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A number of new ternary rhenium chalcogenides $\text{A}_4\text{Re}_6\text{X}_{12}$ with A = Tl, Cu, Na, Cs, X = Se; A = Tl, Rb, X = S; and $\text{A}_2\text{Re}_6\text{X}_{12}$ with A = Pb, X = S, Se, have been prepared using high temperature solid state reaction or ion exchange methods. These new phases are isostructural with $\text{K}_4\text{Re}_6\text{S}_{12}$ (Space Group C2/c). The observed semiconducting and diamagnetic properties of these phases are consistent with the valence electron count (VEC) of 24. Tl and Re in $\text{Tl}_4\text{Re}_6\text{X}_{12}$ (X = S, Se) have been confirmed by XANES to be in the +1 and +3 oxidation state, respectively. Ru can partially substitute for Re in $\text{Tl}_4\text{Re}_6\text{Se}_{12}$ forming solid solutions of $\text{Tl}_4\text{Re}_6\text{Ru}_x\text{Se}_{12}$. For $x \geq 0.5$, $\text{Tl}_4\text{Re}_6\text{Ru}_x\text{Se}_{12}$ shows metallic and antiferromagnetic behavior which suggest the possibility of VEC greater than 24.			
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New Rhenium Chalcogenides With
[Re₆X₈]-Cluster Units

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Abstract

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A number of new ternary rhenium chalcogenides $A_4\text{Re}_6\text{X}_{12}$ with $A = \text{Tl}, \text{Cu}, \text{Na}, \text{Cs}$, $X = \text{Se}$; $A = \text{Tl}, \text{Rb}$, $X = \text{S}$; and $A_2\text{Re}_6\text{X}_{12}$ with $A = \text{Pb}$, $X = \text{S}, \text{Se}$, have been prepared using high temperature solid state reaction or ion exchange methods. These new phases are isostructural with $\text{K}_4\text{Re}_6\text{S}_{12}$ (Space Group C2/c). The observed semiconducting and diamagnetic properties of these phases are consistent with the valence electron count (VEC) of 24. Tl and Re in $\text{Tl}_4\text{Re}_6\text{X}_{12}$ ($X = \text{S}, \text{Se}$) have been confirmed by XANES to be in the +1 and +3 oxidation state, respectively. Ru can partially substitute for Re in $\text{Tl}_4\text{Re}_6\text{Se}_{12}$ forming solid solutions of $\text{Tl}_4\text{Re}_{6-x}\text{Ru}_x\text{Se}_{12}$. For $x \geq 0.5$, $\text{Tl}_4\text{Re}_{6-x}\text{Ru}_x\text{Se}_{12}$ shows metallic and antiferromagnetic behavior which suggest the possibility of VEC greater than 24.

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Key Words: ternary rhenium chalcogenides, octahedral cluster units, of rhenium (III), ruthenium, substitution, for rhenium, electronic transport, magnetic, and XANES studies.

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1. Introduction

Since 1978, thirteen ternary rhenium chalcogenides with the general formula $A^I/A^{II}_2 \text{Re}_6\text{X}_{11+n}$ ($A^I = \text{Li, Na, K, Rb, Cs}$; $A^{II} = \text{Sr, Ba, Eu}$; $\text{X} = \text{S, Se}$, $n = 0, 1, \text{ or } 2$) have been reported [1-7] (Table 1).

The major structural features of these compounds are Re_6 octahedra inscribed in X_8 cubes forming Re_6X_8 cluster units, which are interconnected three dimensionally by X/X_2 bridges. The ternary metal ions (A) are located in the interstitial positions of these skeletal structures. The rhenium ions are 5-coordinated by X atoms (dsp^3) [1,2] and thus each Re atom has 4 remaining d-orbitals to form Re-Re bonds within the cluster. Of the 24 Re-Re orbitals available, 12 are bonding orbitals forming the valence band, and 12 are anti-bonding orbitals forming the conduction band [8-12]. It has been assumed that Re atoms in these compounds are in the +3 oxidation state (d^4) which leads to complete filling of the valence band, and leaving the conduction band empty. As a result of 24 electrons per cluster unit, the so-called magic number, the Re_6 octahedra should be almost regular, and semiconducting or insulating, as well as diamagnetic behavior is expected. Indeed, detailed structural analyses of these compounds by X-ray diffraction have confirmed the regularity of Re_6 octahedra, and physical measurements, although very few, have shown for example, that $\text{Na}_4\text{Re}_6\text{S}_{12}$ is insulating [3] and $\text{Li}_4\text{Re}_6\text{S}_{11}$ is diamagnetic [6]. The only exception found so far is $\text{Cs}_4\text{Re}_6\text{S}_{13}$, which is paramagnetic [13]. The latter behavior has been attributed to 23 valence electron count (VEC) due to the presence of terminal sulfide [1, 13], i.e. $\text{Cs}_4[\text{Re}_6\text{S}_8]\text{S}_{2/2} (\text{S}_2)_{3/2}$.

We have focused our research in this area on some of the interesting issues still remaining:

- (1) Is it possible to change the number of electrons per cluster unit, i.e. to populate the conduction band or to produce holes in the

valence band by substitution chemistry? If the answer to this question is yes, what effects the change in VEC might have both on the structure and on physical properties?

- (2) Is the oxidation state of Re +3?
- (3) Is it possible to prepare new ternary rhenium chalcogenides with novel A cations possibly leading to interesting new properties?

In this communication, we report on the synthesis and properties of a number of new ternary rhenium chalcogenides $A_4Re_6X_{12}$ with A = Tl, Cu, Na, Cs, X = Se; A = Tl, Rb, X = S; and $A_2Re_6X_{12}$ with A = Pb, X = S, Se, and the substitution chemistry of $Tl_4Re_6Se_{12}$.

2. Experimental

2.1. Synthesis

We have successfully prepared two new Tl analogs: $Tl_4Re_6S_{12}$ and $Tl_4Re_6Se_{12}$ by conventional high temperature solid state reactions from stoichiometric TlX (X = S, Se), Re metal and elemental X. The starting materials were intimately mixed and sealed in evacuated quartz tubes. The mixtures were slowly heated to $\sim 1000^\circ C$, kept at this temperature for a few days, and then cooled down to room temperature in a week.

$A_4Re_6X_{12}$ (A = Na, K; X = S, Se) were prepared either directly from the corresponding elements or by replacement of Tl in $Tl_4Re_6X_{12}$ by ion exchange method. All the other ternary phases reported here were obtained by ion exchange method [14].

