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Preparation and Properties of the System $Co_{1-x}Rh_xS_2$

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Members of the system $Co_{1-x}Rh_xS_2$ ($0 \le x \le 0.6$) were prepared, and their crystallographic and magnetic properties were studied. The observed ferromagnetic moments for compositions where $x \le 0.2$ indicate a ferromagnetic alignment between Co($3d^7$) and Rh($4d^7$) electrons. This is the first observation of localized behavior of 4d electrons in the pyrite structure. For larger concentrations of rhodium, there is a reduction in the observed moment which can be attributed to a lack of magnetic homogeneity in these samples with the possible formation of rhodium clusters. The paramagnetic data are consistent with the results obtained in the ferromagnetic region.

Introduction

In recent years, numerous studies have reported the effect of anion, and cation substitution on the electrical and magnetic properties of CoS_2.[1-7] This compound crystallizes in the cubic pyrite structure (space group *P*3*a*) and exhibits the property of metallic ferromagnetism which may be attributed to a partially filled σ^* band.[8-10] The observed ferromagnetic moment has been reported to be 10% lower than the calculated value. The reduced moment has been attributed[5] to an overlap of the spin-up and spin-down bands below the Fermi level.

Recent studies have shown that the disulfides of Fe($3d^6$) and Ni($3d^8$) crystallize with the pyrite structure. In addition, these disulfides can form solid solutions with CoS_2. The cation-substituted system $Co_xFe_{1-x}S_2$ exhibits ferromagnetic behavior for $x \ge 0.05$.[5] The ferromagnetic moment is proportional to the cobalt concentration over the range $0 \le x \le 0.95$; at larger values of x, the moment is reduced as was observed for pure CoS_2. Members of the system $Co_{1-x}Ni_xS_2$ where $x > 0.1$ showed antiferromagnetic behavior, although no well-defined Néel temperature could be observed.[5]

No magnetic studies have been made on compounds where platinum metals have been substituted for cobalt in CoS_2. The possibility of Co($3d^7$) and Rh($4d^7$) orbital interaction and the effect of this interaction on the magnetic properties of CoS_2 have motivated this study. In addition, it is known that RhS_2 does not exist,[11] and therefore the extent to which rhodium ($4d^7$) can be stabilized in the pyrite structure is of interest.

Experimental Section

Preparation of Materials. Polycrystalline samples of the system $Co_{1-x}Rh_xS_2$ ($0 \le x \le 0.6$) were synthesized either by direct combination of the elements in sealed evacuated silica tubes or by heating stoichiometric quantities of pentaamminechlorocobalt(III) chloride and ammonium hexachlororhodate(III) with hydrogen sulfide.

Direct Combination of the Elements. Pretreatment of the starting materials was carried out as follows: The high-purity metals (Co 99.999% (Leico Inc.) and Rh 99.999% (Engelhard Inc.)) were reduced in a 15% H_2/85% Ar atmosphere (Co at 650 °C for 4 h, ground, further reduced at 850 °C for 8 h; Rh for 8 h at 800 °C). Freshly sublimed sulfur was used.

Stoichiometric quantities of the elements were ground thoroughly and transferred to a silica tube. To this mixture were added an additional 10% by weight of excess sulfur and approximately 0.01 g of iodine, and the tube was sealed after evacuation. Each sample was heated slowly to 400 °C, maintained at this temperature for 12 h, and then raised gradually to 800 °C. Once each week, the sample was extracted with CS_2 and then with CCl_4 to remove the excess sulfur and iodine, respectively. After approximately 5 weeks of heating at 800 °C, single-phase products were obtained.

Synthesis of $Co_{1-x}Rh_xS_2$ by the Precursor Method. Stoichiometric quantities of $(NH_4)_3RhCl_6$ (Engelhard Inc. 99.999%) and $[Co(NH_3)_5Cl]Cl_2$[12] were dissolved in 10 mL of 0.10 M NH_4OH by warming with constant stirring to 85 °C. When complete solution was achieved, the solvent was evaporated by means of an infrared lamp. The product was ground thoroughly and transferred into a flow-bed reactor (Figure 1) in which sulfurization took place. The system was purged at a flow rate of 55 cm^3/min with nitrogen for 1 h. The mixture was then treated with hydrogen sulfide for 10 min at room temperature and then the temperature was raised slowly to 350 °C and maintained at this temperature for 4 h. After sulfurization, the product was extracted with hot methanol in order to remove the white crystals of NH_4Cl which were formed. The material was then extracted with CS_2 to remove any sulfur which may have formed. The product was dried under vacuum.

