THE MATERIALS RESEARCH LABORATORY

THE PENNSYLVANIA STATE UNIVERSITY

SECOND QUARTERLY REPORT
ON
CRYSTAL CHEMISTRY STUDIES

For the period

13 August 1965 to 13 November 1965

U. S. Army Electronics Laboratories

Contract Number DA28-043 AMC-01304(E)

Order Number FR-28-043-J5-20495(E)

January 1966

Rustum Roy
S. Kachi
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Code 1

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UNIVERSITY PARK, PENNSYLVANIA

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ABSTRACT

Work during the quarter has been: (i) An examination of the crystal chemistry of a series of rare earth-rhenium oxide compounds. Some six new compounds have been prepared. (ii) Work on the vanadium-oxygen system has been completed and is included here as Technical Report Number 1. Work has continued on the Sm-O and Eu-O systems with many attempts to duplicate literature preparation methods for SmO and EuO. SmO and probably Sm_3O_4 have been prepared.

PURPOSE

It is now generally acknowledged that the preparation and characterization of the material is as important a part of a solid state research or development problem, as the physical measurements made on the material. Clearly one of the major aspects of materials preparation is the ability to predict conditions under which new materials may be prepared, and to delineate the physico-chemical conditions which define the stability and reproducibility of a phase. The purpose of this contract is to provide such crystal chemical information to complement solid state physics and device development research. Because materials with interesting magnetic, electric and optical properties usually involve elements with unfilled shells, the research is concentrated on systems involving transition metals such as Mn-O, Cr-O, Tc-O and V-O, and rare earth systems such as Nd-O, Eu-O and Sm-O. Two approaches are used. In one the thermodynamics of the pertinent binary and ternary systems are determined using careful control of composition, temperature and oxygen activity and the most refined methods of phase analysis.

In the other, principles of crystal chemistry are systematically applied to predict and prepare new phases with important structures in poly-component systems. Combination of the two approaches allows a systematic preparation of examples of important structures containing unusual ions such as Cr^{4+}, Fe^{4+}, Eu^{2+}, etc.

PUBLICATIONS, REPORTS AND CONFERENCES

The following paper, supported by the previous contract appeared during the quarter:

"Stability of Ni_2TiO_4", by R. K. Datta and Rustum Roy. Zeits. für Krist. 121, 410-417 (1965).

FACTUAL DATA

1. Search for New Ferrimagnetic Compounds

A. The System $MgO-Cr_2O_3-O_2$

Further studies have been carried out in the system $MgO-Cr_2O_3-O_2$ at high oxygen pressures, especially near the $MgCrO_x$ region. This study will be continued especially in the 1-2 kb region.

B. The Systems $Nd_2O_3-ReO_2$, $Dy_2O_3-ReO_2$ and $Yb_2O_3-ReO_2$

The systems $Nd_2O_3-ReO_2$, $Dy_2O_3-ReO_2$ and $Yb_2O_3-ReO_2$ have been studied at the temperatures 1130°C and 1300°C. The appropriate oxide mixtures were sealed into Pt tubing and heated in an argon atmosphere to prevent air oxidation of the samples in case of leakage. In general, it was found that for rare earth/rhenium ratios < 1, the ReO_2 disproportionates, yielding Re metal and a hygroscopic rhenium rich phase (probably containing heptavalent Re). For rare earth/rhenium > 1, black or nearly black compounds were obtained. These probably contain tetravalent rhenium.

The following phases have been identified both by x-ray diffraction and by electron microprobe analysis:

1. Yb_2ReO_5. Apparently this phase is isostructural with the previously reported orthorhombic phases "$Dy_2Re_2O_7$" and "$Er_2Re_2O_7$". It is now apparent that the true stoichiometry of these orthorhombic phases is Dy_2ReO_5 and Er_2ReO_5.

2. $Nd_4Re_3O_{12}$, $(2Nd_2O_3 \cdot 3ReO_2)$. The x-ray pattern of this phase is rather complex and has not yet been identified as belonging to any known structure.

3. Nd_2ReO_5. The powder pattern of this phase has been indexed on the basis of a tetragonal unit cell with $a_0 = 12.28Å$, $c_0 = 5.886Å$.

4. $Nd_6Re_2O_{13}$, $(3Nd_2O_3 \cdot 2ReO_2)$. This phase has a distorted fluorite structure.

The following phases have been identified by x-ray diffraction only:

1. Dy_2ReO_5. This phase is orthorhombic with $a_0 = 23.69Å$, $b_0 = 7.514Å$, $c_0 = 5.647Å$. It was formerly erroneously designated as "$Dy_2Re_2O_7$".

2. Dy_4ReO_8. This phase has an undistorted fluorite structure. This phase is stable only at high temperatures ($\sim$1300°C).

3. At lower temperatures a distorted fluorite structure forms in the system ReO_2-Dy_2O_3 with a Dy/Re ratio > 4.

In many runs the resulting products were off the starting stoichiometry due to the volatility of ReO_2 and the other rhenium oxides. Even the use of platinum tubing protected by an argon atmosphere could not always prevent leakage of rhenium oxides.

2. The Vanadium-Oxygen Systems

The study of the binary system V-O was completed during the quarter. A description of the work is included there as Technical Report Number 1. The report demonstrates that any of the Magneli-Type phase in the vanadium-oxygen system may be prepared easily under open-system equilibrium conditions by use of controlled oxygen-activity atmospheres. Secondly, it should be possible to grow single crystals of the electrically interesting compound VO_2 from a self-fluxing system by melting V_2O_5 in an atmosphere of the proper oxygen activity.

3. The Samarium and Europium-Oxygen Systems

During the past quarter, work has continued on the preparation of SmO and EuO. These compounds have been previously prepared by several other researchers, but their results have been generally irreproducible in our Laboratories. The following is a summary of the procedures used, and their results.

A. Reduction of the Sesquioxide with the Metal

Sm_2O_3 and Sm metal were chosen for these initial experiments because of the comparative ease of handling Sm over Eu metal. The metal and sesquioxide were mixed in various proportions, sealed into evacuated silica capsules (10^{-2} mmHg), and fired at temperatures of 1100° to 1180°C. The products were always multiphased, consisting of the high temperature monoclinic form of Sm_2O_3 and an unknown phase which will be described later. The SmO reflections were absent from the powder patterns of the products.

B. Reduction of the Sesquioxides with Hydrogen

Sm_2O_3 and Eu_2O_3 turn black at approximately 2100° and 1800°C respectively when heated in an iridium element strip furnace in a hydrogen atmosphere. The only reflections on the powder patterns are those of the monoclinic forms of the sesquioxides, but with extensive intensity variations. The color changes and the intensity variations probably indicate massive oxygen defects in the sesquioxide structure.