The preparation of substituted phases was carried out using the same procedure as that for $Tl_4Re_6Se_{12}$.

2.2. Phase Identification

Phases were identified by powder X-ray diffraction using graphite monochromatized CuK_α radiation with a computer controlled Scintag PAD V diffractometer. Si was used as internal standard. Unit cell parameters were determined by fitting the observed X-ray powder pattern by a least

were determined by fitting the observed X-ray powder pattern by a least square program. Chemical analysis was carried out by a dc - Argon plasma emission spectrometer.

2.3. Transport Property Measurements

Temperature variation of the resistivity of sintered pellets was measured using the Van der Pauw technique [15] in a conventional cryostat.

Magnetic susceptibility measurements were performed using a SQUID, Quantum design, magnetometer.

2.4. XANES

The X-ray absorption near-edge spectra (XANES) were recorded on the Cl beam line at the Cornell High Energy Synchrotron Source (CHESS). The monochromator used consists of two Si crystals with their diffracting surface cut parallel to the (111) planes. Samples were first ground to a fine powder and then dusted uniformly onto scotch tape. In order to obtain the energy positions of the Re-L₃ "white line" (WL) and Tl-L₃ absorption edge, ReO₂ or Tl₂O₃ was always used at the second detector for standard.

3. Results

3.1. The Ternary Phases

Tl₄Re₆S₁₂ and Tl₄Re₆Se₁₂ form as grey polycrystalline materials with metallic luster. Single crystal growth, structure determination and physical property measurements will be reported in a separate paper [16]. The ion exchange products appear in grey powder form. These phases can only be dissolved in oxidizing acids. The Tl ions located in interstices are highly mobile as shown by their partial removal upon treatment with I₂/CH₃CN or in dilute HCl at room temperature. The low limit for x in Tl_xRe₆Se₁₂ was found to be 1.8. Further oxidation results in decomposition.

All the phases are isostructural with $K_4Re_6S_{12}$ and may be indexed on space group $C2/c$. Cell parameters of the compounds prepared in this work along with those of previously reported $A_4Re_6X_{12}$ phases given for comparison are summarized in Table 2.

Fig. 1 shows the results of selected resistivity measurements. All of the phases measured show semiconducting behavior. The resistivity of $Tl_4Re_6S_{12}$ is much higher than that of $Tl_4Re_6Se_{12}$. The only pathway for conduction in this system is via the Re-X/ X_2 bridges. Thus the increased conductivity of the selenium compound may be attributed to the larger radial distribution of the Se 4p orbitals compared to the 3p orbitals of S leading to better overlap of the former with the 5d orbitals of Re.

$Tl_4Re_6Se_{12}$ shows diamagnetic behavior (Fig. 2). From room temperature down to 120K, the susceptibility is almost temperature independent, followed by an upturn at low temperature which is most likely related to the presence of impurities. This is in agreement with previously reported results for $Li_4Re_6S_{11}$ [6].

It has been well established that the core level absorption edges (as determined in XANES measurements) manifest as chemical shift to higher energy with increasing cation valence. [17-20] We will define the relative chemical shift (RCS) in our materials as $\Delta E = E(\text{compound}) - E(\text{reference compound})$, where the reference compound was chosen to be $ReCl_3$ for Re- L_3 edge and $TlSe$ for Tl- L_3 edge respectively. Here E is defined as the half absorption step position for Tl- L_3 absorption edge and the peak position of the intensive Re- L_3 white line, respectively.

The Re- L_3 and Tl- L_3 spectra are shown in Fig. 3 and Fig. 4, respectively. By convention these spectra are normalized to the height of the step in the continuum absorption across the X-ray absorption edge. The (RCS) values are listed in Table 3 for the Re- L_3 edges and

Table 4 for Tl-L₃ edges. One can see that the WL peak position of the Re⁴⁺ compound, ReO₂ is obviously shifted to the higher energy side of the Re³⁺ compound ReCl₃. The RCS value is about 1.7 eV (see Table 3). On the other hand, the absorption peak positions of the compound Tl₄Re₆Se₁₂ and Tl₄Re₆S₁₂ are almost the same as that of ReCl₃ (RCS values are -0.2 and 0.1, respectively), indicating that the Re valence in these two compounds is close to +3 as in ReCl₃.

Turning to the Tl-L₃ results in Fig. 4, we note that the Tl₄Re₆Se₁₂ spectrum has a chemical shift quite close to the Tl⁺ compound (TlSe) and that the Tl³⁺ compound Tl₂O₃ is dramatically shifted to higher energy (by 8.9 eV). Thus the association of the Tl⁺ state in our ternary compound seems certain. We note that the nearly featureless step nature of the Tl⁺ compound Tl-L₃ edges is due to the absence of empty Tl-6s which are strongly favored in the 2p absorption process. The small maximum at the Tl₂O₃ edge is presumably related to the appearance of empty 6s states in the Tl³⁺ compound.

3.3 The Quarternary Phases

All our attempts to produce holes in the valence band were unsuccessful. None of the valence electron deficient elements such as Nb, Ta, W, and Mo substituted even partially, for Re, even though some of them are chemically very similar to Re. In contrast, Ru which has one more valence electron than Re, was found to replace Re partially forming solid solutions of Tl₄Re_{6-x}Ru_xSe₁₂ (x = 0.25 - 1.50). The electrical conductivity increases with increasing x in Tl₄Re_{6-x}Ru_xSe₁₂; for x ≥ 0.5, samples show metallic behavior as illustrated in Fig. 5. This is an interesting finding, since all of the previously reported ternary rhenium chalcogenides are insulating or semiconducting. The magnetic susceptibility data of Tl₄Re₆Se₁₂ are also very interesting as seen in Fig. 6. In the range 300 to 70K the data can be fitted to the

equation $\chi_M = C_M/(T-\theta)$ with $\theta = -612 \pm 6K$ and $C_M = 0.641 \pm 4K$ emu/mole. $\mu_{eff} = (8 \times C_M)^{1/2}$ yields a value of 2.26 and from $C_M = 1/8g^2S(S+1)$ we obtain $S = 0.71$ which suggests 1.5 electrons/mole. This is in excellent agreement with 24 of 25.5 electrons of $Tl_4Re_{4.5}Re_{1.5}Se_{12}$ filling the valence band and 1.5 electrons occupying some localized level(s). In the low temperature region, the $1/\chi$ values drop possibly due to some type of magnetic ordering (Fig. 6).

