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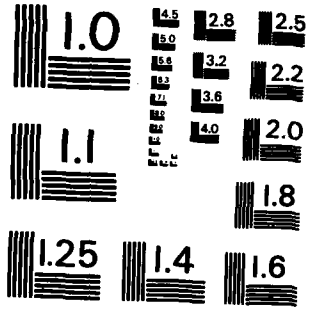

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Solid solutions of the end members Fe_2WO_6, Cr_2WO_6, and Rh_2WO_6 have been prepared and their crystallographic and magnetic properties have been studied. All solid solutions crystallize with the trirutile structure, and their magnetic behavior is characterized by the existence of antiferromagnetic interactions and effective molar Curie constants corresponding to those expected from contributions of the spin-only moments of high-spin Fe^{3+}, Cr^{3+}, and diamagnetic low-spin Rh^{3+} ions. Fe_2WO_6 crystallizes with the (over)

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tri-α-PbO_2 structure and is antiferromagnetic and conducting. The random rutile Rh_2WO_6 is conducting, and the difference between its magnetic and electric properties and those of the inverse trirutile Cr_2WO_6 are discussed in terms of possible interactions between Cr^{3+}(3d) or Rh^{3+}(4d) orbitals and W^{6+}(5d) orbitals.

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Preparation and Properties of the Systems $Fe_{2-x}Cr_xWO_6$, $Fe_{2-x}Rh_xWO_6$, and $Cr_{2-x}Rh_xWO_6$

by

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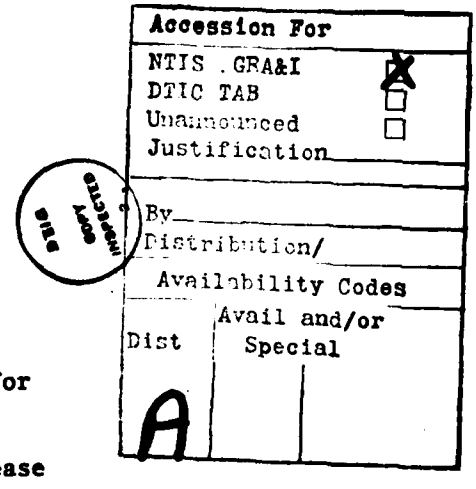

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INTRODUCTION

It has been reported (1-3) that Fe_2WO_6 crystallizes with the tri-α-PbO_2 structure when prepared at temperatures above 800°C. This phase shows high conductivity as a result of the formation of a small amount of $FeWO_4$ and its solid solution in Fe_2WO_6 (3). The existence of both Fe^{2+} and Fe^{3+} is assumed to be the basis for the observed conductivity.

Cr_2WO_6 and Rh_2WO_6 crystallize with the trirutile and the rutile structures, respectively. The magnetic structure of Cr_2WO_6 derived from neutron diffraction data (4,5) shows antiferromagnetic behavior with a Néel temperature at 69°K. However, bulk susceptibility measurements at elevated temperatures have not been made. In addition, there has been no report concerning the electronic properties of this phase. Rh_2WO_6 was first prepared by Badaud and Omaly (6). The structure assignment was based on analysis of x-ray diffraction patterns from polycrystalline samples as well as infrared spectra studies. There have been no reported studies of either the magnetic or electronic properties of Rh_2WO_6.

In both the random rutile and trirutile structures, there is edge sharing of MO_6 octahedral units in such a way that straight chains are formed parallel to the c-direction. Separate chains are linked together by means of corner sharing. For both Cr_2WO_6 and Rh_2WO_6, these chains contain tungsten and either chromium or rhodium ions. It was the main purpose of this study to measure the crystallographic, magnetic, and electronic properties of these compounds in order to determine if there was any significant interaction between $Cr^{3+}(3d)$

or Rh^{3+}(4d) orbitals and W^{6+}(5d) orbitals. Such interactions, if present, might allow some delocalization of the d-electrons to take place, resulting in conducting materials. Solid solutions of the end members Fe_2WO_6, Cr_2WO_6, and Rh_2WO_6 were prepared, and their crystallographic and magnetic properties were determined.

EXPERIMENTAL

All materials in the systems $Fe_{2-x}Cr_xWO_6$, $Fe_{2-x}Rh_xWO_6$, and $Cr_{2-x}Rh_xWO_6$ were prepared from the solid state reactions of the reactants: Fe_2O_3 (Mapico Red); Cr_2O_3, which was obtained by the decomposition in air of ammonium dichromate (Mallinkrodt, analytical reagent) for 36 h at 600°C; WO_3, which was prepared by heating 99.9% tungsten foil (Schwarzkopf Dev. Co.) under flowing oxygen for 80 h at 1000°C; and Rh_2O_3, which was obtained by heating rhodium metal at 800°C under flowing oxygen until constant weight was obtained. A finely ground mixture of stoichiometric amounts of the starting materials was placed either in a covered platinum crucible (system $Fe_{2-x}Cr_xWO_6$) or in a silica tube (systems $Fe_{2-x}Rh_xWO_6$ and $Cr_{2-x}Rh_xWO_6$) and heated in air at the temperature and time indicated in Table I. Each sample was x-rayed, reground, and then reheated. This process was repeated until x-ray diffraction patterns of the products indicated the formation of a single phase. A Philips-Norelco diffractometer with $CuK\alpha_1$ radiation (λ=1.5405Å) was used at a scan rate of 0.25°2θ/min and a chart speed 30 in/h. Cell parameters were obtained from a least-squares refinement of the data with the aid of a computer.