C. Reduction of the Sesquioxide with Carbon

Graphite and the sesquioxide were ground together and compressed to pellets. These were placed in an iridium container, and fired in a graphite tube resistance furnace in both argon and carbon monoxide atmospheres. The reduction of Sm_2O_3 was shown not to occur with either atmosphere, up to approximately 2050°C. Here the sample and the iridium containers reacted to form an alloy and/or carbide. Initial attempts with Eu_2O_3 to 1600°C in an argon atmosphere were unsuccessful.

D. Oxidation of Samarium Metal

"SmO" was first discovered as a coating on heat treated samarium metal, and its powder pattern was recorded. In an attempt to reproduce this experiment, small chunks of samarium metal were placed in a silica tube which was sealed at one end, and held horizontal. The metal was spread from the closed end to the open end, and fired to white heat in oxyhydrogen flame for five minutes. The metal nearest to the open end oxidized to the sesquioxide, but that near the closed end gave a product whose reflections match the powder pattern of "SmO". It is strongly suspected that this product is a mixed oxide-nitride phase. As lattice parameters are available for the oxide and nitride end members, this hypothesis can be checked with precise measurement of the lattice parameter of the product.

Last quarter, it was reported that a samarium silicate was probably forming from reaction the metal and/or sesquioxide with the silica glass capsules. To test this hypothesis runs were carried out in three inch zirconia tubes placed inside large evacuated silica capsules. The products were the same as those for similar compositions fired in silica capsules alone. It was found that when the sesquioxide was run alone in the zirconia tube without the metal, it partially reacted with the zirconia and was itself partially reduced to the new phase mentioned above. Sm metal, having a large positive oxidation potential, will rapidly react with the silica of the capsules in a hydrogen flame, reducing it probably to metallic silicon. However, when Sm and Sm_2O_3 are both present in either the silica or zirconia containers, the thermodynamically favorable reaction is the one between the metal and the sesquioxide.

The unknown phase from the Sm-Sm_2O_3 reactions was a white powder when the amount of Sm in the starting materials was near that necessary to react with Sm_2O_3 to form SmO. However, when metal was in the mixtures in a considerable excess, this phase had the form of a brick red powder and of blade-like single crystals, which were sometimes several millimeters in length, and which appear to be orthorhombic. Orthorhombic Eu_3O_4 has been known for several years, and it is believed that our unknown phase is Sm_3O_4. Single crystal and lattice parameter determinations will soon be carried out to test if these single crystals are isostructural with Eu_3O_4. As Sm_3O_4 would almost surely be isostructural with Eu_3O_4, this will serve as one test of the hypothesis.

An oxidation experiment on the crystals using a precision balance should also serve to test this hypothesis.

PROGRAM FOR NEXT INTERVAL

The research on the vanadium-oxygen system is regarded as complete and no further work on this system is contemplated. Work on the topics of systematic crystal chemistry of rhenium and of chromium compounds and the study of the Sm-O and Eu-O systems will continue.

PERSONNEL

Dr. Rustum Roy, Director of the Materials Research Laboratory, and Dr. William B. White continue to direct the project. Mr. O. Muller and Mr. G. J. McCarthy are graduate students working on their Ph.D. degrees. Dr. S. Kachi has returned to his permenant position at Kyoto University and left the project in September.

PHASE EQUILIBRIUM STUDIES AND TRANSITIONS
IN THE SYSTEM V_2O_3-V_2O_5

by

Sukeji Kachi and Rustum Roy

FIRST TECHNICAL REPORT

ON

CRYSTAL CHEMISTRY STUDIES

U. S. Army Electronics Command
Contract Number DA28-043 AMC-01304(E)
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Materials Research Laboratory
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Phase Equilibrium Studies and Transitions in the System V_2O_3-V_2O_5

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ABSTRACT

Quenching and differential thermal analyses, x-ray diffraction studies and magnetic susceptibility measurements were used to establish the binary phase relations in the V_2O_3-V_2O_5 system.

Seven intermediate phases V_3O_5, V_4O_7, V_5O_9, V_6O_{11}, V_7O_{13}, VO_2 and V_6O_{13} have been shown to be stable between V_2O_3 and V_2O_5 and in the temperature range from liquid nitrogen to 1400°C. These phases, with the exception of V_6O_{11} and V_6O_{13} behave like antiferromagnetic substances exhibiting different Neél points at lower temperatures. There is an eutectic reaction between V_2O_5 and V_6O_{13} at 650°C, and the V_6O_{13} phase decomposes incongruently into VO_2 and a liquid phase at 708°C.

Some discussions on the nature of the phase transitions involving resistivity changes of 10^{-1} to 10^{-6} in the intermediate phases at lower temperature a: presented, in the light of the new data.

Presented in part at the Sixty-Seventh Annual Meeting, The American Ceramic Society, Philadelphia, Pennsylvania, May 15, 1965 (Basic Science Division, #80-B-65). At the time this work was done, the writers were, respectively, research associate and Director of the Materials Research Laboratory, The Pennsylvania State University. Sukeji Kachi is a Professor of Solid State Chemistry, Kyoto University, Japan.

I. INTRODUCTION

Since V_2O_5 in an important oxidizing catalyst, the physico-chemical aspects of the V_2O_3-V_2O_5 system have been extensively studied. However, some discrepancies exist in the literature concerning the phase relations due to the complexity of the system. Hoschek and Klemm(1) who first studied this system suggested the presence of three phases, $\alpha(VO_{1.80}\text{-}V_{2.00})$, $\beta'(VO_{2.09}\text{-}VO_{2.33})$ and $\gamma(VO_{1.05}\text{-}VO_{1.80})$ between V_2O_3 and V_2O_5. Anderson(2,3), Magneli, et al.(4) and Aebi(5) reexamined this system by x-ray techniques and identified eight oxides whose compositions are expressed by a general formula $V_nO_{2n\pm1}$ where n is an integer. These oxides are listed in Table 1. This series of phases with compositions expressed as V_nO_{2n-1}, are sometimes called Magneli phases after the main investigator. The structure of the Magneli phases is based on the rutile structure, with periodic defects resembling stacking faults which effectively introduce extra planes of metal atoms(6). The structure of V_3O_5, V_5O_9 and V_6O_{13} have been determined respectively by G. Anderson(3), Aebi(5) and S. Anderson(6).

Since then, other significant investigations by Burdese(7) and by Grossman(8) have supported the results of Anderson(2) and contributed much to the understanding of the phase relations in this system. However, these studies have been limited to experiments in the temperature range from 600 to 1000°C, with no control of the oxygen pressure; phase relations outside this region are still in doubt.