4. Discussion

4.1. Unit Cell Volume

Fig. 7 shows the variation of cell volumes for $A_I/A_{II}Re_6X_{12}$ phases with effective ionic radii of the ternary elements. It is clear that the cell volume (V) increases almost linearly with ionic radius (r) when A = alkali metals or $A = Cu^+, Pb^{2+}$ and Tl^+ , respectively. The slopes of the V vs. r lines are almost the same indicating that the major factor effecting the volume for a different class of ions is the size of the ternary element. It should be noted that the cell volumes of the alkali metal rhenium chalcogenides are larger than the volumes of other corresponding ternary rhenium chalcogenides with comparable A ionic radius; for example, $r_{K^+} < r_{Tl^+}$ but the volume of $K_4Re_6X_{12}$ is larger than that of $Tl_4Re_6X_{12}$ (Table 2). This may be attributed to the greater polarization by the Tl^+ ions compared to that of the K^+ ions, leading to more covalent $Tl-X$ bonds. This argument applies to Cu^+ and Pb^{2+} as well. Furthermore, the a cell parameter increases considerably with increasing effective ionic radii while the b and c dimensions change only a small amount (Table 2). In the case of $A_4Re_6Se_{12}$ ($A = K, Rb$, and Cs), b is constant. This may be ascribed to the fact that the Se_2 bridges are located along the a direction [1,2] and are expected to be more flexible than the Se bridges.

For the Ru-substituted phases, the cell volumes are nearly unchanged. Although the Ru ion is slightly smaller than Re ion, which might be expected to lead to some volume contraction, the extra electrons introduced by partial replacement of Re by Ru (presumably populating the conduction band, antibonding orbitals), will weaken the metal-metal bonding within clusters, leading to expansion of the unit cell. Thus, on the whole, the cell volume remains constant.

4.2. Valence Electron Counting

24 electrons per cluster unit corresponds to a filled valence band (magic number). Up to date, only two compounds have been considered to have VEC greater than 24 [11,21]. Although extended Huckel calculations [22] show that cluster dimers should be stable for 25 electrons per cluster, and that 26 electrons per cluster is favorable for one dimensional polymers, our efforts in attempting to condense thallium rhenium chalcogenides were not successful. It has been suggested on the basis of crystal structure determination that $\text{Mo}_{1.5}\text{Re}_{4.5}\text{Se}_8$ has a 24.5 electrons per cluster unit [11]. However, the semiconducting behavior [23] recently confirmed by photoelectrochemical experiments [24] does not support this assumption. $\alpha\text{-(TMTTF)}_2\text{Re}_6\text{Se}_5\text{Cl}_9$ (TMTTF = tetramethyltetrathiofulvalene) is another example where a VEC of 25 has been suggested [21]. However, this compound was prepared under non-equilibrium conditions (room temperature electrocrystallization).

In order to explain the electrical transport and magnetic properties of $\text{Tl}_4\text{Re}_{4.5}\text{Ru}_{1.5}\text{Se}_{12}$ (Figs. 4, 5), one should consider the following facts: binary ruthenium selenide RuSe_2 is semiconducting and there is no report on the existence of ternary ruthenium selenide. Thus, a mixture of RuSe_2 and $\text{Tl}_4\text{Re}_6\text{Se}_{12}$ should not result in metallic behavior; moreover, if there were small amounts of unreacted Ru in the bulk sample which might account for the metallic behavior, the

antiferromagnetic ordering observed of the sample, cannot be explained since Ru metal is weakly paramagnetic. Thus, there is strong evidence that Ru is incorporated in the lattice and that the VEC is greater than 24. A single crystal X-ray structural analysis of $Tl_4Re_{6-x}Ru_xSe_{12}$ would be helpful to resolve unambiguously the question of Ru substitution.

Acknowledgments

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Table 1. Three types of Known Ternary Rhenium Chalcogenides

$A_4/A_2[Re_6X_8]X_{6/2}$	$A_4[Re_6X_8]X_{4/2}(X_2)_{2/2}$	$A_4[Re_6X_8]X_{2/2}(X_2)_{4/2}$
$Li_4Re_6S_{11}$ $Sr_2Re_6S_{11}$ $Ba_2Re_6S_{11}$ $Eu_2Re_6S_{11}$	$Na_4Re_6S_{12}$ $K_4Re_6S_{12}$ $K_4Re_6Se_{12}$ $Rb_4Re_6Se_{12}$	$K_2Rb_2Re_6S_{13}$ $Rb_4Re_6S_{13}$ $Cs_4Re_6Se_{13}$ $Cs_4Re_6S_{9.45}Se_{3.55}$

* $Cs_4Re_6S_{13} = Cs_4[Re_6S_8]S_{2/2}(S_2)_{3/2}$

Table 2. Cell Constants of Some New $A_4^{II}/A_2^{II}ReO_3^{12}$ Phases

Compound	Prep. Method	a (Å)	b (Å)	c (Å)	β (°)	V (Å ³)	Remark
$Tl_4Re_6Se_{12}$	H.S.	17.205 (2)	9.865 (2)	12.206 (2)	90.72 (2)	2071.7 (4)	This work
$Na_4Re_6Se_{12}$	H.S.	16.424 (5)	9.864 (3)	11.823 (3)	91.67 (3)	1925.9 (9)	This work
$K_4Re_6Se_{12}$	H.S.	17.195 (8)	10.020 (7)	12.286 (5)	91.35 (5)	2116.3 (12)	This work
$K_4Re_6Se_{12}$	$K_2CO_3 + Re + Se$	17.167 (5)	10.029 (7)	12.293 (1)	91.37 (6)	2115.9 (11)	(11)
$Rb_4Re_6Se_{12}$	I.E.	17.509 (8)	10.020 (3)	12.352 (5)	90.67 (4)	2166.8 (10)	This work
$Rb_4Re_6Se_{12}$	$Rb_2CO_3 + Re + Se$	17.487 (8)	10.024 (1)	12.350 (1)	90.59 (6)	2164.7 (11)	(11)
$Cs_4Re_6Se_{12}$	I.E.	18.078 (7)	10.019 (3)	12.430 (6)	91.51 (4)	2250.5 (9)	This work
$Cu_4Re_6Se_{12}$	I.E.	17.141 (6)	9.857 (7)	10.288 (6)	90.41 (5)	1738.1 (10)	This work
$Pb_2Re_6Se_{12}$	I.E.	16.544 (7)	9.741 (4)	12.041 (8)	90.52 (5)	1940.4 (12)	This work
$Tl_4Re_6S_{12}$	H.S.	16.632 (2)	9.586 (1)	11.786 (2)	90.59 (1)	1879.0 (3)	This work
$Na_4Re_6S_{12}$	H.S.	15.843 (5)	9.576 (3)	11.492 (4)	92.46 (7)	1741.8 (7)	This work
$Na_4Re_6S_{12}$	$Na_2CO_3 + Re + H_2S$	15.830 (8)	9.582 (4)	11.816 (6)	91.13 (4)	1884.3 (1)	This work
$Rb_4Re_6S_{12}$	I.E.	16.829 (4)	9.745 (3)	11.948 (2)	91.08 (2)	1963.0 (5)	This work
$Pb_2Re_6S_{12}$	I.E.	15.845 (10)	9.602 (9)	11.527 (8)	92.19 (8)	1752.5 (15)	This work