Sintered discs of Fe_2WO_6 were prepared as described previously (3). Sintered discs of Cr_2WO_6 were formed by pressing aliquots of 200 mg at 90,000 psi; 10 drops of Carbowax were added to the powder before pressing in order to facilitate the formation of a well-sintered disc. The pressed discs were placed on a bed of powder having the same composition in an alumina crucible, were heated at a rate of 50°C/h to 975°C, and were maintained at that temperature for 36 h. At the end of the sintering process, the discs were cooled at the same rate. They were x-rayed with $CuK\alpha_1$ radiation and their x-ray diffraction patterns were compared to those of polycrystalline Cr_2WO_6 to confirm that the phase did not undergo any changes during the sintering process. Similarly, sintered discs of Rh_2WO_6 were formed by pressing aliquots of 200 mg at 90,000 psi. The pressed discs were placed on a bed of polycrystalline Rh_2WO_6 in an opened silica tube. The discs were heated at a rate of 50°C/h to 975°C and were maintained at that temperature for 36 h. At the end of the process, the discs were cooled at the same rate and were x-rayed with $CuK\alpha_1$ radiation, as described for Cr_2WO_6.

Magnetic susceptibilities were measured using a Faraday balance (7,8) at a field strength of 10.4 kOe. Honda-Owens (field dependency) plots were also made to determine the presence or absence of ferromagnetic impurities. The data were then corrected for core diamagnetism (9). When observed, Néel temperatures (T_N) were estimated from the minima of the plots of inverse molar magnetic susceptibility versus temperature.

The electrical resistivities were measured using the van der Pauw technique (10). Contacts were made by the ultrasonic soldering of indium

directly onto the samples, and their ohmic behaviors were established by measuring their current-voltage characteristics. The Seebeck coefficient was obtained by applying a temperature gradient to a disc and recording the resulting voltage difference. The sign of this coefficient was used to determine the sign of the majority carriers.

RESULTS AND DISCUSSION

Structure and Crystallography

Fe_2WO_6 has been reported to crystallize with the columbite structure when prepared below 800°C (11) and with the tri-α-PbO_2 structure when prepared at a higher temperature (1-3). Both of these structures have been discussed previously (12) and may be regarded as superlattice variants of α-PbO_2. In this study, the tri-α-PbO_2 phase was prepared and characterized. This structure consists of hcp planes of oxygen anions in which only half of the octahedral sites are occupied by the metal atoms, Fe or W. As shown in Figure 1, each of the resulting octahedra shares a pair of skew edges in such a way that zigzag chains are formed parallel to the c-direction. The separate chains are linked to each other by means of corner sharing. Senegas and Galy (2) have indicated that in the tri-α- PbO_2 form of Fe_2WO_6 one third of the zigzag chains contain only iron atoms, and two thirds of the chains show a 1:1 ordering of iron and tungsten atoms. The 2:1 cation order results in a tripling of the b-parameter. Fe_2WO_6 crystallizing with the tri-α-PbO_2 structure is orthorhombic (space group Pbcn) with the following cell constants: a=4.577(4)Å, b=16.75(4)Å, c=4.965(4)Å

The crystallographic structure of Cr_2WO_6 has been described by Bayer (13). The compound crystallizes with the "inverse trirutile structure," which may be regarded as a superlattice variant of the fundamental rutile structure. It consists of an hexagonal close-packed array of oxygen anions in which one half of the octahedral interstices are occupied by the metal atoms, Cr or W, in a regular 2:1 distribution. The structure is shown in Figure 2. Each of the resulting octahedra shares a pair of opposite edges in such a way that straight chains are formed parallel to the c-direction. Separate chains are corner linked to each other. Within these chains, a 2:1 cation order results in a tripling of the c-parameters. Cr_2WO_6 is tetragonal (space group $P4_2/mnm$) with a=4.580(4)Å and c=8.865(4)Å.

The existence of Rh_2WO_6 has been first reported by Badaud and Omaly (6). Rh_2WO_6 crystallizes with the rutile structure, in which the Rh and W atoms are statistically distributed in the lattice. Rh_2WO_6 is tetragonal (space group $P4_2/mnm$, with a=4.608(4)Å and c=3.033(4)Å.

The crystallographic cell parameters obtained for Fe_2WO_6, Cr_2WO_6, and Rh_2WO_6 are in close agreement with those reported previously (2-6,14). The precise cell parameters obtained for some members of the systems $Fe_{2-x}Cr_xWO_6$, $Fe_{2-x}Rh_xWO_6$, and $Cr_{2-x}WO_6$ are indicated in Table II. Chromium cannot be substituted into the tri-α-PbO_2 structure, but the system $Fe_{2-x}Cr_xWO_6$ does form a solid solution crystallizing with the trirutile structure over a composition range of $2 \geq x \geq 0.3$. The decrease in cell volume with increasing chromium content follows Végard's law and is consistent with the difference in the ionic radii of Fe^{3+}(0.65Å) and Cr^{3+}(0.615Å) (15). Similarly for the system $Fe_{2-x}Rh_xWO_6$, rhodium cannot be substituted into the tri-α-PbO_2 phase, but a solid solution does form with the trirutile structure over the range $2 > x \geq 0.3$. The slight change in the cell volume with composition is consis-

tent with the similarity between the ionic radii of Fe^{3+}(0.65Å) and Rh^{3+}(0.665Å) (15). In the system $Cr_{2-x}Rh_xWO_6$, there are two compositional ranges crystallizing with the trirutile structure: the range $0.4 \gtrsim x \gtrsim 0$ represents the solubility of rhodium in Cr_2WO_6; the range $2 \gtrsim x > 1.7$ may be regarded as representing the solubility of Cr atoms in Rh_2WO_6. In the range $1.7 > x \gtrsim 0.4$, two trirutile phases are observed to be present. The increase of the cell volume with increasing rhodium content is consistent with the difference between the ionic radii of Cr^{3+} and Rh^{3+}.