Recently, much interest has been directed from quite different sources toward the electrical properties of V_2O_3 and VO_2. Morin(9) found that V_2O_3 and VO_2 are the representative of the class of oxides which exhibit a metal-to-insulator phase transition at lower temperatures. Since then, the conduction mechanism has been discussed by Morin(9) and Goodenough(10) has used them as one of the primary examples for his narrow-band conduction model. Others(11,12,13) have also discussed this theory although it is not yet generally accepted. Additional conductivity data have been published by Kachi, Takada and Kosuge(14). Though these conflicting theories remain to be solved in the future, it may be expected that other interesting electrical properties will be found as these materials are further developed. Before such detailed measurements were interpreted we felt it was essential that the detailed crystal chemical information be obtained. Phase equilibrium studies relating composition and structure to temperature and partial oxygen pressure have, therefore, been carried out in the temperature range from liquid nitrogen to 1400°C. In the present studies phase identification of the intermediate oxides has been augmented by magnetic measurements and resistivity measurements in addition to the usual x-ray diffraction methods.

II. EXPERIMENTAL PROCEDURES

(1) Starting Materials

V_2O_3 and V_2O_5 were used as starting materials for the sample preparations. V_2O_5 was obtained from the thermal decomposition of ammonium metavanadate NH_4VO_3 at 550°C in air. V_2O_3 was prepared by reducing V_2O_5 in hydrogen at 850°C. The x-ray powder patterns of the starting materials showed no extraneous lines. Ferromagnetic impurities in the V_2O_5 and V_2O_3 were estimated at less than 0.01%.

(2) Preparation and Reaction of Samples

Specimens were reacted in sealed platinum tubes or in platinum in the controlled oxygen atmosphere. For the studies of the phase relations in the closed system, about 30 specimens of different compositions were prepared by mixing V_2O_3 and V_2O_5 in the required proportions. To ensure homogeneity, each sample was shaken for 10 minutes in a Wig-L-Bug, using a polystyrene vial and agitator. Each mixture was sealed in a silica or platinum tube and heated to the desired temperature ranging from 800°C to 1400°C. The dissociation pressure of oxygen in these samples was less than one atmosphere in the temperature range used, being well below the strength of seals. The controlled oxygen atmospheres were generated by using $CO-CO_2$ gas mixtures in the temperature range from 1100°C to 1300°C. In order to approach equilibrium from both sides, V_2O_3 and V_2O_5 were always used as dual starting materials. The starting materials were heated in a platinum furnace in a circulating atmosphere of the $CO-CO_2$ mixtures.

The compositions of the gas mixtures were respectively 3%, 1%, 0.1% CO and pure CO_2, and total pressure was one atmospheric pressure. The product phase was identified by x-ray diffraction after quenching from reaction temperature. The gas mxitures were obtained by mixing CO and CO_2 in a high pressure storage tank. The composition of the mixture was then determined by a gas chromatograph. Adequate precautions were taken to obtain equilibrium by varying the duration of heating depending upon the reaction temperature.

(3) Phase Identification

The phase characterization was done by x-ray diffraction, magnetic susceptibility of quenched specimens and D.T.A. measurements. X-ray powder patterns [illegible] taken on a Norelco diffractometer using nickel filtered CuK radiation. Magnetic susceptibility of the specimens was measured by a Faraday type torsion balance in the temperature range from liquid nitrogen to 200°C. D.T.A. was performed in the temperature range from liquid nitrogen to 1000°C. For the low temperature D.T.A., a special sample holder made of α brass was devised. The holder had a cold finger whose end was immersed in liquid nitrogen during measurement. Heating curves were taken from the high temperature range, and cooling curves for low temperatures at the rate of 4°/min and 15°/min, respectively.

III. RESULTS AND DISCUSSIONS

(1) Phases Present

As a result of the x-ray studies, the presence of seven Magneli-phases V_3O_5, V_4O_7, V_5O_9, V_6O_{11}, V_7O_{13} and V_6O_{13} was confirmed in agreement with the results of Anderson, but the V_8O_{15} phase could not be prepared in the present experiments. Moreover, the data established that these phases, with the exception of V_6O_{13} and V_4O_7, are stable up to at least 1400°C. The V_6O_{13} phase is only stable below 708°C and V_4O_7 dissociates at 1230°C. The x-ray powder patterns obtained on these phases were in very good agreement with those of Anderson(2). The patterns were reporduced in an earlier paper by Kosuge, Takada and Kachi(15). The patterns of the homologous series V_nO_{2n-1}, especially those for V_4O_7 and V_7O_{13}, are quite similar to each other. Hence, it turned out that in such cases, magnetic analysis was actually more effective for phase identification.

Table III shows the symmary of susceptibility measurements on the Magneli phases prepared at 800°C.*(16) The presence of seven intermediate phases was also confirmed from the measurements. All the phases, except V_6O_{11} and V_7O_{13}, behave like antiferromagnetic substances having different Neél points. In spite of a marked kink in the susceptibility vs. temperature

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* Except the V_6O_{13} phase which was prepared at 650° below its melting point.

curves of V_2O_3 and VO_2, it is still in doubt whether these phases are truly antiferromagnetic or not. Neutron diffraction studies by Paoletti, et al.(17) gave no positive evidence of antiferromagnetic spin alignment in these oxides.* Goodenough(10) suggested that the magnetic anomaly in V_2O_3 comes from the crystalline distortion accompanying the transition. However, as a matter of phase identification, the presence of two phases in the specimens could be identified by the observation of two kinks in the susceptibility vs. temperature curves. Figure 1 shows such an example: two kinks can be observed for the two phase mixture of V_4O_7 and V_3O_5, each corresponding to the unchanged transition temperatures of V_4O_7 and V_3O_5, respectively.

Figure 2 shows a summary of D.T.A. results of all the phases. No phase transitions except those corresponding to the above mentioned magnetic transitions can be observed. Figure 3 shows D.T.A. curves in the samples $VO_{2.08}$, $VO_{2.17}$ (V_6O_{13}), $VO_{2.28}$ and $VO_{2.38}$ whose compositions are in the VO_2-V_2O_5 region. In curves of $VO_{2.28}$ and $VO_{2.38}$ of Figure 3, the first discontinuity at 650°C was assigned to an eutectic reaction between V_6O_{13} and V_2O_5, and the

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* Minomura, Tomon, et al.(18) also studied NMR spectra of V^{51} in V_2O_3, but could not observe the spin alignment below the transition point. Meanwhile, Jones(19) has reported that the V^{51} NMR signal disappears at the transition point with decreasing temperature. Recently Kosuge(20) reported that Fe^{57} imbedded in V_2O_3 shows a hyperfine structure in the Mössbauer spectra below the transition temperature. These could indicate the onset of the spin ordering. These conflicting results seem to come from the compositional differences of the samples; these results remain to be checked carefully again, using well characterized samples.

second to a peritectic reaction $V_6O_{13} \rightarrow VO_2 + V_2O_5$-rich liquid, and the third to mean a primary liquidus point at which VO_2 precipitates out from the melt. Figure 3 suggests that the peritectic reaction extends as far over as the composition of $VO_{2.38}$, which also means, at least, that the eutectic composition is beyond $VO_{2.38}$ being very close to V_2O_5.