Note: H.S. High temperature synthesis
I.E. Ion exchange method

Table 3. Relative Chemical-Shift of the Re
L₃-Absorption Edge in its Compounds

Absorber (Compound)	Formal Oxidation State	Relative Chemical-Shift ΔE (eV)*
Tl ₄ Re ₆ Se ₁₂	3 ⁺	-0.2
ReCl ₃	3 ⁺	0.0
Tl ₄ Re ₆ S ₁₂	3 ⁺	0.1
ReO ₂	4 ⁺	1.7

*Energy values are taken relative to ReO₂ (standard),
Re-L₃ peak position E=10526.2 eV.

Table 4. Relative Chemical-Shift of the Tl
L₃-Absorption Edge in its Compounds

Absorber (compound)	Formal Oxidation State	Relative Chemical-Shift ΔE (eV)*
Tl ₄ Re ₆ Se ₁₂	1 ⁺	-1.1
TlSe	1 ⁺	0.0
Tl ₂ O ₃	3 ⁺	8.8

*Energy values are taken relative to Tl₂O₃ (standard) Tl-L₃ edge
position E=12686.0 eV, where the edge position E refers to the
half absorption step maximum position.

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Figure Captions

Fig. 1. Temperature dependence of the resistivity for selected $A_4\text{Re}_6\text{X}_{12}$ phases:

(a) $\text{Tl}_4\text{Re}_6\text{Se}_{12}$ dashed line, $\text{Cs}_4\text{Re}_6\text{Se}_{12}$ solid line; (b) $\text{Tl}_4\text{Re}_6\text{S}_{12}$.

Fig. 2. Temperature variation of the magnetic susceptibility for $\text{Tl}_4\text{Re}_6\text{Se}_{12}$.

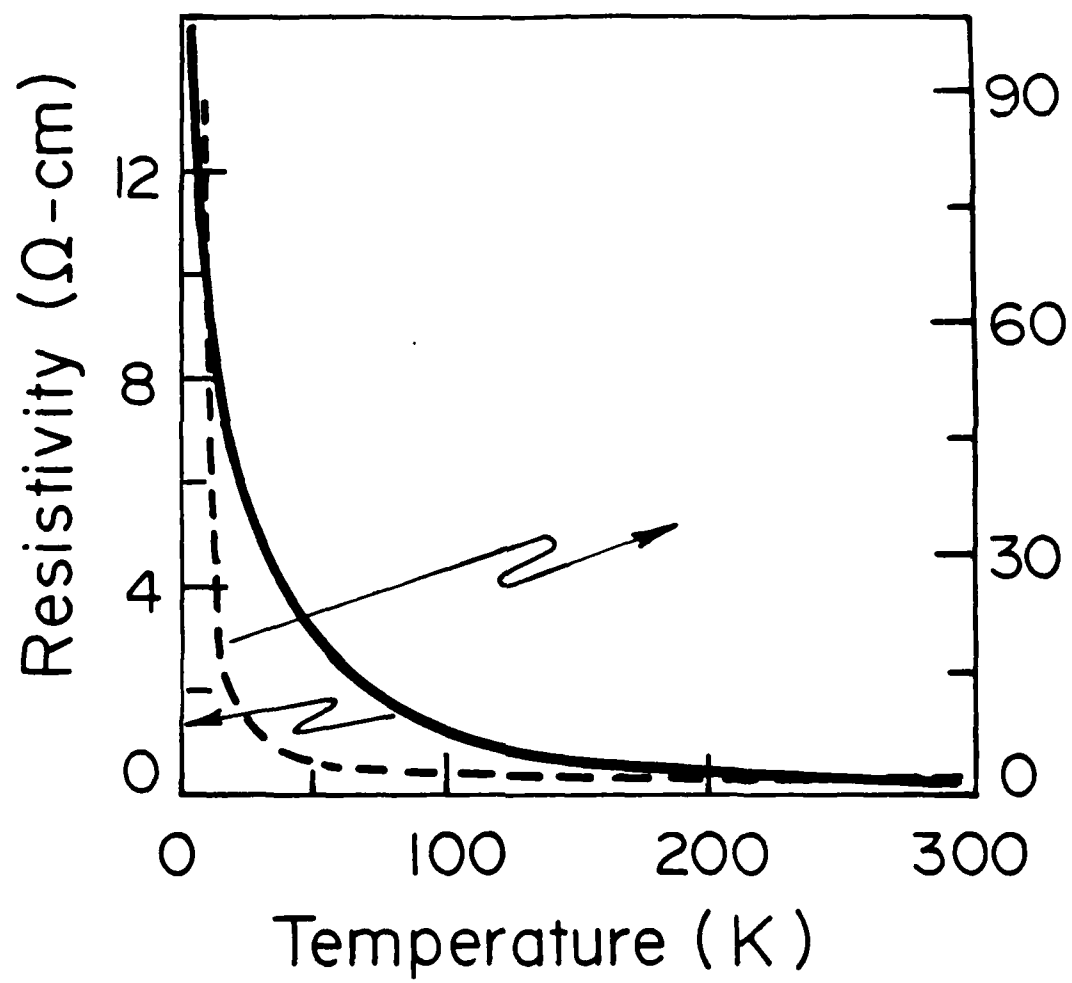
Fig. 3. Re- L_3 X-ray absorption spectra for selected Re compounds.

