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Acoustic Emission during Metal–Insulator Phase Transition in V_2O_3

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Acoustic emission experiments have been performed on V_2O_3 undergoing the metal–antiferromagnetic insulator transition near 150 K. The release of stress in the transition generates acoustic pulses which change on repeated thermal cycling. The observations are consistent with formation of nuclei of the insulating phase in the metallic matrix approximately 5 to 6 degrees above the transition. The observed rise and spread of the transition temperature on thermal cycling indicates the importance of thermoelastic martensitic effects in the course of the transition. © 1997 Academic Press

INTRODUCTION

The most striking features in the doped V_2O_3 system are the many metal–insulator transitions (MIT) which arise simply by varying temperature, altering composition, or applying hydrostatic pressure (1). Pure, stoichiometric V_2O_3 on cooling undergoes a first-order MIT at temperature $T_c \sim 150\,K$, with a drastic increase in electrical resistivity, antiferromagnetic ordering of the vanadium spins, and a concomitant structural transition. Despite a vast literature on the subject, a reliable picture of the nature of the MIT is still unavailable. For a more complete understanding of the driving forces for the MIT in V_2O_3 the properties of the antiferromagnetic insulating (AFI) phase must be more thoroughly investigated.

There is considerable scatter in the many experiments which have been performed on the conductivity, Seebeck coefficients, ultrasound characteristics, and optical properties of the AFI phase. One of the reasons for the variety of reported results is the volume change at the first-order MIT, which causes the crystals to fracture when thermally cycled. The fracture process in V_2O_3 single crystals during the MIT is not understood; hence this problem should be more closely investigated. Since fracturing results in a change in elastic energy within the crystal, the influence of this energy on the MIT parameters is of considerable interest.

One well-known method for the study of fracture is acoustic emission (AE) (2). AE signals are produced by transient elastic waves accompanying the sudden, localized change of stress and strain in a material. In this work we study the AE caused by the M $\leftrightarrows$ AFI phase transition in V_2O_3, and the effects of fracture on the MIT parameters, such as the phase transition temperature.

EXPERIMENT

A special piezoelectric transducer was designed for the study of AE in V_2O_3 single crystals (see Fig. 1). The piezoelectric transducer is composed of a brass box, 1; piezoelectric ceramic sensor, 10 mm in diameter and 1 mm thick, 2; insulating fused quartz plate, 3; spring, 4; thermocouple, 5; and cover 6.

The V_2O_3 single crystal, $5 \times 5 \times 0.1$ mm in dimension, was grown under carefully controlled conditions as described elsewhere (9). The crystal was held between the sensor and quartz plate by the spring. The piezoelectric transducer was then mounted in a temperature-controlled cryostat.

Computer-controlled programs had been previously designed to test and to study failure processes in variety of solids by the AE method (3–8). This program was used in the present experiments.

RESULTS

Figure 2 displays the temperature dependence of the AE, recorded as the number of acoustic pulses in a 10 s time interval as the sample was cooled from room temperature to

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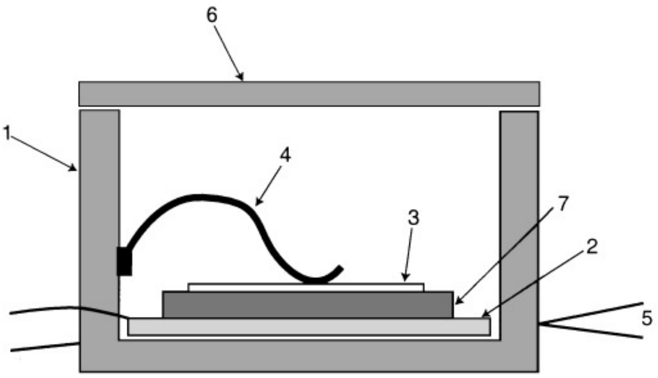

FIG. 1. Schematic diagram of a piezoelectric transducer. For numbering see text.