(2) Proposed Phase Diagram

Figure 4 is, then, the proposed phase diagram for the V_2O_3-V_2O_5 system. The liquidus for most of the diagram is still unknown. The homogeneous range of each intermediate phase is very narrow, except for V_3O_5 and V_6O_{13}. In the V_3O_5 phase, a homogeneous range appears to extend from $VO_{1.64}$ to $VO_{1.71}$. An eutectic reaction at 650°C between V_2O_5 and V_6O_{13} was confirmed from D.T.A. The eutectic composition may be near $VO_{2.45}$. The V_6O_{13} phase incongruently decomposes into VO_2 and a V_2O_5-rich liquid at 708°C.

Figure 5 shows the result of equilibrium oxygen activity studies. The oxygen activity pO_2 corresponding to those of CO-CO_2 gas mixtures were read from Porter's$^{(21)}$ table. It should be noted that, unfortunately, there are no appropriate gas mixtures available for obtaining pO_2 between 10^{-2} and 10^{-5} conveniently and hence for studying the high Magneli phase (V_7O_{13}) and VO_2 fields.

The data obtained from these experiments and the closed system data are combined to give the oxygen isobar curves of Figure 4. The oxygen isobar curves shown at the V_2O_5 side of the diagram are calculated from Milan's$^{(22)}$ and Flood and Kleppa's$^{(23)}$ data, since they were in good agreement with the liquidus curve data determined herein by D.T.A. The most important result of this study is to establish that V_2O_5 can be melted essentially congruently at 1 atm. O_2. Indeed most V_2O_5 rich glasses and compounds melted in air or oxygen will, therefore, show essentially no reduction whatever.

(3) Electrical Conductivity and the Nature of Phase Transitions in the Intermediate Phases

Figure 9 shows a summary of the electrical conductivity measurements taken from reference (14). V_2O_3 and VO_2 exhibit the expected metal-to-insulator transition with an abrupt change of a factor of 10^5 in good agreement with Morin's(9) experiments made on single crystal specimens. Meanwhile, V_4O_7 and V_6O_{13} have a transition with a conductivity change by a factor of 10^2. V_3O_5 and V_5O_9 do not show any significant changes. The abrupt change in the conductivity of V_2O_3, VO_2, V_4O_7 and V_5O_{13} does not, of course, necessarily mean that these phase changes are first-order. Recently Minomura and Nagasaki(24) studied the changes in volume of V_2O_3 and VO_2 at the transition temperature and found a discontinuity in V_2O_3 but no discontinuity in VO_2. This suggests that the transition in V_2O_3 is certainly first-order and that the transition in VO_2 is possibly second-order. Our D.T.A. results indicate, however, a finite ΔH for the VO_2 transition and thereby confirm a first-order nature for the change. It appears then that VO_2 is another example of the mixed first- and second-order behavior common to many transitions as shown in the studies by Majumdar and Roy(25). Kachi, Minomura, et al.(26) also studied the volume change in V_6O_{13} at the transition temperature and found no discontinuity in the volume, but only a change in slope of the curve, again suggesting a second-order transition. However, here also D.T.A. shows a symmetrical endotherm, which can only result from a definite, discontinuous enthalpy of transition making this also a first-order change. In the study of Majumdar and Roy(25) it was noted that the ΔV term was usually the most difficult to determine accurately. The V_2O_3 and VO_2 metal-to-insulator transitions have been discussed by many authors(9,10,11,12,13). In these discussions, V_2O_3 and VO_2 are normal semiconductors below the transition points with valence and conduction band separated by an energy gap. There are two possible explanations for the changes in the energy gap at the transition,--one is the antiferromagnetic spin ordering(9), the other is overlapping of "d" orbitals due to crystalline distortion. In analogy with the volume-enthalpy dichotomy, these two processes are, of course, not mutually exclusive. The antiferromagnetic ordering provides a conceptual mechanism for a continuous change in the function which correlates with the volume change. Superimposed on this is the noncontinuous crystallographic change accompanied by a finite ΔH in both cases, but which requires only a very small extra ΔV (unmeasurable in the case of VO_2). This mixed-transition theory may also explain the discrepancy that exists among results of NMR, neutron diffraction and Mössbauer spectra with respect to the magnetism of these oxides.

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Table I. Vanadium Oxides Phases

Structure	Phase	Crystal System
Corundum	V_2O_3	Rhombohedral
Anosovite	V_3O_5	Monoclinic
V_nO_{2n-1} Magneli phases based on the rutile structures	V_4O_7	Triclinic
	V_5O_9	Triclinic
	V_6O_{11}	Triclinic
	V_7O_{13}	Triclinic
	V_8O_{15}*	Triclinic
	VO_2	Monoclinic
	V_6O_{13}	Monoclinic
	V_2O_5	Orthorhombic

* This phase was not encountered in this study.

Table II. Compositions of Specimens and Phases Identified Between 800°C and 1400°C in Closed System Runs of 2-48 Hour Duration.

X in VO_x	Phases Identified in Quenched Specimens
1.50 1.54	V_2O_3
1.64 1.67 1.68 1.70	V_3O_5
1.72	$V_4O_7 + V_3O_5$
1.74 1.75	V_4O_7
1.76 1.79	$V_5O_9 + V_4O_7$
1.80 1.81	V_5O_9
1.82 1.83	V_6O_{11}
1.84 1.85	V_7O_{13}
1.90 2.00	VO_2
2.08	$VO_2 + V_6O_{13}$
2.13 2.16	V_6O_{13}
2.28 2.38	$V_6O_{13} + V_2O_5$
2.50	V_2O_5

Table III. Magnetic Data on Vanadium Oxides

Phase	Magnetism	Neél Point (Transition Point)	Weiss Temperature	$\mu_{Ob.}$ (Bohr Magneton Number)
V_2O_3	antiferro. (?)	168°K	- 72°K	2.63
V_3O_5	antiferro. (?)	235 ± 3	-302	2.77
V_4O_7	antiferro. (?)	130 ± 3	-142	2.82
V_5O_9	antiferro. (?)	162	-142	2.60
V_6O_{11}	para.	---	- 47	2.14
V_7O_{13}	para.	---	-107	2.30
VO_2	antiferro. (?)	345 ± 3	-292	2.16
V_6O_{13}	antiferro. (?)	154	-177	2.13
V_2O_5	dia.	---	---	0

FIGURE LEGENDS

Figure 1. Magnetic susceptibility curves of two phase mixtures.