Magnetic Properties

The magnetic structure of Fe_2WO_6 was determined by means of neutron diffraction by Pinto et al. (16); they reported antiferromagnetic ordering at 4.2K with a Néel temperature of approximately 240K. They confirmed the existence of antiferromagnetic ordering by measuring the magnetic susceptibility from 80 to 298K. In this present study, high temperature susceptibility measurements indicate that the inverse magnetic susceptibility varies linearly with temperature above 600K. The susceptibility data obtained between 298 and 800K are shown in Figure 3; a Weiss constant of approximately -450K and an effective molar Curie constant of 7.7 (emu-mole^{-1}K) were determined. The latter value corresponds to a spin-only moment of about $5.6\mu_B$, which is in agreement with the spin-only value of $5.9\mu_B$ for Fe^{3+}(S=5/2). Between 300K and 600K, the temperature dependency of the inverse magnetic susceptibility is not linear because of the presence of some short-range magnetic order.

The magnetic structure of Cr_2WO_6 has been determined previously by Montmory (4) and Kunnmann (5). It was found from both neutron diffraction and bulk susceptibility measurements that Cr_2WO_6 is ordered antiferromagnetically at 4.2K, with a Néel temperature of 69K (4) and a Weiss constant of -196K. In this present study, high-temperature susceptibility measurements were made between 298 and 800K. Above 300K, there is a linear dependency of the inverse magnetic susceptibility on temperature. A Curie constant of 3.7 gives a calculated magnetic moment of $3.9\mu_B$ which agrees with the spin-only value of $3.87\mu_B$ for $Cr^{3+}(S=3/2)$.

The molar magnetic susceptibility of Rh_2WO_6 is 3.8×10^{-4} (emu/mole) at 298K and shows a small temperature dependency in the range from 77 to 298K ($\chi_{77K} \sim 2[\chi_{298}]$). This result suggests the existence of a small number of unpaired electrons which may arise from the presence of trace amounts of $Rh^{4+}(3d^5)$ in the sample.

The magnetic data for the system $Fe_{2-x}Cr_xWO_6$ are summarized in Table III. All compositions in this system show a Curie-Weiss behavior above room temperature. The effective molar Curie constants, C_M, agree with those values expected from the contributions of the spin-only moments of high-spin Fe^{3+} and Cr^{3+}. Below room temperature, all members order antiferromagnetically, as indicated by negative values of the Weiss constant, θ, and by the presence of distinct Néel temperatures in the inverse susceptibility-versus-temperature plots. Figure 4 shows the inverse magnetic susceptibility versus temperature for the compositions $Fe_{1.7}Cr_{0.3}WO_6$. From similar plots, T_N and θ values were calculated for the other members

of the system. The strength of the antiferromagnetic interactions in the iron-containing members of the system increases with increasing iron content. This is seen from the values of θ and T_N indicated in Table III. The increase in the strength of the antiferromagnetic interaction is related to the availability of half-filled $Fe^{3+}(3d^5)$ e_g orbitals. (17)

The magnetic data for the systems $Fe_{2-x}Rh_xWO_6$ and $Cr_{2-x}Rh_xWO_6$ are so summarized in Table III. Members of both systems show Curie-Weiss behavior, with effective molar Curie constants corresponding closely to those calculated from contributions from the spin-only moments of either high-spin $Fe^{3+}(3d^5)$ or $Cr^{3+}(3d^3)$ and diamagnetic low-spin $Rh^{3+}(3d^6)$. All compounds indicate the presence of antiferromagnetic interactions as indicated by the negative θ values. The decrease of the magnitude of θ upon rhodium substitution is consistent with the weakening of these interactions by the presence of diamagnetic Rh^{3+} ions. The magnetic susceptibility data for the composition $Fe_{1.6}Rh_{0.4}WO_6$ is shown in Figure 5; there are sufficient antiferromagnetic interactions present so that the Néel temperature is clearly observed.

Electrical Properties

The electrical properties of Fe_2WO_6 have been determined previously (3). Fe_2WO_6 is an *n*-type semiconductor with an activation energy of 0.17(1) eV and a room temperature resistivity of $\sim$50(Ω-cm). This extrinsic semiconducting behavior is consistent with the existence of a solid solution of small amounts of $FeWO_4$ in Fe_2WO_6, thereby introducing iron(II) and iron(III)

on equivalent sites; conduction may therefore occur by electron transfer along the chains containing pure iron in the tri-α-PbO_2 structure.

Cr_2WO_6 was found to be non-conducting ($\rho_{298K} \sim 2 \times 10^6 \Omega$-cm). This result is consistent with the presence of both Cr^{3+} and W^{6+} ions in all the chains of the trirutile structure.

Rh_2WO_6 was found to be conducting ($\rho = 22\Omega$-cm at room temperature and the conductivity is almost temperature independent. In addition, a small Seebeck coefficient was measured, which is also indicative of metallic behavior. The sign of this coefficient indicates p-type conductivity, which is consistent with the existence of Rh^{4+} as an impurity. The electrical conductivity observed in Rh_2WO_6 may be a result of Rh(4d)-W(5d) interactions which make some electron transfer possible in the "disordered" rutile structure. In Cr_2WO_6, Cr(3d)-W(5d) interactions do not occur, and hence a high resistivity is observed. Some delocalization of electrons is possible in Rh_2WO_6 because of overlap of Rh(4d) orbitals with W(5d) orbitals. This observation is also consistent with the magnetic behavior observed in Rh_2WO_6.

CONCLUSIONS

Fe_2WO_6, Cr_2WO_6, and Rh_2WO_6 have been prepared, and crystallize with the tri-α-PbO_2, trirutile, and rutile structures, respectively. Fe_2WO_6 is conducting as a result of the formation of a small amount of $FeWO_4$ and its solid solution in Fe_2WO_6. When Fe_2WO_6 crystallizes in the tri-α-PbO_2

structure, zigzag chains are formed by the linking of FeO_6 octahedra, and along them, electron transfer from Fe^{2+} to Fe^{3+} may give rise to conductivity. Measurements above 600K of the magnetic susceptibility of Fe_2WO_6 yield an effective molar Curie constant whose value corresponds closely to that expected for spin-only Fe^{3+} ions. In addition, the large, negative Weiss constant indicates the existence of strong antiferromagnetic interactions.