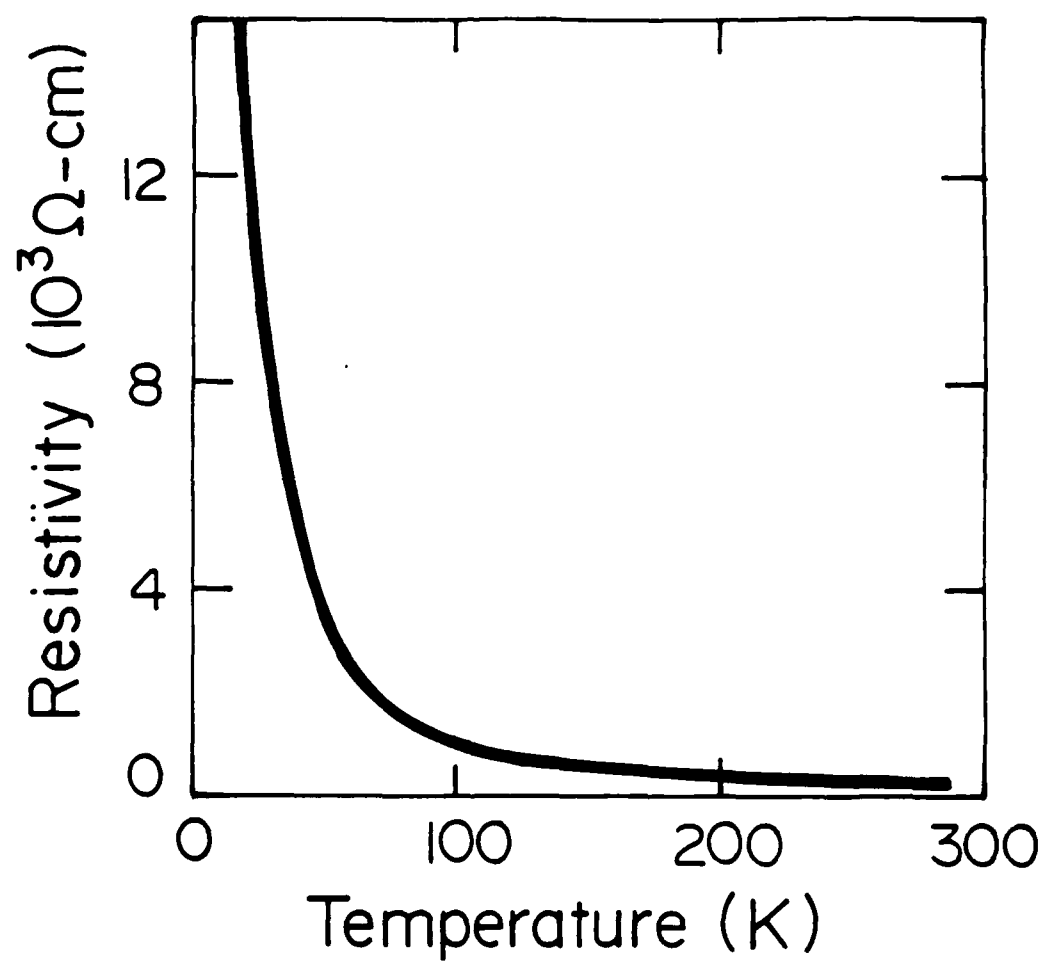
Fig. 4. Tl- L_3 X-ray absorption spectra for selected Tl compounds.

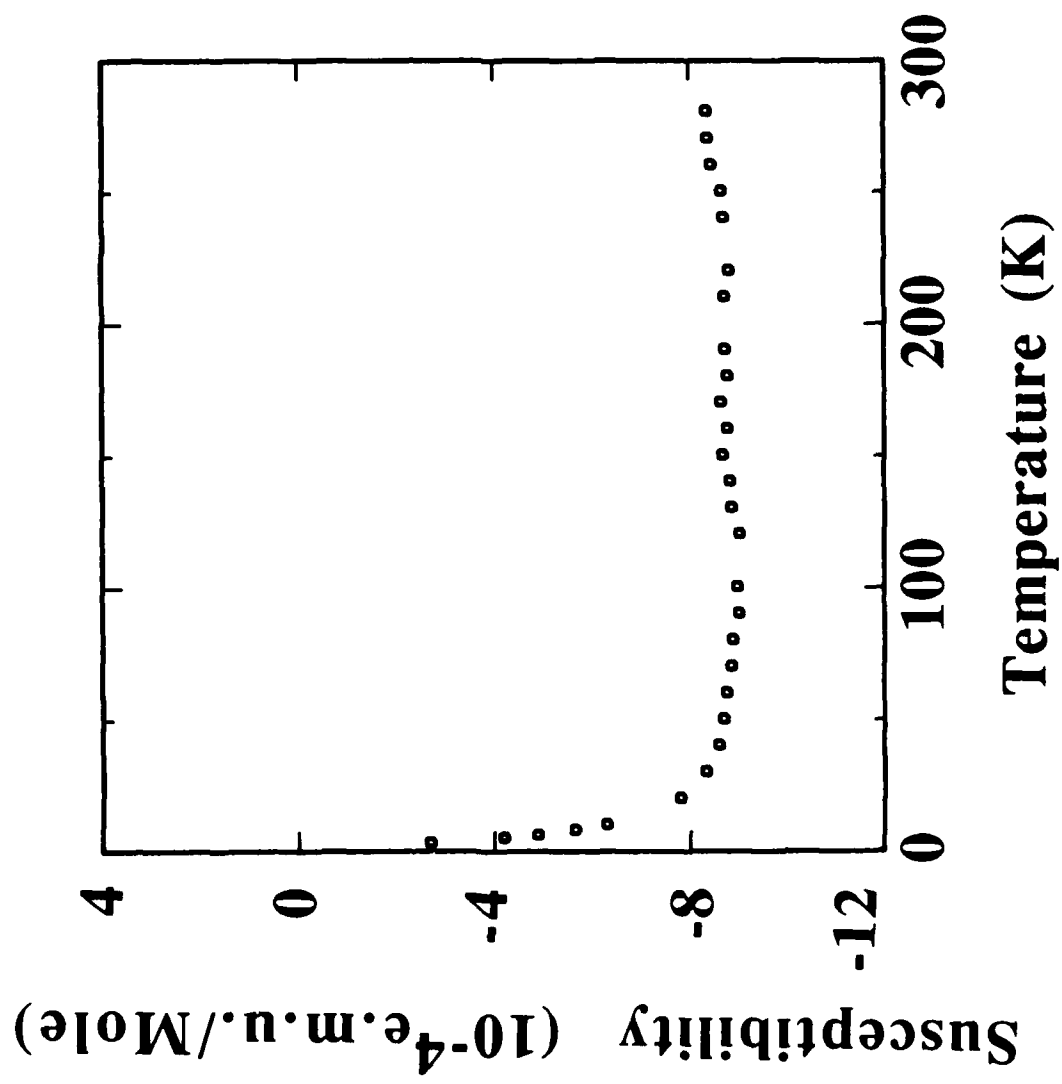
Fig. 5. Temperature dependence of the resistivity of $\text{Tl}_4\text{Re}_{6-x}\text{Ru}_x\text{Se}_{12}$ for $x=0.25$ and 1.50.