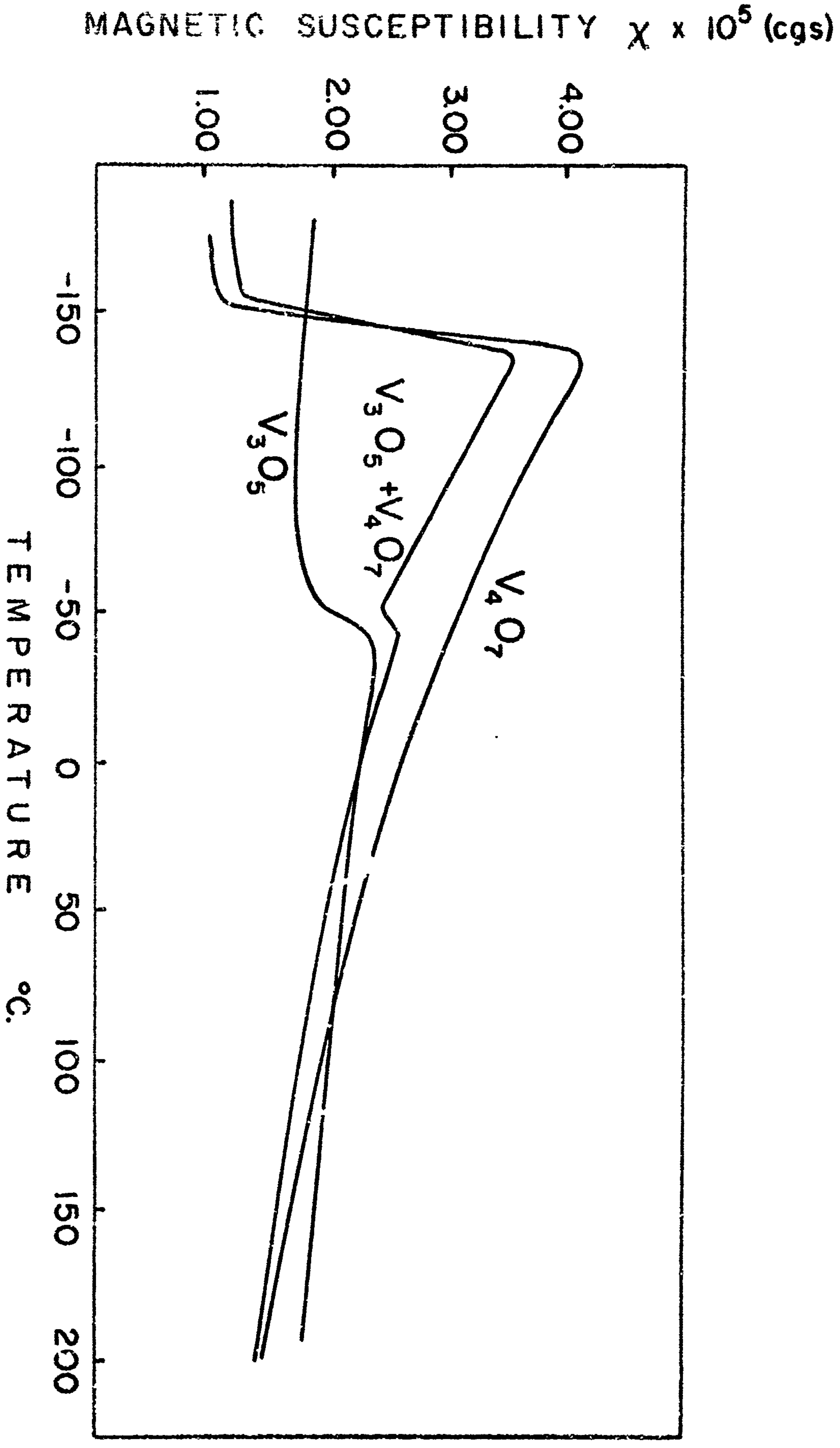
Figure 2. D.T.A. curves of vanadium oxides.

Figure 3. D.T.A. curves of vanadium oxides, in the composition range of VO_2-V_2O_5.

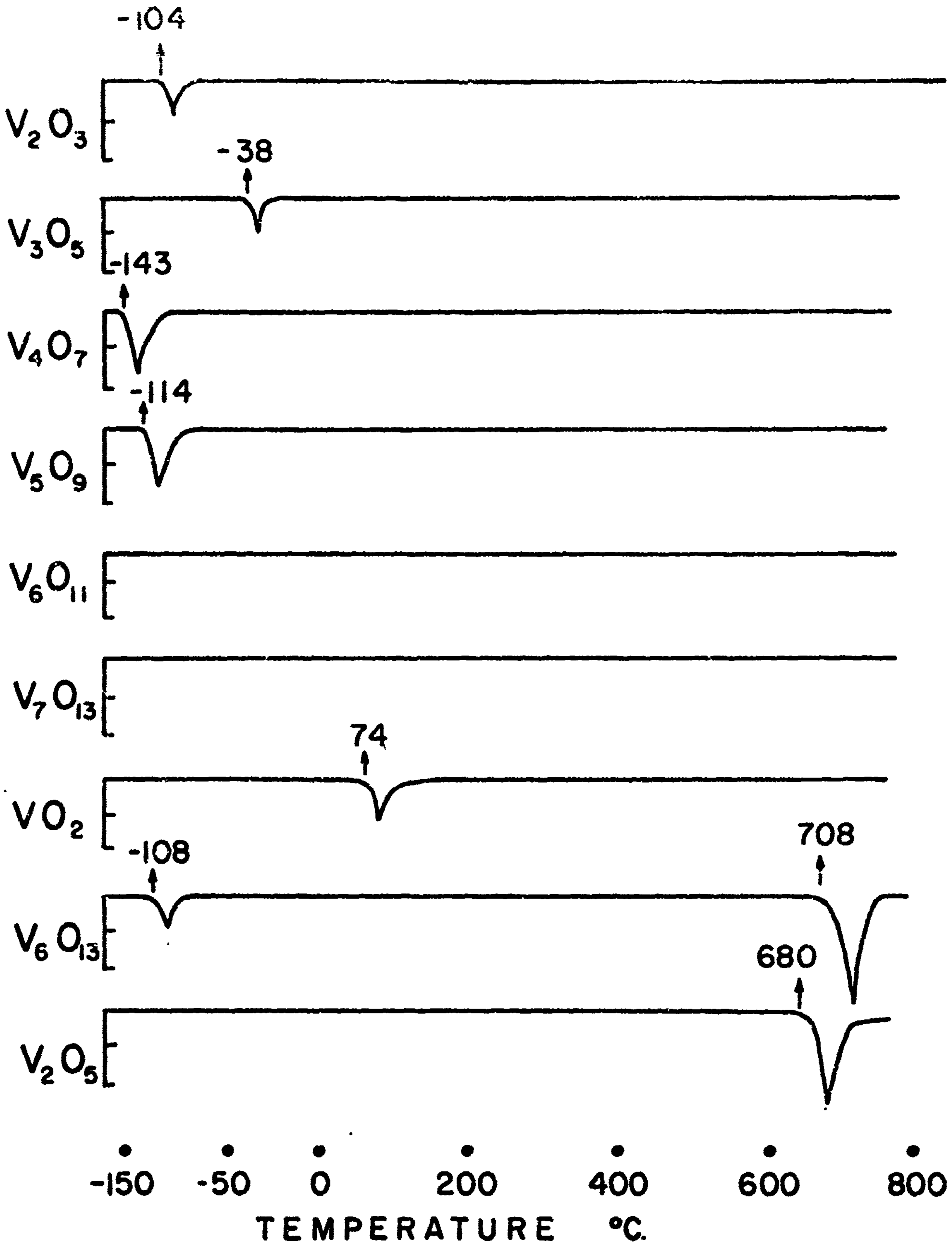
Figure 4. Partial phase diagram for the system V_2O_3-V_2O_5. Closed system runs are indicated by circles. Open circles are one-phase regions, black circles are two-phase regions. Light dashed lines are oxygen isobars, with pressures indicated in atmospheres. The isobars on the left are derived from the p-T relations of Figure 5. Isobars on right are calculated from Milan's(22) data. The two points on the liquidus were obtained by D.T.A.