Cr_2WO_6 crystallizes with the trirutile structure which is characterized by both tungsten and chromium ions beings located in MO_6 octahedra which are linked together to form straight chains. Measurements of the magnetic susceptibility of Cr_2WO_6 above 300K yield an effective molar Curie constant whose value corresponds to that expected for spin-only Cr^{3+}.

Rh_2WO_6 also crystallizes in the random rutile structure, and shows small temperature dependencies in its magnetic susceptibility and its electrical conductivity. The Seebeck coefficient indicates p-type conduction. This behavior of Rh_2WO_6 is consistent with the presence of Rh^{4+} as an impurity and with the existence of interactions between Rh(4d) orbitals and W(5d) orbitals in the rutile structure.

Solid solutions of the end members Fe_2WO_6, Cr_2WO_6, and Rh_2WO_6 can be prepared, and crystallize with the trirutile structure over different compositional ranges. Magnetic susceptibility measurements for all the resulting solid solutions yield effective molar Curie constants corresponding closely to those calculated from the contributions of the spin-only

moments of high-spin Fe^{3+}, Cr^{3+} and diamagnetic low-spin Rh^{3+} ions. In addition, negative Weiss constants indicate the existence of antiferromagnetic interactions in these compounds.

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TABLE I

Reaction Conditions for the Synthesis of Single Phase Compounds

Nominal Composition	Reaction Temperature/Time
Fe_2WO_6	950°C/5 days
$Fe_{1.7}Cr_{0.3}WO_6$	950°C/6 days
$Fe_{1.5}Cr_{0.5}WO_6$	950°C/4 days
$FeCrWO_6$	950°C/4 days
Cr_2WO_6	950°C/6 days
Fe_2WO_6	950°C/5 days
$Fe_{1.6}Rh_{0.4}WO_6$	900°C/1.5 days, 950°C/2 days
$FeRhWO_6$	850°C/3 days, 900°C/1.5 days
$Fe_{0.8}Rh_{1.2}WO_6$	850°C/9 days
$Fe_{0.6}Rh_{1.4}WO_6$	850°C/12 days
$Fe_{0.3}Rh_{1.7}WO_6$	850°C/3.5 days, 875°C/14.5 days
Rh_2WO_6	850°C/3.5 days, 875°C/16 days, 900°C/2 days, 930°C/2 days
Cr_2WO_6	950°C/6 days
$Cr_{1.8}Rh_{0.2}WO_6$	850°C/2.5 days, 900°C/2 days, 950°C/1.5 days
$Cr_{1.6}Rh_{0.4}WO_6$	900°C/6 days, 950°C/2 days
Rh_2WO_6	850°C/3.5 days, 875°C/16 days, 900°C/2 days, 930°C/2 days

Table II

CRYSTALLOGRAPHIC PROPERTIES

System $Fe_{2-x}Cr_xWO_6$

Compound	a(Å)	b(Å)	c(Å)	V(Å)^3	Structure	Space Group
Fe_2WO_6	4.577(4)	16.75(4)	4.965(4)	380.6	tri-α-PbO_2	Pbcn
$Fe_{1.7}Cr_{0.3}WO_6$	4.627(4)	-	8.964(4)	192.0	trirutile	$P4_2/mnm$
$Fe_{1.5}Cr_{0.5}WO_6$	4.619(4)	-	8.941(4)	190.8	trirutile	$P4_2/mnm$
$FeCrWO_6$	4.607(4)	-	8.916(4)	189.2	tritutile	$P4_2/mnm$
$CrWO_6$	4.580(4)	-	8.865(4)	186.0	rutile	$P4_2/mnm$

System $Fe_{2-x}Rh_xWO_6$

Compound	a(Å)	b(Å)	c(Å)	V(Å)^3	Structure	Space Group
Fe_2WO_6	4.577(4)	16.75(5)	4.965(4)	380.6	tri-α-PbO_2	Pbcn
$Fe_{1.6}Rh_{0.4}WO_6$	4.633(4)	-	8.974(4)	192.6	trirutile	$P4_2/mnm$
$FeRhWO_6$	4.631(4)	-	9.002(4)	193.1	trirutile	$P4_2/mnm$
$Fe_{0.8}Rh_{1.2}WO_6$	4.629(4)	-	9.015(4)	193.2	trirutile	$P4_2/mnm$
$Fe_{0.6}Rh_{1.4}WO_6$	4.622(4)	-	9.031(4)	192.9	trirutile	$P4_2/mnm$
$Fe_{0.3}Rh_{1.7}WO_6$	4.615(4)	-	9.062(4)	193.0	trirutile	$P4_2/mnm$
Rh_2WO_6	4.608(4)	-	3.033(4)	64.4(*)	rutile	$P4_2/mnm$

System $Cr_{2-x}Rh_xWO_6$

Compound	a(Å)	c(Å)	V(Å)^3	Structure	Space Group
$CrWO_6$	4.580(4)	8.865(4)	186.0	trirutile	$P4_2/mnm$
$Cr_{1.8}Rh_{0.2}WO_6$	4.585(4)	8.879(4)	186.7	trirutile	$P4_2/mnm$
$Cr_{1.6}Rh_{0.4}WO_6$	4.590(4)	8.895(4)	187.4		$P4_2/mnm$
Rh_2WO_6	4.608(4)	3.033(4)	64.4(*)		$P4_2/mnm$