The products obtained after the extractions with methanol and carbon disulfide were annealed with 10% by weight excess sulfur and approximately 0.01 g of iodine in evacuated sealed silica tubes at 800 °C. The temperature was raised from room temperature to 800 °C over a period of 2 days. Samples were held at 800 °C for 4 days and then cooled slowly to room temperature. The samples were extracted with CS_2 and CCl_4, ground, resealed in evacuated silica tubes as before, and rereacted under the same conditions. The process was repeated in order to ensure homogeneity and reaction completeness.

Sample Characterization

X-ray Diffraction. Powder diffraction patterns were obtained with a Norelco diffractometer using monochromatic high-intensity Cu Kα_1 radiation ($\lambda = 1.5405$ Å). Fast scans at 1°[2θ]/min were examined for the possible presence of extraneous phases. Slow scans of 0.25°[2θ]/min were obtained for all single-phase samples in the range of $12° \le 2\theta \le 120°$. Lattice parameters for the well-crystallized materials were determined by least-squares analysis using 2θ values from 26 to 105°. For members of the system $Co_{1-x}Rh_xS_2$ ($0 \le x \le 0.6$), the patterns showed a single-phase product which could be indexed on the basis of a cubic pyrite structure (space group *P*3*a*). Powder patterns of the composition $x > 0.6$ indicate the presence of a second phase which could be indexed as Rh_2S_3.[13]

Magnetic Measurements. Magnetic measurements were made with a PAR FM-1 vibrating-sample magnetometer

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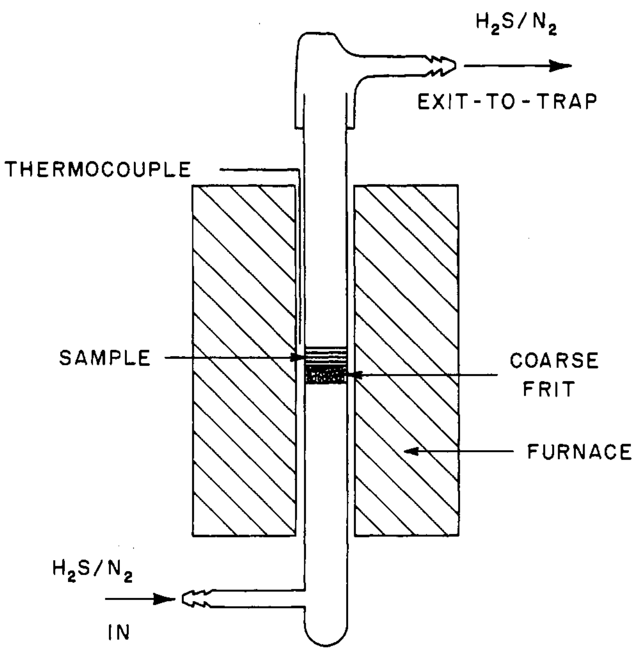

Figure 1. Flow-bed reactor for the preparation of members of the system $Co_{1-x}Rh_xS_2$.

(Princeton Applied Research Co.) in conjunction with a variable-temperature control Dewar which is described elsewhere.[3] Field-dependent measurements were made with fields up to 8 kOe with a 9-in. Varian magnet (V3400) (Varian Associates). The magnetometer was calibrated relative to a cylinder of high-purity nickel single crystal obtained from Material Research Corp. Nickel has temperature-dependent values of magnetic moment of 58.57 emu/g at absolute zero, 58.2 emu/g at 77.3 K, and 55.8 emu/g at 293 K,[14] which were the values used for the calibration. Temperature-dependent magnetization plots were taken with the use of a solid-state temperature controller (type MPRY Thermac Controller, R.I. Controls) to program the temperature at a desired rate from 4.2 to 300 K. The temperature was measured with a 0.005-in. Teflon-coated Au + 0.07% Fe vs. Chromel-P thermocouple (Sigmund Cohn). The thermocouple was located on the outside of the sample chamber and within 6.5 mm of the sample.

In addition, magnetic susceptibility measurements were made from 77 to 540 K with a Faraday balance described elsewhere.[15] Measurements were performed at field strengths between 6.22 and 10.40 kOe. The balance was calibrated with platinum wire ($\chi_g = 0.991 \times 10^{-6}$ emu/g at 275 K). So that it could be ensured that there was no loss of sulfur upon heating, each sample was encapsulated in a silica bubble under vacuum. So that these measurements could be supplemented, susceptibilities were also calculated from magnetometer measurements made in the range of 4.2–77 K.