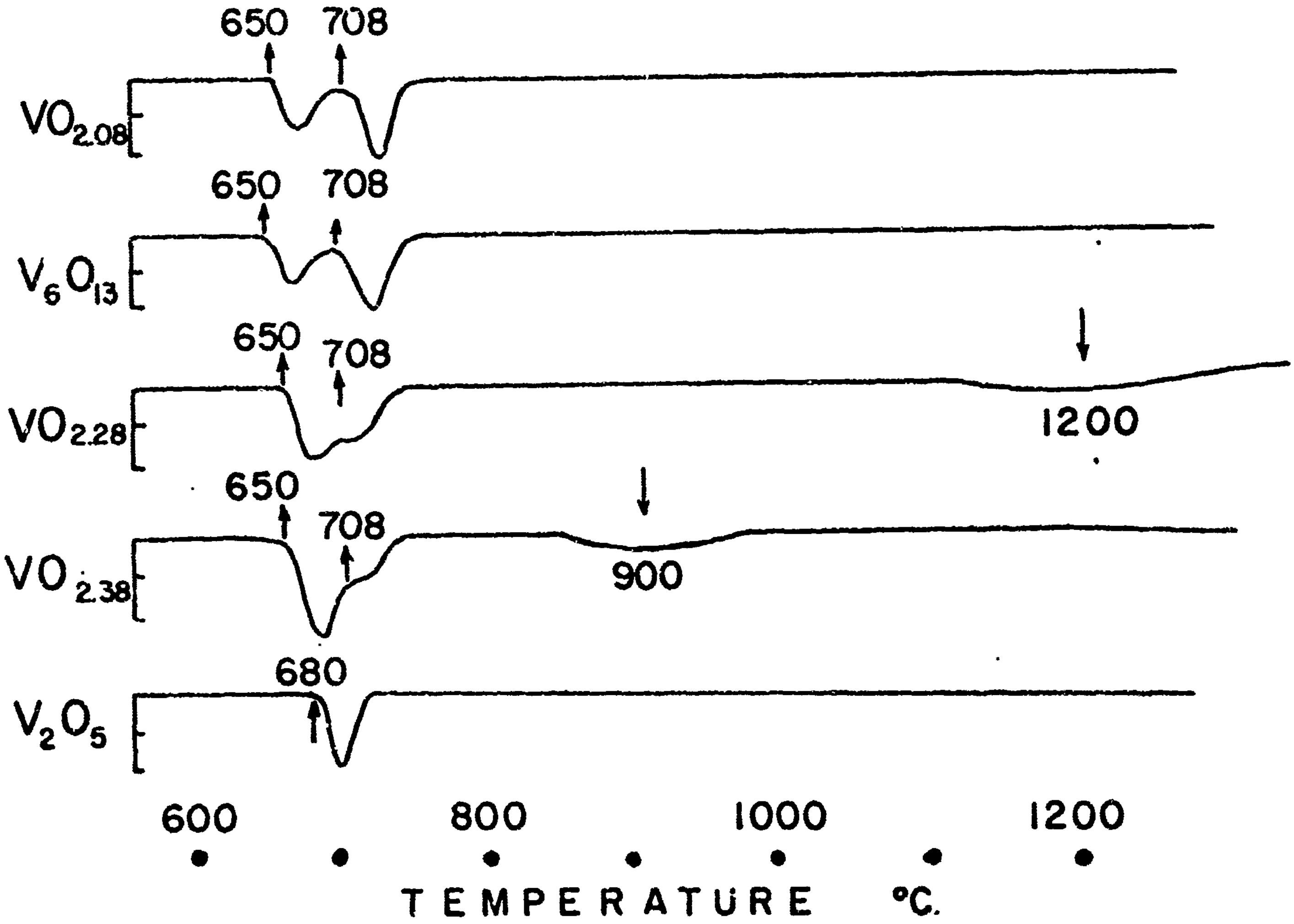
Figure 5. pO_2-T diagram for Magneli phase region. Boundaries are based on open-system runs shown by various symbols. All solid phases co-exist with vapor.

