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Preparation and Properties of Some Ternary Selenides and Tellurides of Rhodium[1]

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The compounds MRh_2X_4 (M = Cr, Co, Ni; X = Se, Te) and Rh_3Te_4 have been prepared and found to have the monoclinic Cr_3S_4-type structure (space group I2/m) except for $CoRh_2Te_4$, and $NiRh_2Te_4$ which are trigonal (space group $P\bar{3}m1$). The symmetry of these compounds with defect NiAs structure depends upon whether the metal ion vacancies are ordered or randomly arranged in alternate metal layers. Electrical resistivity and Seebeck coefficient measurements reveal metallic behavior. This may arise from partially filled σ^* conduction bands formed as a result of interactions between the metal e_g and anion s,p_σ orbitals.

Introduction

The monoclinic defect NiAs structure (space group I2/m) was first proposed by Jellinek[2] for Cr_3S_4. This structure is intermediate between the NiAs ($B8_1$) and CdI_2 (C6) types. The idealized packing sequence of the cations and vacancies in this ordered structure with AB_2X_4 stoichiometry is shown in Figure 1. The transition metal cations, A and B, occupy three-fourths of the octahedral sites between the layers of hexagonal close-packed anions. The packing sequence is such that B^{3+} layers alternate with layers containing the A^{2+} cations and vacancies. It can be seen that ideally the A^{2+} cations are ordered with respect to the vacancies.

A large number of sulfides,[3-7] selenides,[5-9] and tellurides[10,11] of the type AB_2X_4 have since been reported to be isostructural with Cr_3S_4. Structural, electrical and magnetic properties have been investigated for many of these compounds. All these compounds with the monoclinic defect NiAs structure, however, contain only the first transition series metals Ti, V, Cr, Fe, Co, and Ni.

The present investigation was undertaken to determine whether the Cr_3S_4-type structure could also accommodate the second transition series metal, rhodium. Both the ionic radius of octahedrally coordinated Rh^{3+} and the stability of this oxidation state appeared to favor the existence of compounds such as $NiRh_2Se_4$ and $NiRh_2Te_4$. In addition to their preparation, the structural and electrical properties of these new compounds were also studied.

Experimental Section

Preparation.—Attempts were made to prepare the compositions MRh_2Se_4 (M = Cr, Fe, Co, Ni) and $M'Rh_2Te_4$ (M' = Ti, V, Cr, Fe, Co, Ni, Rh). High-temperature reactions of stoichiometric amounts of the high-purity elements were carried out in evacuated silica tubes. The sources of supply and purity of the starting materials were as follows: Fe, Co, Ni, Cr (all 99.99+%), Se, and Te (99.999%) were obtained from Gallard-Schlesinger Corp.; Ti (99.9%) was obtained from Metal Hydrides, Inc.; and Englehard supplied the Rh (99.9+%). The iron, cobalt, and nickel were freshly reduced prior to use. The reactants were heated at 600 and 800° for 3 days with intermediate grinding under dry nitrogen. When X-ray diffraction analysis indicated other than a single phase following this treatment, additional grindings of the products and firings at temperatures from 900 to 1000° were performed. All final products were studied by X-ray diffraction.

X-Ray Measurements.—Crystallographic parameters were determined on powder samples of the single-phase products using a Norelco diffractometer. Radiation was obtained from a high-intensity copper source (λ(Cu Kα_1) 1.5405 Å) and monochromatized with an AMR-202 focusing monochromator. Cell parameters were calculated and refined using an IBM 360 computer program of a modified Cohen's least-squares method.[12]

Chemical Analysis.—Each of the elements was determined for two of the single-phase tellurides, Rh_3Te_4 and $NiRh_2Te_4$. Samples weighing approximately 50 mg were dissolved by refluxing several hours with concentrated sulfuric acid, the only effective solvent. After the solution was made 2 *N* in hydrochloric acid in a total volume of 200 ml and heated to boiling, tellurium was quantitatively precipitated with sulfur dioxide and hydrazine, dried, and weighed according to standard techniques.[13,14] Rhodium was determined on aliquots of the filtrate by a spectrophotometric tin(II) chloride method,[15] employing a Bausch and

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TABLE I

ROOM-TEMPERATURE STRUCTURAL AND ELECTRICAL DATA

Compound	System	a (±0.005), Å	b (±0.005), Å	c (±0.005), Å	β (±0.05), deg	Electrical resistivity, ohm-cm	Seebeck coeff, μV/deg
$CrRh_2Se_4$	Monoclinic	6.278	3.612	11.25	92.47	1×10^{-3}	−16
$CoRh_2Se_4$	Monoclinic	6.269	3.644	10.81	92.15	...	...
$NiRh_2Se_4$	Monoclinic	6.280	3.648	10.82	92.22	5×10^{-4}	+0.4
$CrRh_2Te_4$	Monoclinic	6.841	3.951	11.40	91.61	1×10^{-3}	−5
Rh_3Te_4	Monoclinic	6.812	3.954	11.23	92.55	1×10^{-4}	−1.5
$CoRh_2Te_4$	Trigonal	3.953	...	5.429	...	...	...
$NiRh_2Te_4$	Trigonal	3.966	...	5.457	...	3×10^{-4}	−2