Results and Discussion

Results on Preparation. Two methods have been used for the preparation of members of the system $Co_{1-x}Rh_xS_2$. Direct reaction of stoichiometric mixtures of cobalt, rhodium, and sulfur in sealed evacuated tubes gave products which were similar in properties to those obtained by the sulfurization of a mixture of $(NH_4)_3RhCl_6$ and $[Co(NH_3)_5Cl]Cl_2$.

CoS_2 crystallizes in the cubic pyrite structure (space group *Pa3*). A value of 5.538 (2) Å was obtained for the cell parameter which compares well with values in the literature of 5.534[16] and 5.536 Å.[17] The system $Co_{1-x}Rh_xS_2$ was reported by Hulliger[11] to have a pyrite structure for $0 \leq x \leq 0.7$. In this study, both direct combination of the elements and sulfurization of stoichiometric mixtures of $[Co(NH_3)_5Cl]Cl_2$ and $(NH_4)_3RhCl_6$ yielded single-phase materials for $x \leq 0.6$. X-ray diffraction patterns of all products could be interpreted on the basis of a cubic unit cell. Figure 2 shows the variation of the cell constant a_0 for the system as a function of composition. For values greater than $x = 0.6$, the orthorhombic phase Rh_2S_3 (space group *Pbcn*[13]) can be detected as an impurity. This is consistent with the findings of Hulliger,[11] where attempts to synthesize RhS_2 always gave Rh_2S_3 as well as other sulfur-deficient phases.

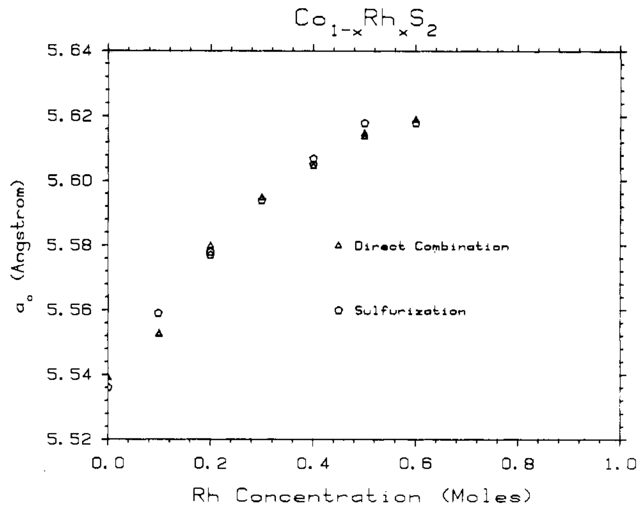

Figure 2. Variation in the cell parameter a_0 with increasing Rh substitution.

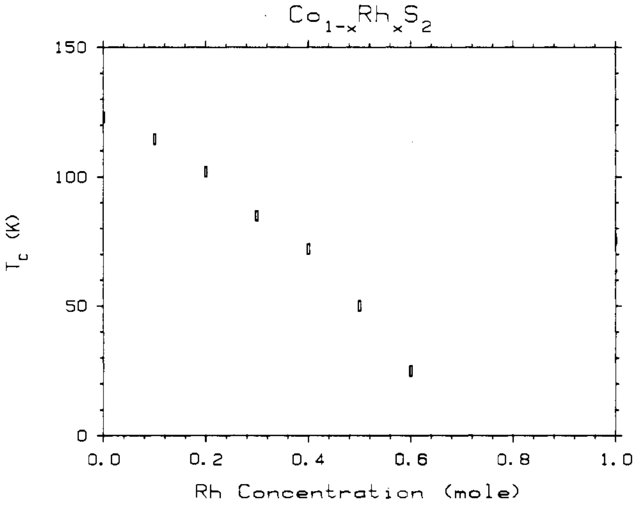

Figure 3. Variation in T_C with increasing Rh substitution.

Thermogravimetric analyses of the compositions $Co_{0.8}Rh_{0.2}S_2$ and $Co_{0.5}Rh_{0.5}S_2$ gave sulfur to total metal ratios of 2.05 (1) and 2.07 (1), respectively. These results indicate that the samples are not sulfur deficient and that the behavior of the lattice parameter shown in Figure 2 is not caused by deviations in stoichiometry.