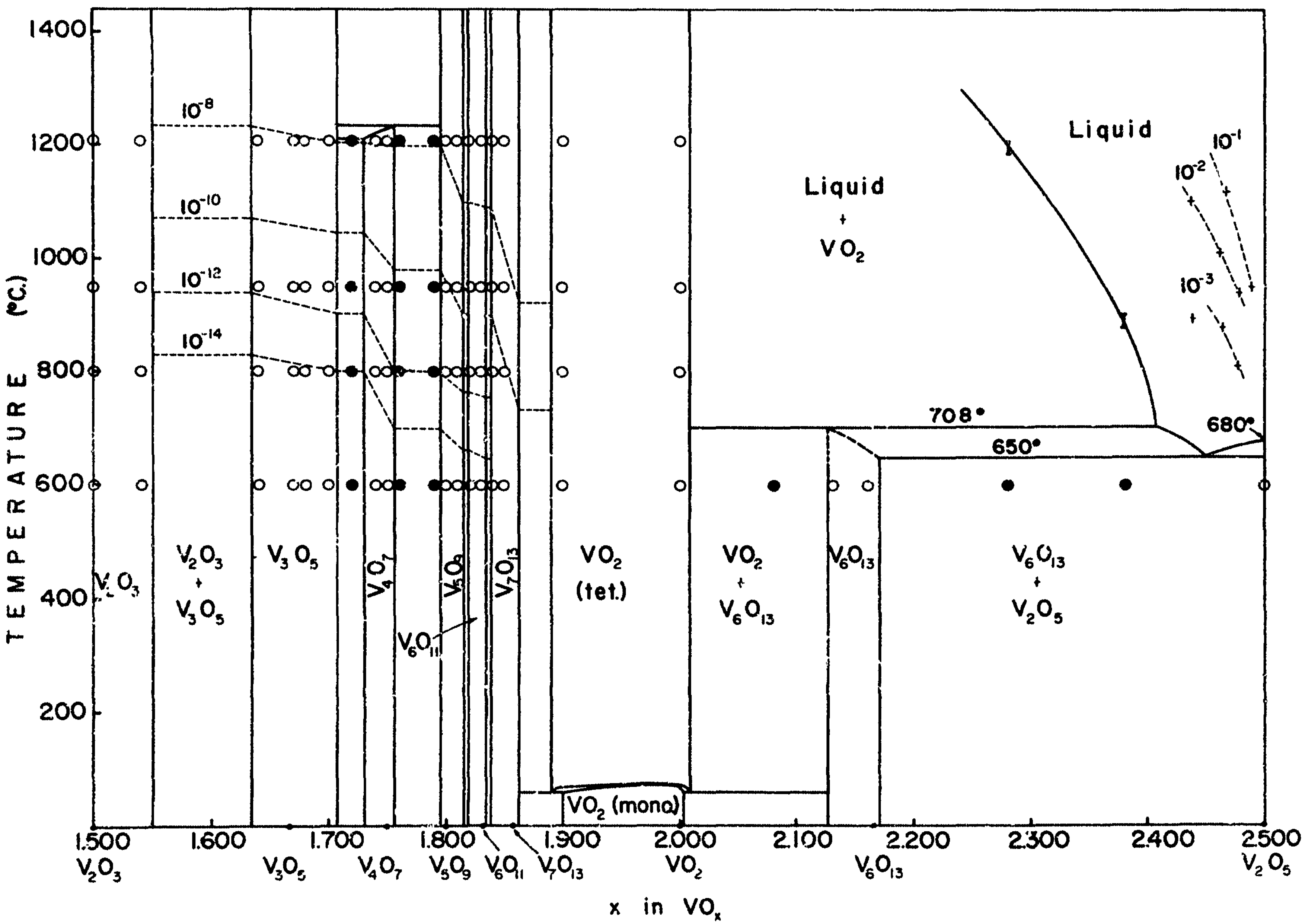
Figure 6. Electrical conductivity of vanadium oxides.