(*) When indexed as a trirutile, Rh_2WO_6 has a calculated cell volume of 193.2(Å)^3

Table III

MAGNETIC PROPERTIES

System $Fe_{2-x}Cr_xWO_6$

Compound	$1/C_M$ Found	$1/C_M$ Expected	T_N(K)	θ(K)
Fe_2WO_6	0.13	0.12	-	∿-450
$Fe_{1.7}Cr_{0.3}WO_6$	0.11	0.12	320	-908
$Fe_{1.5}Cr_{0.5}WO_6$	0.12	0.13	276	-803
$FeCrWO_6$	0.15	0.16	236	-620
Cr_2WO_6	0.27	0.27	∿80	-184

System $Fe_{2-x}Rh_xWO_6$

Compound	$1/C_M$ Found	$1/C_M$ Expected	T_N(K)	θ(K)
Fe_2WO_6	0.13	0.12	-	∿-450
$Fe_{1.6}Rh_{0.4}WO_6$	0.14	0.14	216	-625
$FeRhWO_6$	0.23	0.23	-	-387
$Fe_{0.8}Rh_{1.2}WO_6$	0.32	0.29	-	∿-295
$Fe_{0.6}Rh_{1.4}WO_6$	0.40	0.38	-	-216
$Fe_{0.3}Rh_{1.7}WO_6$	0.78	0.76	-	-102
Rh_2WO_6	-	-	-	-

System $Cr_{2-x}Rh_xWO_6$

Compound	$1/C_M$ Found	$1/C_M$ Expected	T_N(K)	θ(K)
Cr_2WO_6	0.27	0.27	∿80	-184
$Cr_{1.8}Rh_{0.2}WO_6$	∿0.28	0.30	-	∿-200
$Cr_{1.6}Rh_{0.4}WO_6$	0.32	0.33	-	-173
Rh_2WO_6	-	-	-	-

REFERENCES

1. J. Galy and J. Senegas; C.R. Acad. Sc. Paris, C, 275, 665 (1972).

2. J. Senegas and J. Galy; J. Solid State Chem. 10, 5 (1974).

3. H. Leiva, K. Dwight and A. Wold; J. Solid State Chem. 42, 41 (1982).

4. M.C. Montmory, E.F. Bertaut and P. Mollard; Solid State Communications 4, 249 (1966).

5. W. Kunnmann, S. LaPlaca, L.M. Corliss, J.M. Hastings and E. Banks; J. Phys. Chem. Solids 29, 1359 (1968).

6. J.P. Badaud and J. Omaly; C.R. Acad. Sc. Paris 278, 521 (1974).

7. B. Morris and A. Wold; Rev. Sci. Inst. 39, 1937 (1966).

8. A.W. Catalano, Ph.D. Thesis, Brown University (1973).

9. P.W. Selwood, "Magnetochemistry," 2nd ed., Interscience, New York, 1956.

10. L.J. van der Pauw; Philips Res. Rep. 13, 1 (1958).

11. C. Parant, J.C. Bernier and A. Michel; C.R. Acad. Sc. Paris, C, 276, 495 (1973).

12. H. Leiva, K. Sieber, B. Khazai, K. Dwight and A. Wold; J. Solid State Chemistry 44, 113 (1982).

13. G. Bayer; J. Amer. Ceram. Soc. 43, 495 (1960).

14. M. Drillon, L. Padel and J.C. Bernier; J. Chem. Soc. Faraday II, 76, 1224 (1980).

15. R.D. Shannon and C.T. Prewitt; Acta Cryst. B25, 925 (1969).

16. H. Pinto and M. Melamud; Acta Cryst. A33, 663 (1977).

17. J.B. Goodenough; Le Journal de Physique et le Radium 20, 155 (1959).

FIGURE CAPTIONS

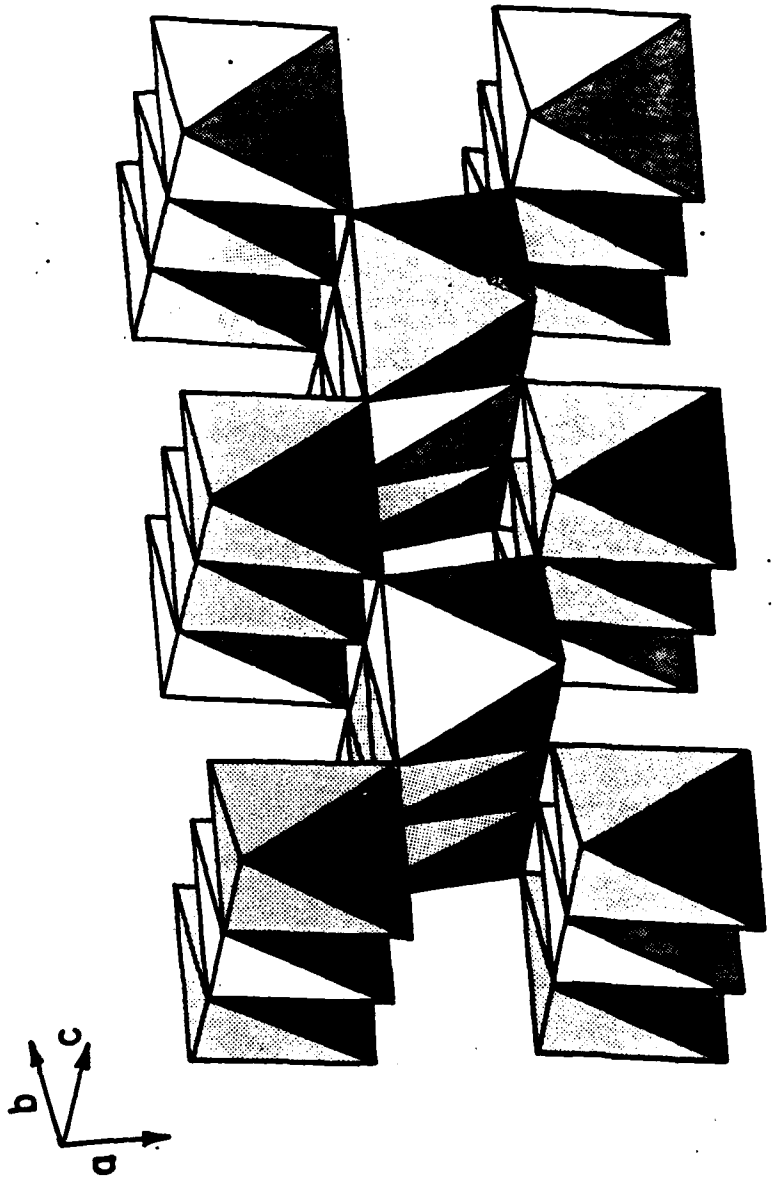
Figure 1 - Perspective view of the tri-α-PbO_2 structure, showing skew-edge linked chains of octahedra.. The lighter octahedra contain the tungsten sites.