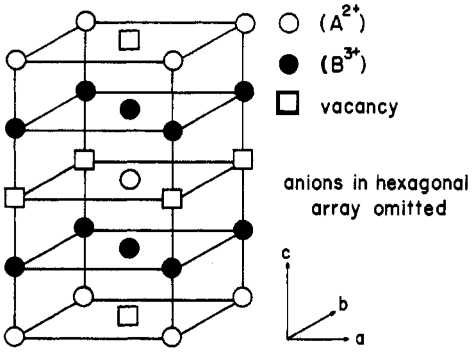

Figure 1.—The metal-packing sequence of the idealized monoclinic defect NiAs structure.

Lomb Spectronic 20 at 470 mμ. Nickel was determined gravimetrically on other portions of filtrate following precipitation with dimethylglyoxime.[16] *Anal.* Calcd for Rh_3Te_4: Rh, 37.69; Te, 62.31. Found: Rh, 37.7; Te, 62.1. Calcd for $NiRh_2Te_4$: Ni, 7.58; Rh, 26.56; Te, 65.86. Found: Ni, 8.0; Rh, 26.9; Te, 65.7.

The other single-phase chalcogenides were analyzed for one element. In all cases, stoichiometry close to the nominal AB_2X_4 was found, as expected, considering the method of preparation.

Electrical Measurements.—Electrical resistivity and Seebeck measurements were carried out on the compositions MRh_2X_4 (M = Cr, Ni; X = Se, Te) and Rh_3Te_4. Samples used in these measurements were pressed at 60,000 psi into bars approximately 0.8 × 0.15 × 0.15 in. and then sintered at 800° in evacuated silica tubes. The measured densities of these bars approached theoretical density. The average grain size was found to be approximately 0.01 mm.

Electrical resistivity as a function of temperature from 80 to 423°K was determined on these bars. A Keithley Model 503 milliohmmeter was used to measure resistance by a four-probe technique to eliminate contact resistance. Spring-loaded gold-plated copper rods were used as current probes, while the voltage probes used were spring-loaded gold-plated stainless steel needles spaced 0.85 cm apart. The shape of the resisitivity *vs.* temperature plot was reproducible from sample to sample with slight variation in the absolute resistivity values.

Seebeck measurements were carried out at room temperature using an ice bath as the cold junction. The values obtained were corrected for the thermal emf of the copper wires used as leads to the samples. This correction was taken to be +3.1 μV/deg at room temperature. In general, the Seebeck coefficients were reproducible from sample to sample.

Results and Discussion

Single-phase products were obtained for the seven compositions listed in Table I. Every reflection observed in their X-ray diffraction patterns could be indexed on the basis of the unit cell parameters given in the table. The other compositions studied ($FeRh_2Se_4$, $TiRh_2Te_4$, VRh_2Te_4, and $FeRh_2Te_4$) failed to yield single-phase products as determined by X-ray analysis. Variation of the preparation conditions did not lead to any improvement.

Each compound on which electrical measurements were carried out was found to exhibit metallic behavior, as indicated by its positive temperature coefficient of resistivity and low Seebeck value. Room-temperature Seebeck coefficients and electrical resistivities are given in Table I. Resistivity *vs.* temperature plots for the nickel compounds and Rh_3Te_4 are shown in Figure 2. Metallic behavior and similar plots were obtained for the chromium compounds.

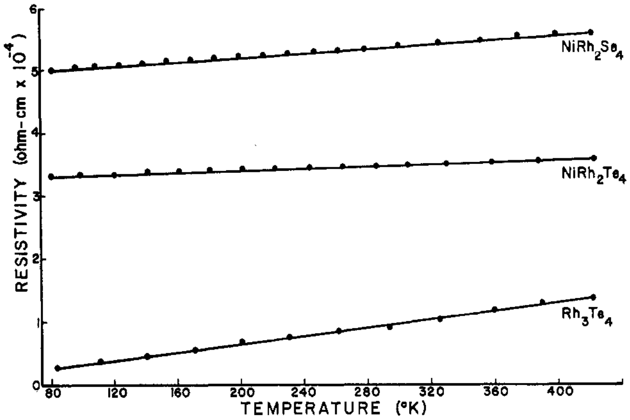

Figure 2.—Electrical resistivity *vs.* temperature for the compounds $NiRh_2Se_4$, $NiRh_2Te_4$, and Rh_3Te_4.

The symmetry of compounds of the general type AB_2X_4 with the defect NiAs structure depends on whether the cation vacancies are ordered or randomly arranged in alternate metal layers.[2,6] When the vacancies are ordered as in Figure 1, the hexagonal symmetry of the parent NiAs structure is lowered to monoclinic. However when the vacancies are randomly arranged in A^{2+} layers, trigonal symmetry results. The crystal class to which a given AB_2X_4 compound belongs is thus indicative of the vacancy arrangement in that compound.