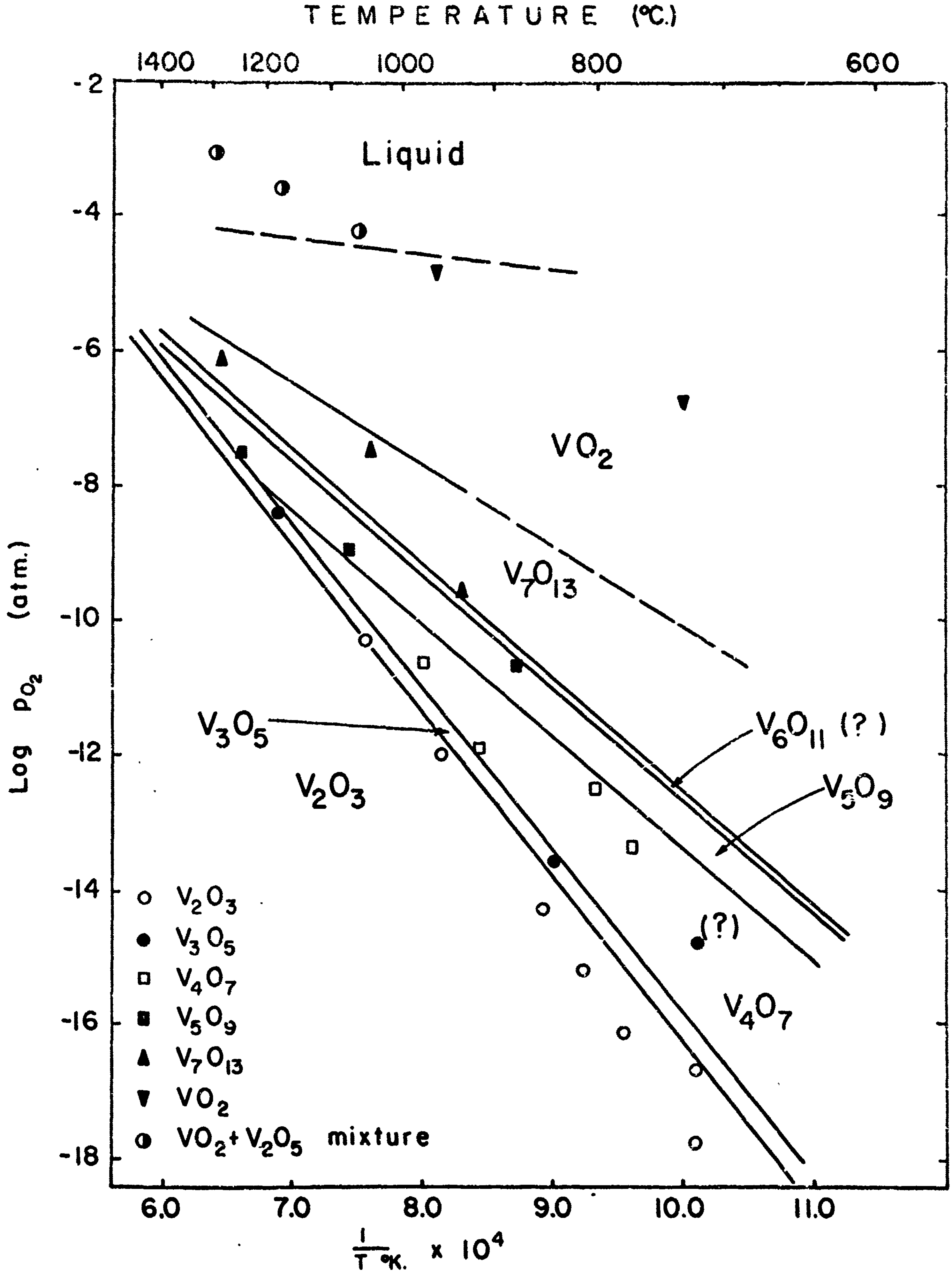


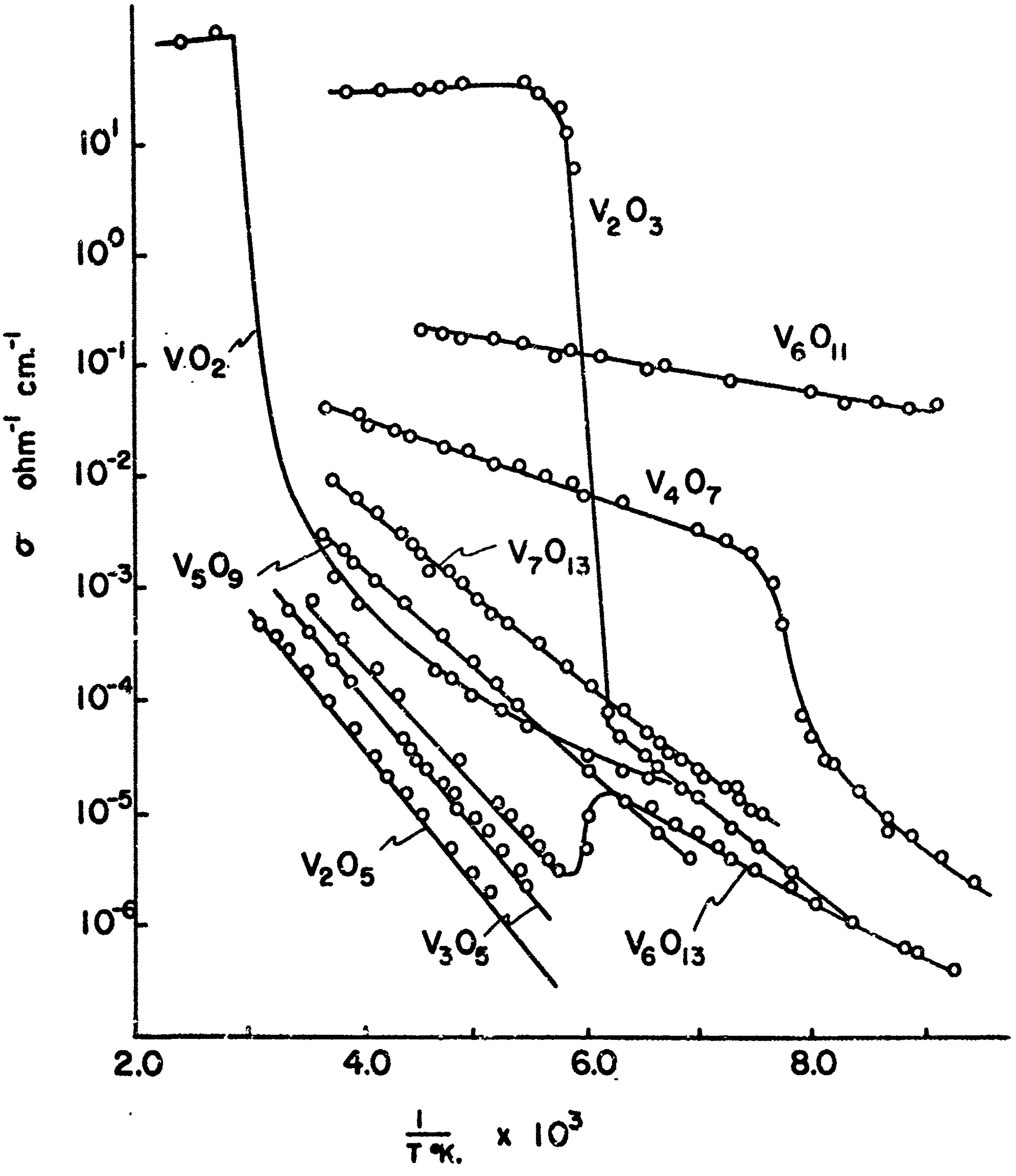
MAGNETIC SUSCEPTIBILITY χ x 10⁵ (cgs)
1.00
2.00
3.00
4.00
-150
-100
-50
0
50
100
150
200
TEMPERATURE °C.
V₃O₅
V₃O₅ +V₄O₇
V₄O₇


-104
V_2O_3
-38
V_3O_5
-143
V_4O_7
-114
V_5O_9
V_6O_{11}
V_7O_{13}
74
VO_2
-108
708
V_6O_{13}
680
V_2O_5
-150
-50
0
200
400
600
800
TEMPERATURE °C.


650
708
$VO_{2.08}$
650
708
V_6O_{13}
650
708
1200
$VO_{2.28}$
650
708
900
$VO_{2.38}$
680
V_2O_5
600
800
1000
1200
TEMPERATURE °C.


TEMPERATURE (°C.)
1400
1200
1000
800
600
400
200
1.500 V2O3
1.600
V3O5
1.700
V4O7
1.800
V5O9
V6O11
V7O13
1.900
2.000 VO2
2.100
V6O13
2.200
2.300
2.400
2.500 V2O5
x in VOx
V2O3
V2O3 + V3O5
V3O5
V4O7
V6O11
V5O9
V7O13
VO2 (tet.)
VO2 (mono)
VO2 + V6O13
V6O13
V6O13 + V2O5
Liquid + VO2
Liquid
10^-8
10^-10
10^-12
10^-14
10^-1
10^-2
10^-3
708°
650°
680°


TEMPERATURE (°C.)
1400
1200
1000
800
600
-2
-4
-6
-8
-10
-12
-14
-16
-18
Log p_{O_2} (atm.)
6.0
7.0
8.0
9.0
10.0
11.0
$\frac{1}{T\,°K.} \times 10^4$
Liquid
VO_2
V_7O_{13}
V_6O_{11} (?)
V_5O_9
V_3O_5
V_2O_3
V_4O_7
(?)
○ V_2O_3
● V_3O_5
□ V_4O_7
■ V_5O_9
▲ V_7O_{13}
▼ VO_2
◐ $VO_2 + V_2O_5$ mixture


σ ohm⁻¹ cm.⁻¹
10¹
10⁰
10⁻¹
10⁻²
10⁻³
10⁻⁴
10⁻⁵
10⁻⁶
2.0
4.0
6.0
8.0
1/T °K. x 10³
V₂O₃
V₆O₁₁
VO₂
V₄O₇
V₇O₁₃
V₅O₉
V₂O₅
V₃O₅
V₆O₁₃

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Research has been concerned with (1) the study of the crystal chemistry of a series of rare earth-rhenium oxide compounds. Six new phases have been found and identified by x-ray and electron probe analysis; (2) Study of the binary system V-O has been completed and described in a Technical Report "Phase Equilibrium Studies and Transitions in the System V_2O_3-V_2O_5". Five out of seven intermediate stable phases found behave like antiferromagnetic materials, having different Neel points; (3) Work has continued to synthesize SmO and EuO. Methods such as reduction of the sesquioxides, oxidation of the metals and reaction of the metal with the sesquioxides have been tried. So far, SmO has been prepared successfully only by the latter method. (U)

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