Figure 2 - Perspective view of the trirutile structure, showing straight chains of octahedra. The lighter octahedra contain the tungsten sites.

Figure 3 - Temperature dependence of the inverse magnetic susceptibility of Fe_2WO_6.

Figure 4 - Temperature dependence of the inverse magnetic susceptibility of $Fe_{1.7}Cr_{0.3}WO_6$.

Figure 5 - Temperature dependence of the inverse magnetic susceptibility of $Fe_{1.6}Rh_{0.4}WO_6$.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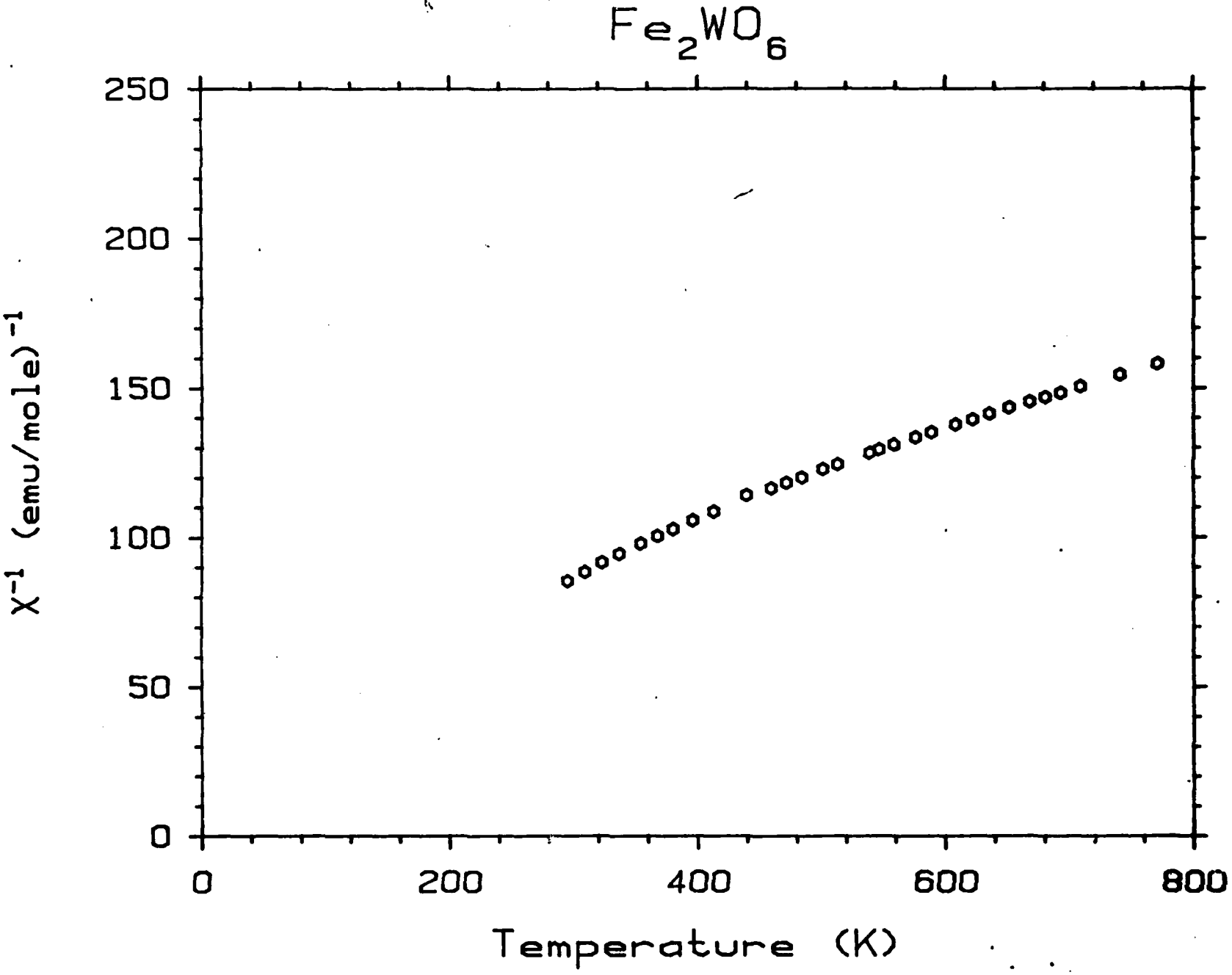
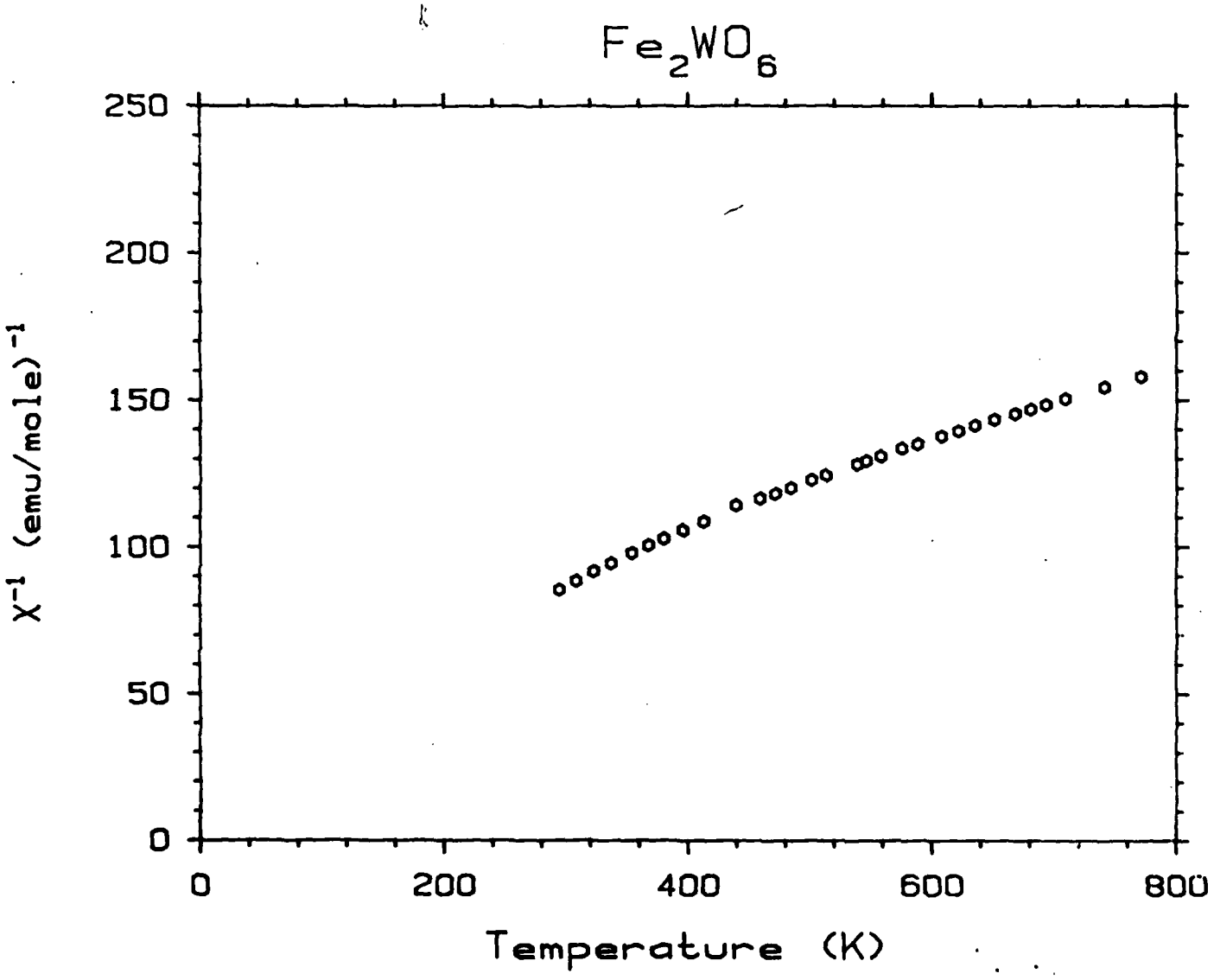