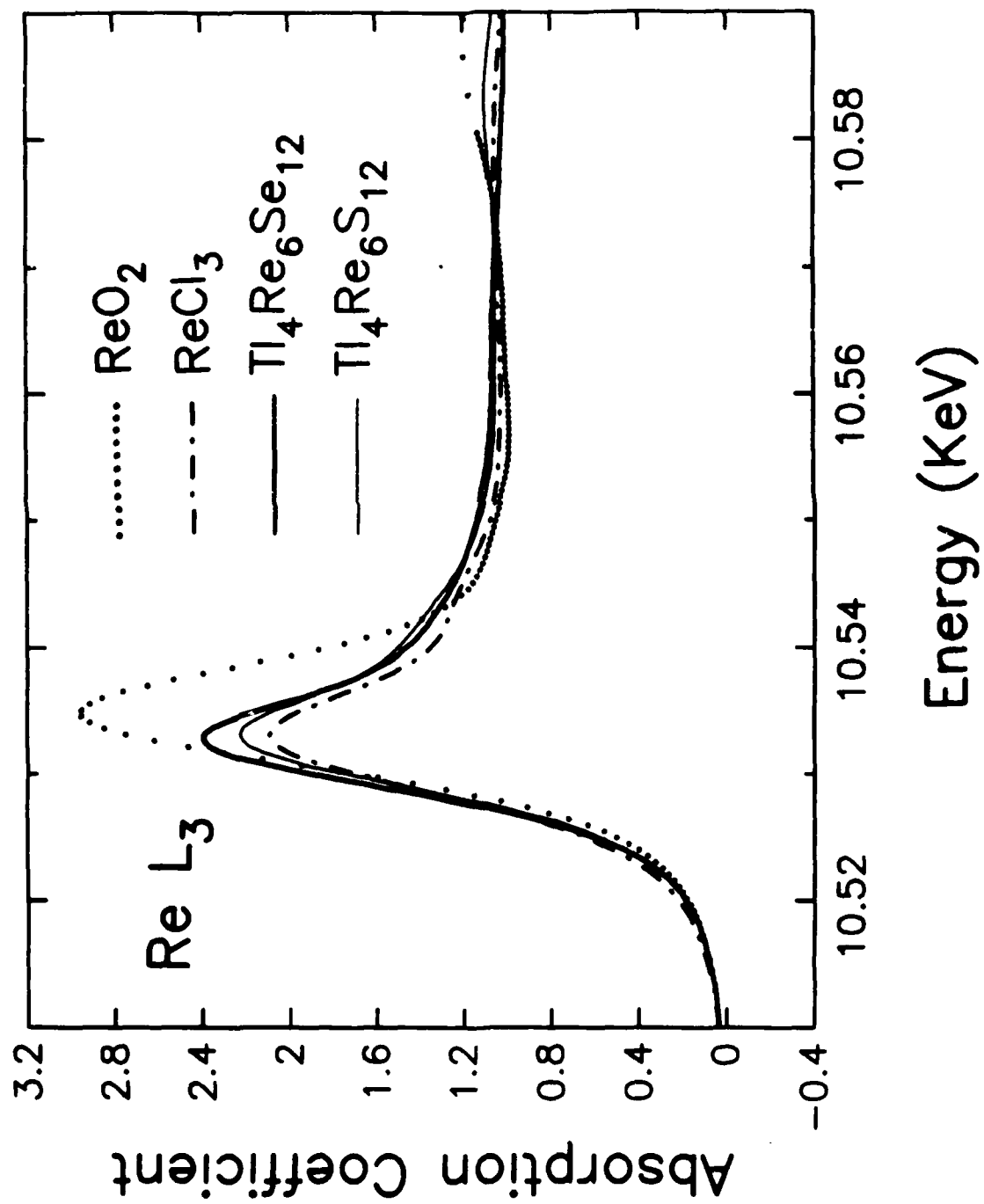
Fig. 6. Temperature dependence of the reciprocal of magnetic susceptibility for $\text{Tl}_4\text{Re}_{4.5}\text{Ru}_{1.5}\text{Se}_{12}$.

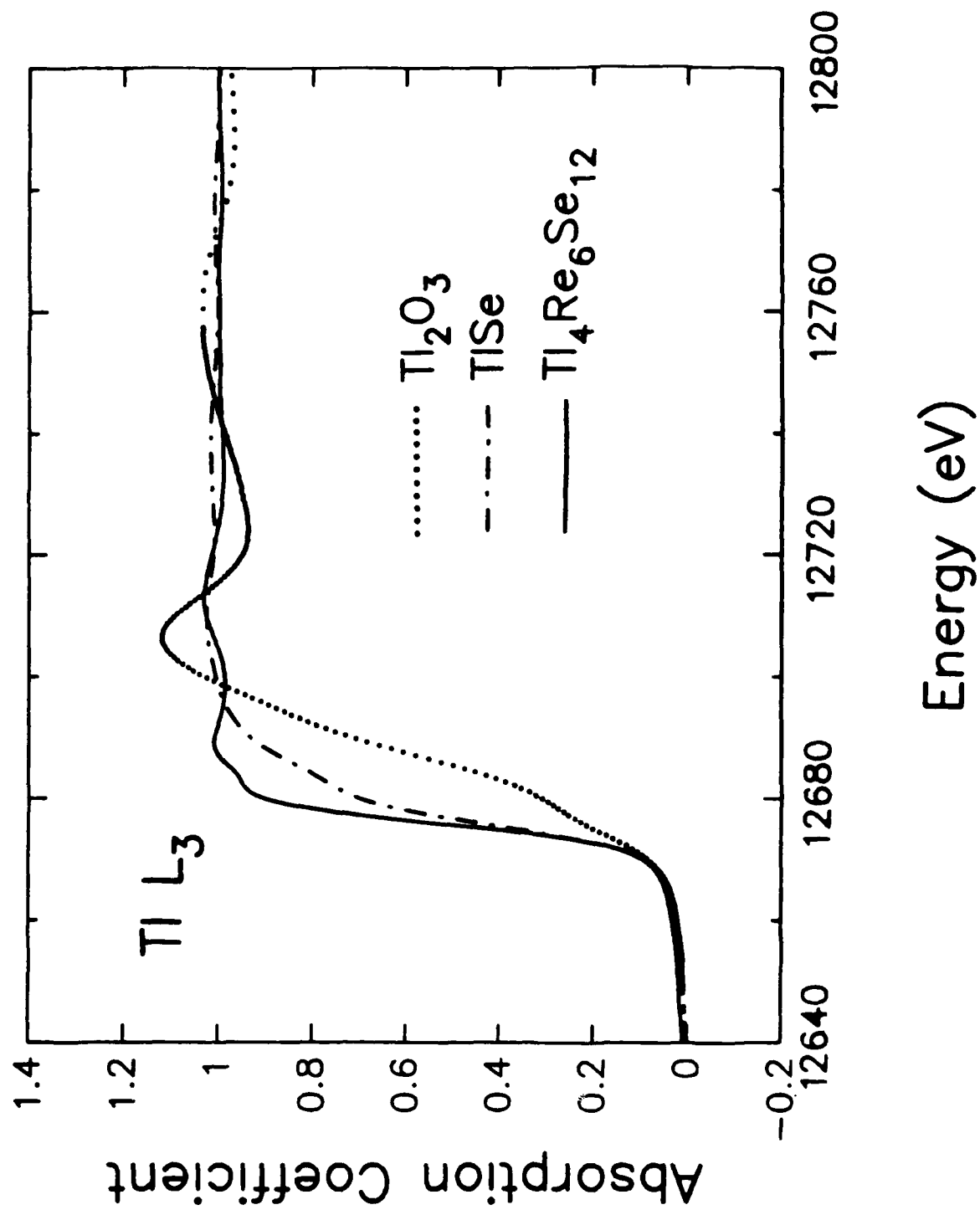
Fig. 7. Variation of cell volumes with effective ionic radii of the ternary elements.