Ferromagnetic Region. CoS_2 is a well-known ferromagnetic material with a well-defined Curie point (T_C). A value of 123 K was measured for T_C which compares well with values in the literature of 124,[18] 130,[19] and 122 K.[20]

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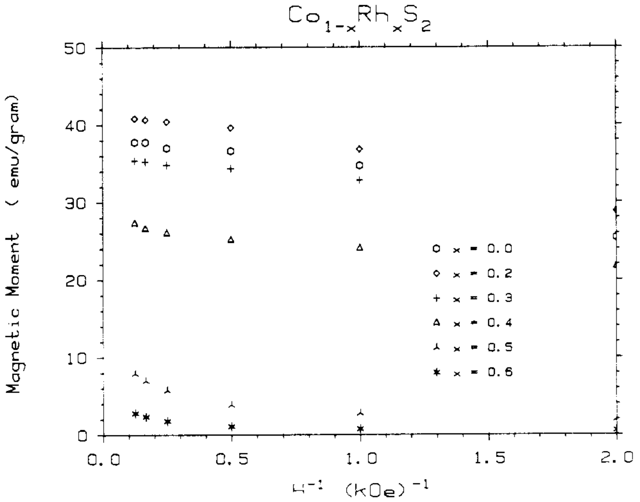

Figure 4. Magnetic moment vs. inverse field for members of the system $Co_{1-x}Rh_xS_2$ ($x \leq 0.6$).

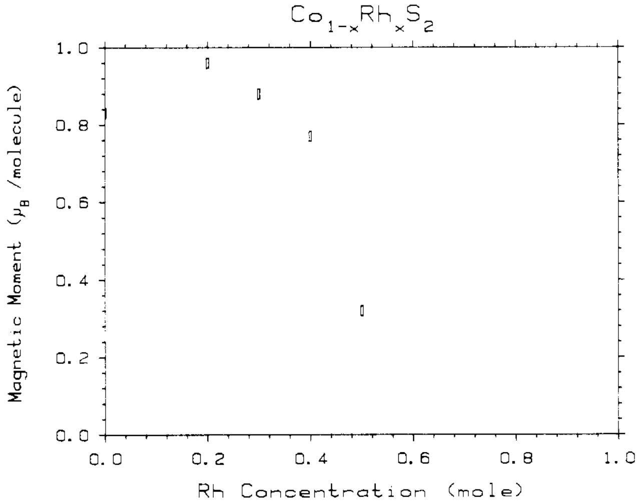

Figure 5. Magnetic moment with increasing Rh substitution.

The observed Curie point for CoS_2 is depressed from 123 K for CoS_2 to 25 K for $Co_{0.4}Rh_{0.6}S_2$; the monotonic decrease for the system $Co_{1-x}Rh_xS_2$ is shown in Figure 3. This decrease in T_C is what is anticipated for a gradual decrease in the strength of the ferromagnetic interactions.

The field dependence at 4.2 K was determined for samples of the system $Co_{1-x}Rh_xS_2$; the values of magnetization vs. reciprocal field are plotted in Figure 4. Samples with compositions greater than $x = 0.3$ did not saturate by 8 kOe, and extrapolation to zero inverse field was necessary in order to estimate the saturation magnetization.

A ferromagnetic moment of 0.83 μ_B was obtained for CoS_2, which is in good agreement with values in the literature.[18,19] The reduced moment observed for CoS_2 has been discussed in terms of partial overlap of the spin-up and spin-down bands.[8-10] The ferromagnetic moment vs. rhodium concentration is plotted in Figure 5. It was observed for members of the $Co_{1-x}Rh_xS_2$ system that the ferromagnetic moment reaches a maximum of 0.96 μ_B/molecule at $x = 0.2$ and then decreases with increasing rhodium content. This maximum moment is larger than the value of 0.8 μ_B obtained for the end member CoS_2, which suggests that there is a ferromagnetic interaction between the Co($3d^7$) and Rh($4d^7$) electrons and a smaller degree of occupancy of the σ^* band.

For $x = 0.5$, a moment of 0.32 μ_B/molecule was measured. This moment is smaller than the value of 0.5 μ_B expected if only cobalt atoms contribute to the moment at the equivalent of one unpaired electron per atom. This large reduction in moment, for large rhodium concentration, can be attributed to a lack of magnetic homogeneity in these samples with the possible formation of rhodium clusters. Formation of such clusters would also tend to reduce the lattice parameters through the formation of metal–metal bonds.