Fe_2WO_6
250
200
150
100
50
0
χ^{-1} (emu/mole)$^{-1}$
0
200
400
600
800
Temperature (K)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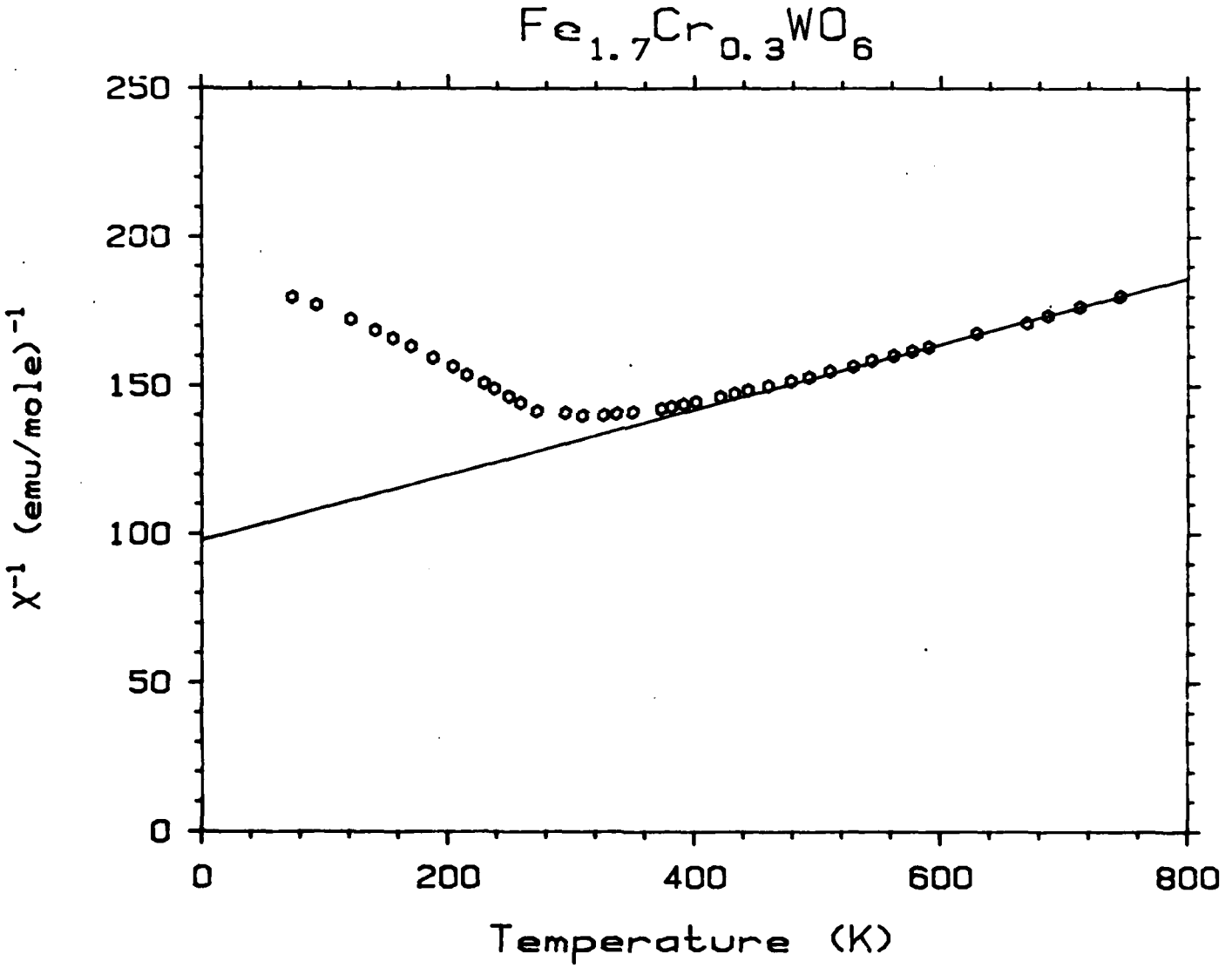
$Fe_{1.7}Cr_{0.3}WO_6$
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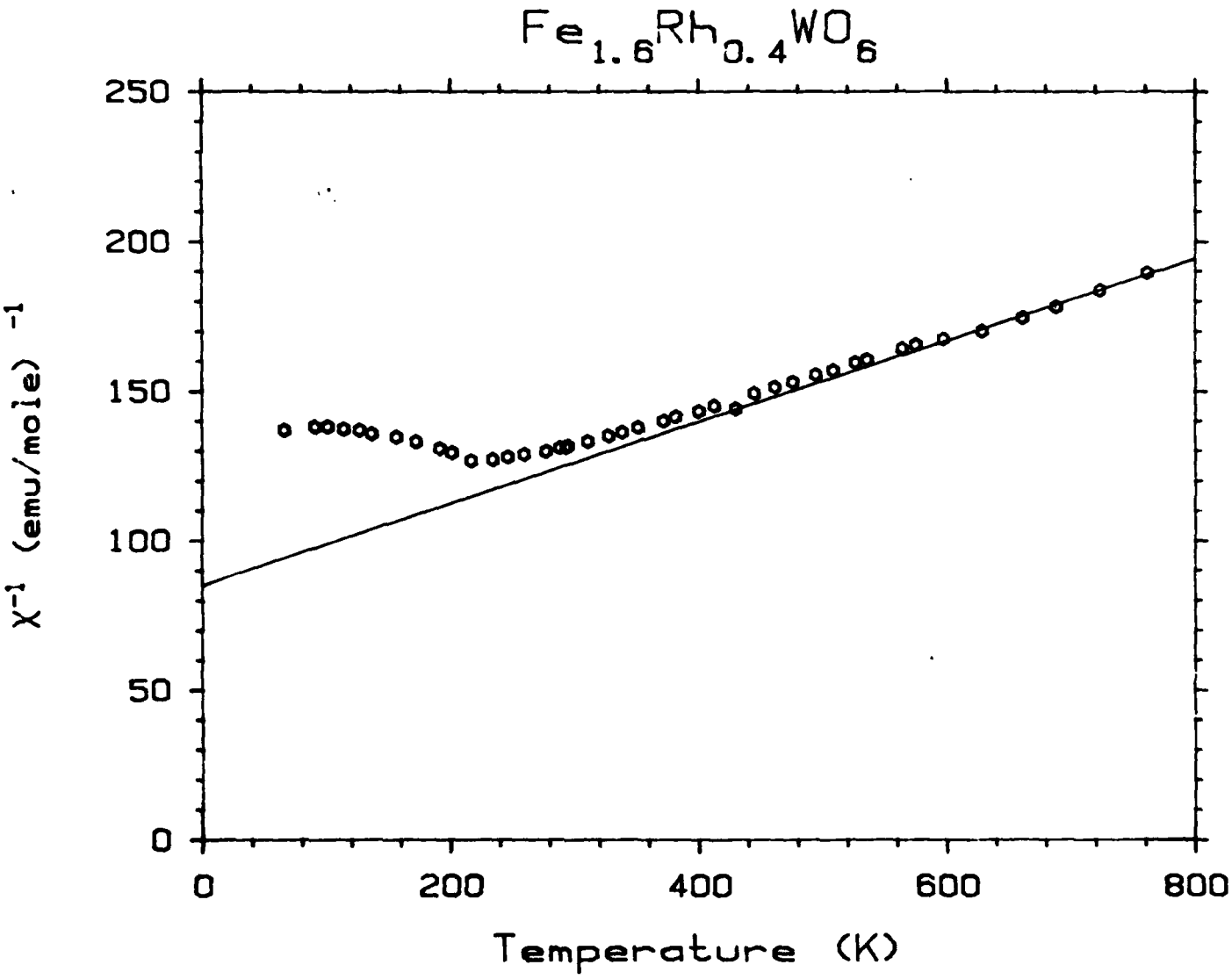
$Fe_{1.6}Rh_{0.4}WO_6$
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Temperature (K)

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