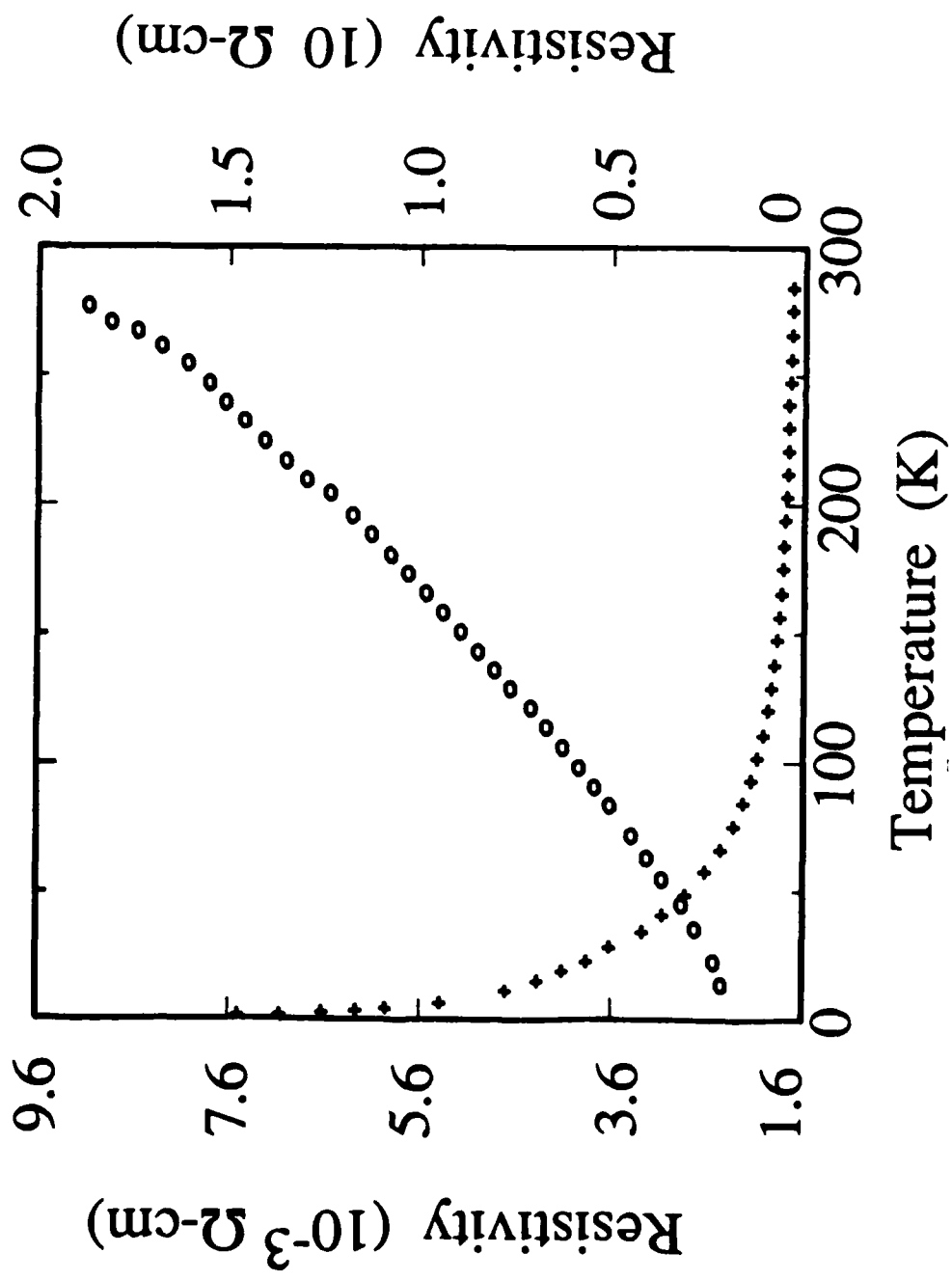


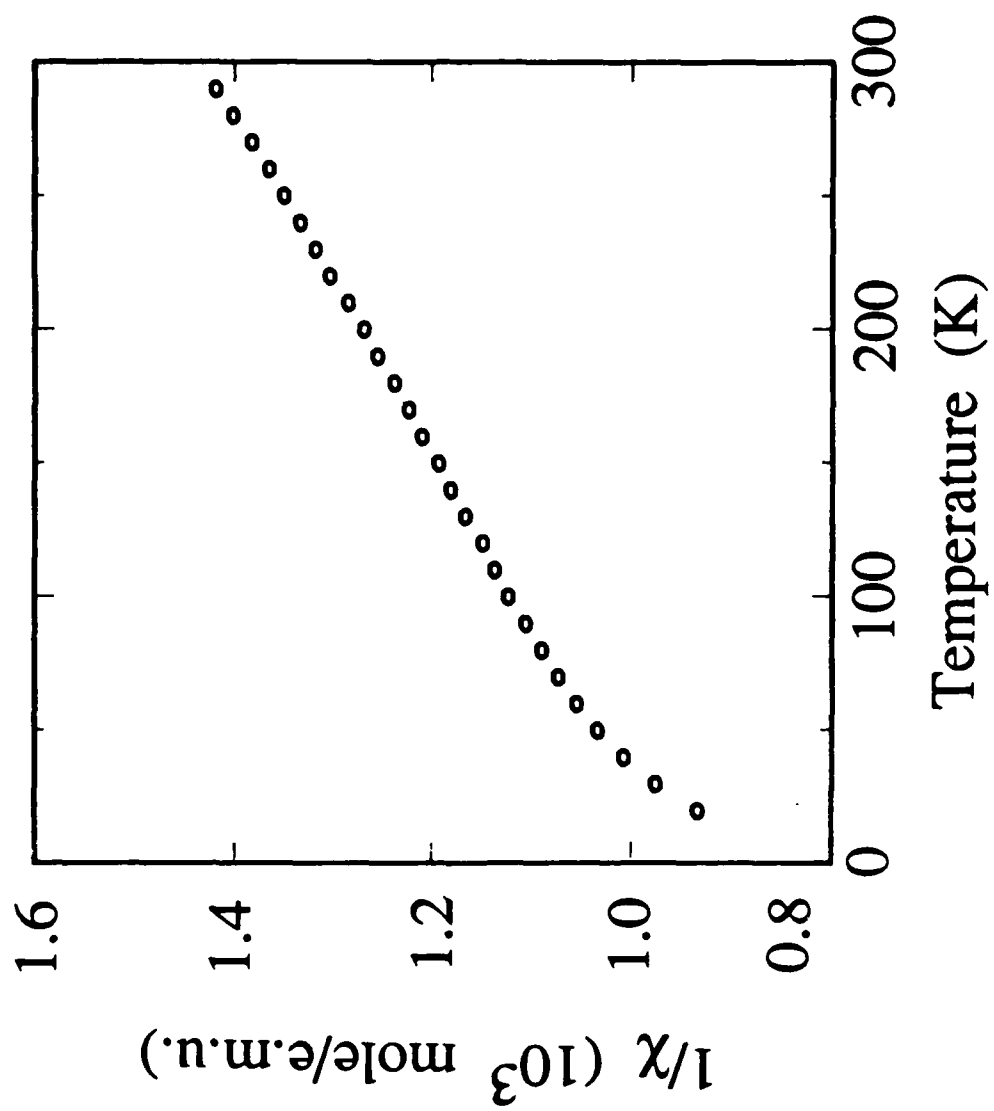