For the five monoclinic compounds reported in Table I, all reflections observed in their X-ray diffraction patterns satisfy the condition $h + k + l = 2n$ (n = integer) for the monoclinic space group I2/m. The choice of I2/m was made to facilitate comparison with the hexagonal cell. These compounds are isostructural with Cr_3S_4, having the ordered vacancy arrangement. In

(16) K. Kodama, ref 14, p 264.

contrast, the compounds $CoRh_2Te_4$ and $NiRh_2Te_4$ are trigonal. The structure of $CoRh_2Te_4$ and $NiRh_2Te_4$ can be described[2] in both space groups $P\bar{3}m1$ and $P6_3/mmc$. The space group $P\bar{3}m1$, however, is the space group applicable here because the presence of all of the $00l$ reflections excludes $P6_3/mmc$. This trigonal structure indicates that the vacancies are randomly distributed in alternate metal layers. That $CoRh_2Se_4$ and $NiRh_2Se_4$ are monoclinic while $CoRh_2Te_4$ and $NiRh_2Te_4$ are trigonal may be compared with findings that Co_3Se_4 and Ni_3Se_4 are monoclinic[8,17,18] whereas Co_3Te_4 and Ni_3Te_4 are trigonal.[10,19–21] Likewise the monoclinic structures observed for $CrRh_2Se_4$ and $CrRh_2Te_4$ are consistent with reports that both Cr_3Se_4 and Cr_3Te_4 are monoclinic.[9,10] It is apparent that in chalcogenides of this type, both the size and d-electron configuration of the cations as well as the size and polarizability of the anion are of importance in determining the relative stability of the ordered *vs.* the random vacancy structure for a given composition.

The monoclinic compound Rh_3Te_4 is of particular interest. Geller[22] determined the crystal structure of RhTe and $RhTe_2$ but did not investigate intermediate compositions. RhTe is hexagonal with the NiAs ($B8_1$) type structure and lattice parameters $a = 3.99$, $c = 5.66$ Å. The high-temperature form of $RhTe_2$ is trigonal with the CdI_2 (C6) type structure and lattice parameters $a = 3.92$, $c = 5.41$ Å. (The low-temperature form of $RhTe_2$ has the cubic pyrite structure.) Geller did not study compositions between RhTe and $RhTe_2$ to determine whether the transformation from the $B8_1$ to the C6 structure with added tellurium is similar to the continuous transformation[21] of CoTe to $CoTe_2$, and no subsequent work appears to have dealt with this question. The present investigation has shown that in the rhodium–tellurium system at the composition Rh_3Te_4, ordering of the vacancies occurs with a consequent lowering of the symmetry to monoclinic. Other systems where the transformation between MX (NiAs type) and MX_2 (CdI_2 type) is discontinuous at the composition M_3X_4(Cr_3S_4 type) as a result of ordering of the vacancies are[23] Ti–Se and Ti–Te. The observation that Rh_3Te_4 and Co_3Te_4 have different vacancy arrangements indicates the influence of cation size in these structures.

Goodenough[24] has proposed a model to account for the electrical properties of ternary chalcogenides of the type AB_2X_4. This involves both direct interactions of cation t_{2g} orbitals and indirect cation e_g–anion s,p_σ interaction. The same model seems applicable to the rhodium chalcogenides. Here it is likely that octahedrally coordinated Rh^{3+} ($4d^4$) has the low-spin configuration $t_{2g}^4e_g^4$ as in the cubic spinel $CuCrRhSe_4$, where low-spin diamagnetic Rh^{3+} has been observed.[25] It is apparent that no contribution to the conductivity by either of the above mechanisms need be considered from Rh^{3+} with filled t_{2g} levels and empty e_g levels. This is not the case, however, for the M cations in the MRh_2X_4 compounds. For example, Ni^{2+} ($t_{2g}^4e_g^2$) may contribute to metallic conductivity *via* formation of partially filled σ^* bands as a result of nickel e_g–anion s,p_σ interactions. Similar considerations apply to the other rhodium chalcogenides. For the compounds $CrRh_2Se_4$ and $CrRh_2Te_4$, Cr^{2+} ($3d^4$) is assumed to have the high-spin configuration $t_{2g}^3e_g^1$ as for[4] Cr_3S_4. Magnetic susceptibility measurements of these compounds indicate deviations from the expected moments for ionic compounds having either purely high or low spin state for the transition metal ions. This is not unusual since there is considerable electron delocalization of the d electrons which is partially responsible for the metallic behavior of these compounds. For example, the expected moment for $CrRh_2Se_4$ assuming high-spin Cr^{2+} is 4.82 μ_B and for low-spin Cr^{2+} it is 2.82 μ_B; the observed value was 3.95 μ_B.

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