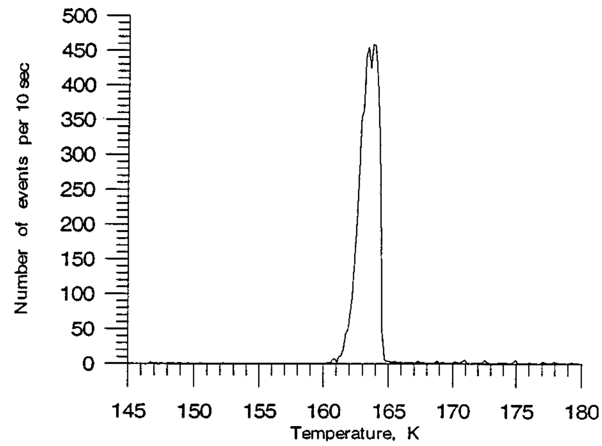

FIG. 3. Temperature dependence of AE during the first heating cycle.

145 K. In Fig. 3 is shown the temperature dependence of the AE when the sample was heated from 145 K to room temperature. Figures 4 and 5 show the temperature dependence of the AE in the fourth "cooling–heating" cycle. As is seen in Figs. 2 and 3, intense AE pulses were observed in the vicinity of MIT phase transition.

Transition temperatures of 148 K upon cooling and 165 K upon heating were obtained from measurements of the sample resistivity during the first cooling–heating cycle. This corresponds well with the peaks observed in the AE experiments.

DISCUSSION

Pure stoichiometric V_2O_3 undergoes a MIT close to 150 K during cooling (1). Accompanying this sharp, first-order phase transition is a change in the symmetry from trigonal ($R\overline{3}c$) to monoclinic ($12/a$) with a $1.6\% \pm 0.03\%$ increase in volume (1). It is known that the monoclinic phase V_2O_3 is composed of threefold twinned domains (10). On cooling below the phase transition, strong mechanical stresses are induced at the domain boundaries, causing fracture of the V_2O_3 crystals (11); this produces the observed acoustic emission.

Sudden relief of internal stresses at the domain boundaries upon heating leads to further fracture of the single crystal and produces more AE pulses. Optical microscopy revealed that after the first cooling–heating cycle, the sample broke into many pieces. With further cycling, these pieces diminish in size.

As can be seen from Figs. 2 and 3, the AE during the first cooling cycle occurs in the form of separate pulses, while in the heating cycle a smoother peaking is evident. In the subsequent cooling–heating cycles, the widths of the AE peaks continue to increase (see Figs. 4 and 5). We propose that AE proceeds simultaneously from all pieces of the sample; as their number increases, the peak in AE is smoothed. Comparison of the transition temperature for the first and the fourth cooling cycles (Figs. 2 and 4) shows that fracture leads to an increase of the transition temperature.

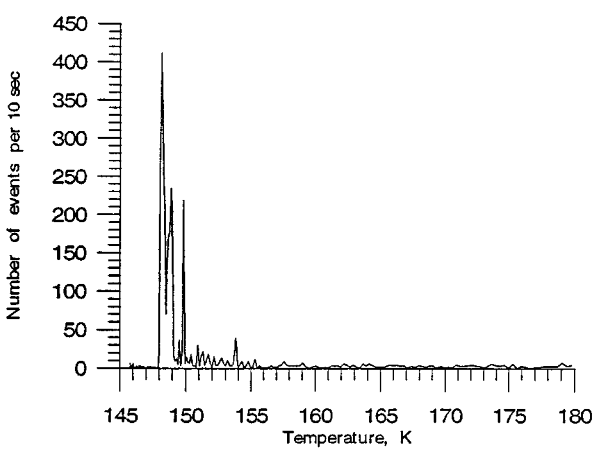

FIG. 2. Temperature dependence of AE during the first cooling cycle.

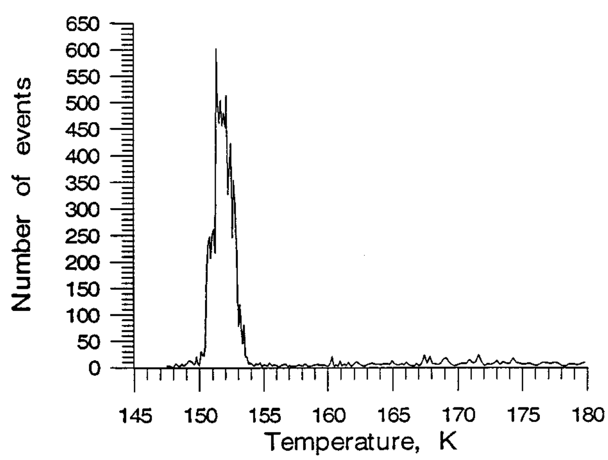

FIG. 4. Temperature dependence of AE during the fourth cooling cycle.

