phase (*1–3*) are understandable; the results cannot be interconnected unless a detailed characterization with respect to the distribution of phases is made.

Acknowledgments

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