Table I. Paramagnetic Properties of $Co_{1-x}Rh_xS_2$

sample	C_M obsd	μ_{eff}, μ_B/molecule	Θ, K
CoS_2	0.37	1.72 (±0.02)	150 ± 10
$Co_{0.9}Rh_{0.1}S_2$	0.43	1.85 (±0.02)	140 ± 10
$Co_{0.8}Rh_{0.2}S_2$	0.44	1.88 (±0.02)	120 ± 10
$Co_{0.7}Rh_{0.3}S_2$	0.58	2.15 (±0.02)	100 ± 10
$Co_{0.6}Rh_{0.4}S_2$	0.42	1.83 (±0.02)	90 ± 10
$Co_{0.5}Rh_{0.5}S_2$	0.29	1.52 (±0.02)	75 ± 10
$Co_{0.4}Rh_{0.6}S_2$	0.20	1.26 (±0.02)	60 ± 10

Paramagnetic Region. A summary of the paramagnetic data is given in Table I. At room temperature, negligible field dependence of the susceptibility was observed. The data was corrected for the diamagnetic contributions of the silica bucket and for the core electrons of cobalt, rhodium, and sulfur. The following core electron diamagnetic correction factors were used:[21] Co^{2+}, 12×10^{-6}; Rh^{3+}, 22×10^{-6}; S^{2-}, 40×10^{-6} emu/mol.

The data obeyed Curie–Weiss behavior at temperatures above 300 K. A least-squares fit of points between 300 and 500 K was used to obtain the molar Curie constant (C_M) from which the paramagnetic moment (μ_{eff}) can be calculated. As can be seen in Table I, μ_{eff} for CoS_2 is 1.72 μ_B/molecule, which is consistent with the spin-only moment for one unpaired electron. As rhodium is substituted for cobalt in CoS_2, μ_{eff} increases to 2.15 μ_B/molecule for the composition $Co_{0.7}Rh_{0.3}S_2$. Orbital contribution of Rh($4d^7$) may account for this high moment. As the concentration of rhodium is increased above $x = 0.3$, the paramagnetic moment decreases and at $x = 0.5$ drops significantly below the spin-only value expected from the combined contributions of cobalt and rhodium. However, the net amount remains greater than could be obtained from the cobalt contribution alone. The large decrease in the moment at high rhodium concentrations is consistent with magnetic inhomogeneity and the possible formation of rhodium clusters. It can also be seen from Table I that the Weiss constant (Θ) decreases almost linearly with increasing rhodium substitution, in agreement with the observed decrease of the Curie temperature determined from the ferromagnetic data.

Conclusion

Synthesis of members of the system $Co_{1-x}Rh_xS_2$ by direct combination of the elements gave materials whose properties were similar to those obtained by the sulfurization of stoichiometric quantities of $(NH_4)_3RhCl_6$ and $[Co(NH_3)_5Cl]Cl_2$. The crystallographic and magnetic properties of the $Co_{1-x}Rh_xS_2$ system behave differently from those observed for the systems $Co_{1-x}Fe_xS_2$ and $Co_{1-x}Ni_xS_2$.[5] Up to 60% rhodium can be stabilized in CoS_2 as opposed to complete solid solutions for the iron and nickel systems.

Both the Curie temperature and the Weiss constant decrease monotonically with increasing rhodium substitution. This can be attributed to a decrease in the efficiency of the ferromagnetic interactions initially present in CoS_2. The behavior of the ferromagnetic moment at low rhodium concentrations is in agreement with cobalt ($3d^7$)–rhodium ($4d^7$) ferromagnetic interactions. This is the first observation of localized behavior of 4d electrons in the pyrite structure. The large reduction in moment at large rhodium concentration can be attributed

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to a lack of magnetic homogeneity in these samples with the possible formation of rhodium–rhodium clusters. The paramagnetic data further supports the possibility of formation of rhodium–rhodium clusters at large rhodium concentrations.

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Registry No. CoS_2, 12013-10-4; RhS_2, 12038-73-2; $(NH_4)_3RhCl_6$, 15336-18-2; $[Co(NH_3)_5Cl]Cl_2$, 13859-51-3.