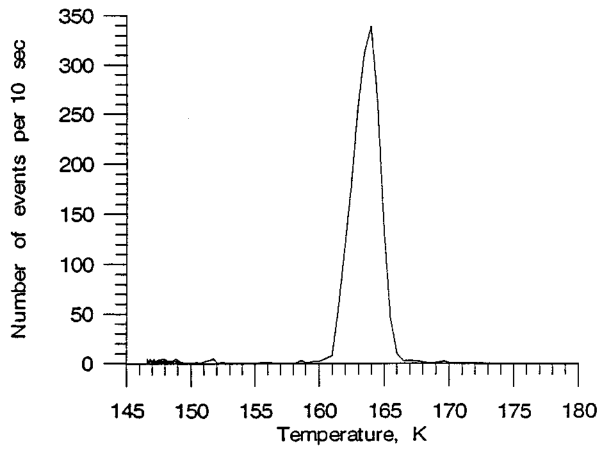

FIG. 5. Temperature dependence of AE during the fourth heating cycle.

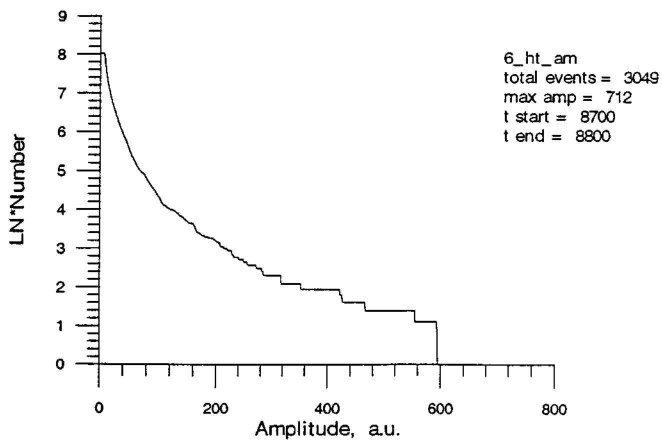

FIG. 7. Amplitude distribution of AE pulses. First heating cycle.

Since fracturing relieves internal stresses, it is evident that the transition temperature depends in part on the thermoelastic stresses. Thus, the model of a thermoelastic martensitic transformation may be used to interpret some aspects of the MIT in V_2O_3. For example, this may explain the mechanism of formation of the hysteresis loop in V_2O_3. During the MIT, the V_2O_3 single crystal is transformed into a polycrystal. According to the martensitic transformation model, an increase in the number of small grains during fracturing increases the spread in transition temperature of each grain (12); this may contribute to the spreading of the AE peak with cycling.

The hypothesis that the AE proceeds simultaneously from various locations within V_2O_3 after fracture is supported by our AE amplitude distribution analysis. Plotted in Figs. 6 and 8 are the amplitude distributions of AE pulses for the first and fourth cooling cycles, respectively. Comparison of these results indicates that in the first cooling cycle, the high-amplitude AE pulses ($A > 800$ a.u.) are created in greater numbers than in the fourth cycle. According to Refs. (4, 5) the amplitude of the acoustic signals can be correlated with the size of cracks associated with the AE pulses. Empirical evidence shows that these AE amplitudes are directly proportional to the size of the cracks.

Along with the decrease in median amplitude of pulses in the fourth cycle the total number of pulses increased considerably. For example, in the first cooling cycle 5394 pulses were registered, and in the fourth cycle 14,041 pulses were registered. Thus, during repeated thermal cycling the repeated fracture of the small crystals increased the number of AE pulses. On comparison of the AE amplitude distribution of the first and fourth heating cycles shown in Figs. 7 and 9 with those of the cooling cycles, the median amplitudes for the cooling cycles were found to be more than twice as large.