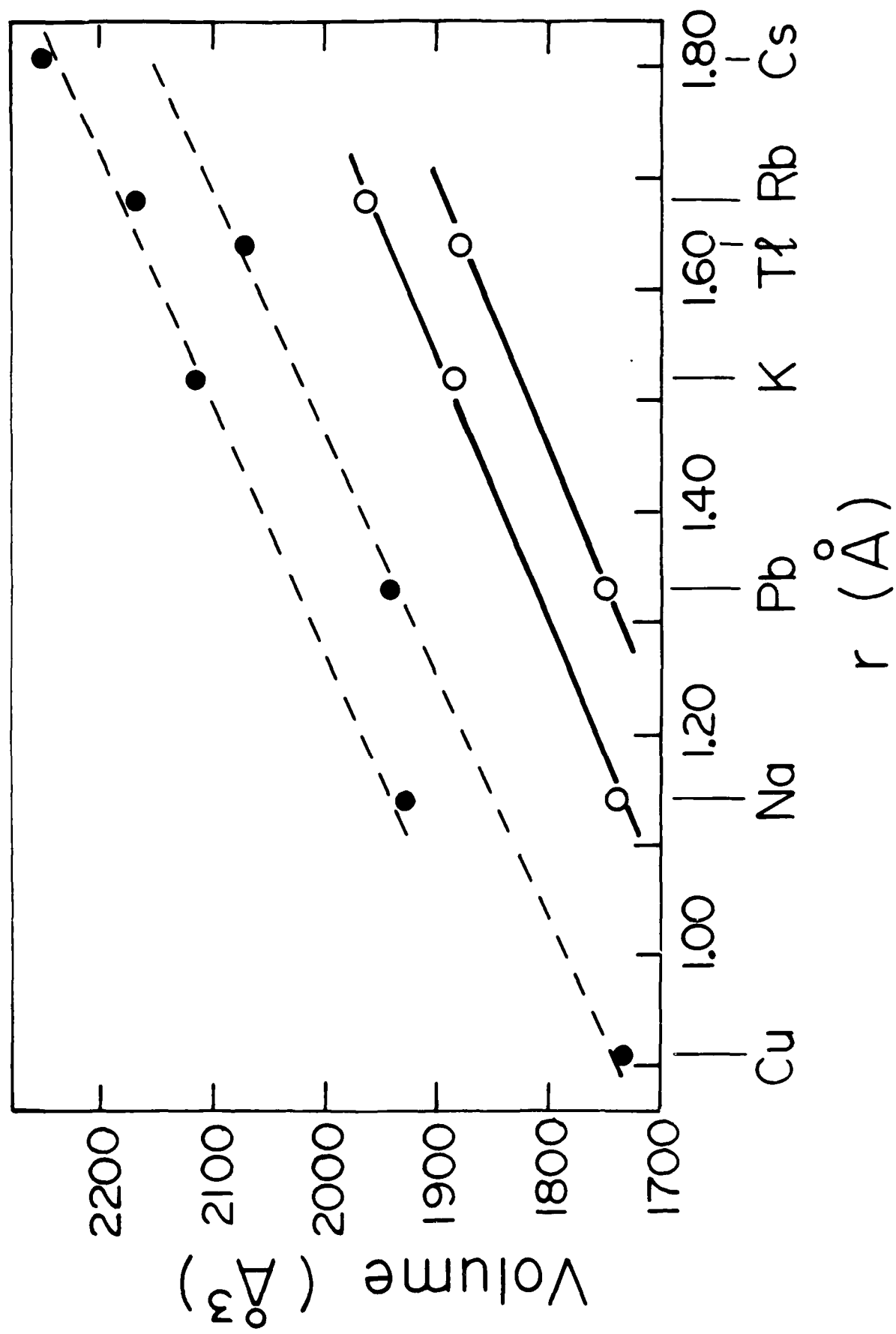












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