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A Second Infinite-Chain Form of Zirconium Diiodide (β) and Its Coherent Intergrowth with α-Zirconium Diiodide

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Syntheses of the previously reported monoclinic (α) ZrI_2 contain a second orthorhombic (β) phase which is isostructural with WTe_2, space group $Pmn2_1$ (No. 31) with $a = 3.7442$ (5) Å, $b = 6.831$ (1) Å, and $c = 14.886$ (2) Å and $Z = 4$. Refinement with 768 unique reflections measured on an automatic diffractometer with monochromatic Mo Kα radiation gave $R = 0.051$ and $R_w = 0.070$. β-ZrI_2 contains sheets in which infinite zigzag chains of zirconium ($d_{Zr-Zr} = 3.185$ (3) Å) lie between puckered iodine layers. The structure is very similar to that reported for α-ZrI_2 and differs principally in shear displacements of adjacent layers. The two phases evidently always intergrow with one another in various proportions, a property which accounts for apparent "superlattice" reflections and for a powder pattern of the "phase" which is much more complex than expected. Both structures may be derived from that in the lattice-equivalent supergroup $Pmnb$ (No. 62) by shear displacements of the layers in second-order phase transitions. A residual electron density which apparently originates in the intergrowth or defect regions of the β-ZrI_2 crystals may imply a substoichiometry, in support of bulk analyses of Zr:I $\simeq$ 1.05:2.

Introduction

Among the zirconium halides with oxidation states below +3 only the cluster phases Zr_6X_{12} are common to chloride, bromide, and iodide;[2-4] otherwise the iodides appear to be quite distinctive. A polymorph of the cluster diiodide Zr_6I_{12} has recently been reported in monoclinic α-ZrI_2 which as the layered β-$MoTe_2$ structure.[5] This may be described as a distortion of a CdI_2-like arrangement in which zirconium atoms have been systematically displaced from the centers of octahedral (trigonal antiprismatic) interstices so as to form infinite zigzag chains of strongly bonded metal atoms ($d = 3.182$ Å) between pairs of iodine layers. A comparable phase has not been found with chloride and bromide; rather these form a sheet structure with $ZrCl_2$ (3R-MoS_2-type), substoichiometric superstructures for $Zr_{1+x}Cl_2$, and a probably related bromide.[6] In addition both the chloride and bromide form a double-metal-layered monohalide with close-packed sheets sequenced X–Zr–Zr–X.[7,8] The equivalent iodide phase has not yet been obtained in spite of extensive investigation.

Continuing studies of the lower iodides have been plagued by a number of complications encountered with the diiodide, namely, (1) Guinier powder patterns for "α-ZrI_2" which are inevitably much more complex than that calculated for the known structure, even for patterns taken of ground "single" crystals, (2) evidence of possible superstructure reflections in Weissenberg photographs of α-ZrI_2, and (3) some analytical evidence for substoichiometry (I:Zr $\approx$ 1.90 $\pm$ 0.05:1) in polycrystalline samples,[9] although no indication of this was found in the reported α-ZrI_2 structure. Most of these problems have now been clarified with the identification of a second orthorhombic form of the layered ZrI_2 structure (β) which shows extensive intergrowth with the monoclinic α form.

Experimental Section

The methods of handling these materials and the synthetic techniques utilized have already been described.[5] Crystals from which the structure of α-ZrI_2 was solved were formed from long-term reactions of ZrI_4 with a large excess of Zr in welded tantalum containers at ca. 750–850 °C which were then cooled by turning off the power to the furnace. Black, lath- to blade-shaped crystals which exhibit a gold reflectance form, presumably via a transport reaction which involves a ZrI_3(g) intermediate. Occasionally crystals were found in earlier studies which were apparently orthorhombic either from indexing on the automatic diffractometer or according to Weissenberg photographs or from both, and these exhibited unit cell axes closely resembling those of the monoclinic α (where $\beta = 95.7°$).

Diffraction data were collected on three different orthorhombic crystals, two of which came from high-temperature reactions at 900–950 °C and gave broad peaks and considerable streaking. The structure of these two, though evidently basically the same as reported herein, would not define below $R \approx 0.20$ because of apparent disorder. A much more suitable crystal came from a relatively low-temperature reaction of a 44:1 mole ratio of Zr strips and ZrI_4 for about 8 weeks at 770 °C. A rectangular prism ~0.74 × 0.081 × 0.056 mm was sealed into a 0.2-mm diameter capillary within the drybox and examined by oscillation and Weissenberg photographic techniques. Diffraction peaks were measured at room temperature in the HKL, $H\bar{K}l$, $\bar{H}KL$, and $\bar{H}\bar{K}L$ octants within the range $2° < 2\theta < 50°$ for a cell ~6.83 × 14.88 × 3.74 Å with the aid of an automated, four-circle diffractometer and monochromatic Mo Kα radiation. Three standards lying approximately out the three reciprocal axes showed

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