The total number of AE pulses in the cooling cycles is also greater than those in the heating cycle. A possible reason for this is that on heating, the stresses are less than on cooling and the fracture process is not so extensive. This may

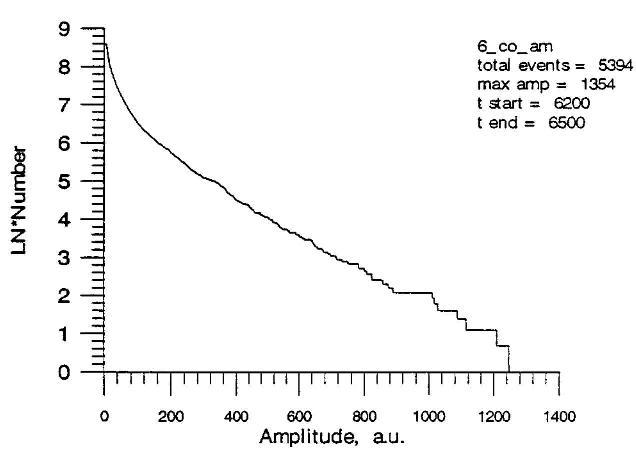

FIG. 6. Amplitude distribution of AE pulses. First cooling cycle.

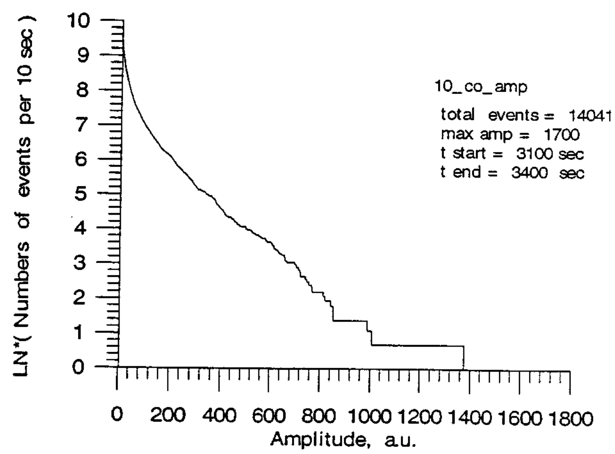

FIG. 8. Amplitude distribution of AE pulses. Fourth cooling cycle.

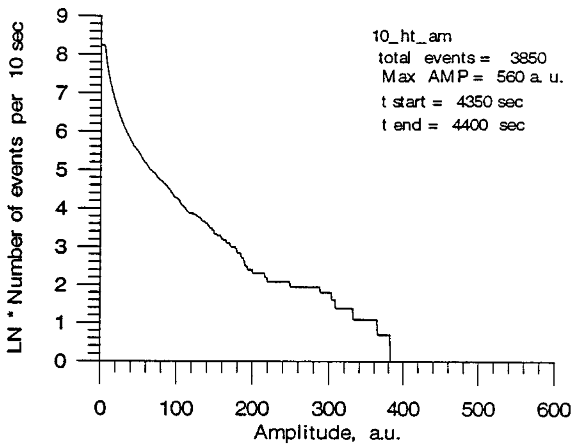

FIG. 9. Amplitude distribution of AE pulses. Fourth heating cycle.

explain why the phase transition temperature upon heating does not change much through several cooling/heating cycles.

One of the most interesting features in the AE is shown in Fig. 2. In the first cooling cycle, the initial AE pulses were detected even in the metallic phase roughly $\sim$5–6 K above the actual transition temperature. The observed behavior may be due to incipient formation of nuclei of the monoclinic phase above the transition temperature. Recent XAFS measurements on V_2O_3 single crystals have shown that local monoclinic distortion persists above the phase transition temperature (13). In Ref. (14) where crystals from the same source as in this work were investigated by the surface acoustic wave method, an increase in surface acoustic wave velocity in the metallic phase was observed at temperatures well above the transition temperature. This effect was also associated with the appearance of nuclei of the monoclinic phase. According to the theory of Ref. (15) the source of ultrasonic waves is attributed to fluctuations occurring in nuclei of the daughter phase in the course of a first-order phase transition.

CONCLUSION

Our study of AE in V_2O_3 has shown the following:

1. AE is associated with the fracture of single crystals as a result of the change in volume during the MIT.

2. AE is observed at temperatures above the transition temperature. A possible reason for this behavior is the formation of nuclei of the monoclinic (insulating) phase within the trigonal (metallic) one.

3. The fracture raises and spreads the transition temperature. This is an indication of the importance of thermoelastic martensitic effects in the MIT in V_2O_3.

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