ter. Line positions were obtained by averaging the results of four scans.

Computations were performed on the IBM/50H computer at the University of Bergen. The graphical output was obtained on a Calcomp Plotter.

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On the Phases Cr_2As, Fe_2As, Co_2As, and Rh_2As

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Despite numerous studies on the metal rich pnictides and chalcogenides of the transition elements there is a general lack of detailed information concerning their chemical and physical properties. The present paper concerns the composition, range of homogeneity, and magnetic properties for the phases Cr_2As, Fe_2As, Co_2As, and Rh_2As (*cf.* Refs. 1 – 22).

Experimental. Samples were prepared from 99.999+ % As (Johnson, Matthey & Co.), 99.999 % Cr (Koch-Light Lab.), 99.9+ % Fe (Riedel-DeHaën AC.), 99.7 % Co (Baker Chemical Co.), and 99.99+ % Rh (Johnson, Matthey & Co.) by heating weighed quantities of the components in evacuated, sealed silica tubes at temperatures between 400 and 900°C for 4 days. (The iron and cobalt powders were obtained by hydrogen reduction (600°C) of their oxides.) The sintered powders were ground and reannealed at temperatures between 500 and 900°C for 4 – 15 day periods and, finally, quenched in iced water.

X-Ray powder photographs of all samples were taken in a Guinier type camera of 80 mm diameter with monochromatized $CuK\alpha_1$-radiation using KCl as internal standard. The lattice dimensions were refined by applying the method of least squares to the diffraction data and the indicated error limits correspond to the standard deviations.

Magnetic susceptibilities were measured between 80 and 1000 K by the Faraday method (maximum field ~8 kØ) using 10 – 100 mg samples.

Results. The compositions of the Cr_2As, Fe_2As, Co_2As, and Rh_2As phases, which have no appreciable ranges of homogeneity, were determined by applying the disappearing phase principle to Guinier photographs of samples with different nominal compositions. The results showed the phases to be stoichiometric according to the general formula T_2X ($T_{2.00\pm0.05}X$). The unit cell dimensions listed in Table 1, are reasonably consistent with those reported in the literature.[2–4,7,11,12,15,17,22]

The magnetic properties of Cr_2As and Fe_2As are well established through earlier magnetic susceptibility, magnetization, and neutron diffraction studies.[5,10,13,14,16–19] The thermomagnetic data for Cr_2As and Fe_2As obtained during the present investigation are consistent with the previous studies, and are accordingly not included here. No magnetic studies have hitherto been reported for Co_2As and Rh_2As.

The temperature dependence of the reciprocal magnetic susceptibility for Co_2As is shown in Fig. 1. The experimental data refer to a single sample, but measurements

Table 1. Unit cell dimensions (at room temperature) for Cr_2As, Fe_2As, Co_2As, and Rh_2As.

Phase	*a* (Å)	*b* (Å)	*c* (Å)	*c*/*a*
Cr_2As	3.618(1)		6.350(1)	1.7551(7)
Fe_2As	3.632(1)		5.981(1)	1.6468(8)
Co_2As	5.990(2)		3.581(2)	0.5978(6)
α-Rh_2As	5.6765(3)			
β-Rh_2As	5.910(2)	3.917(1)	7.367(1)	

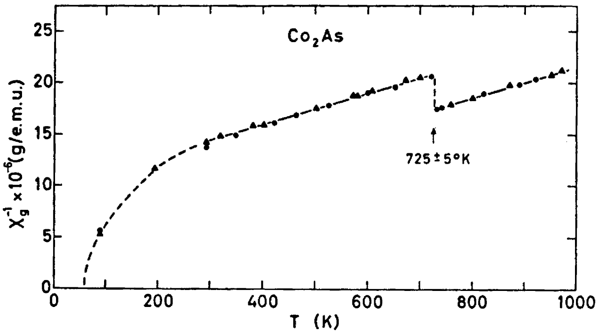

Fig. 1. Reciprocal of the magnetic susceptibility of α- and β-Co_2As as function of increasing (▲) and decreasing (●) temperature.

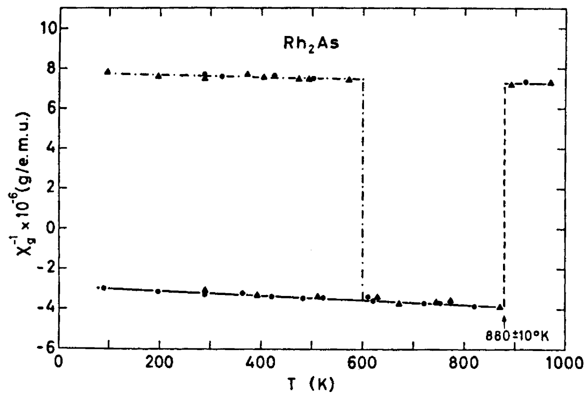

Fig. 2. Reciprocal of the magnetic susceptibility of α- and β-Rh_2As as function of increasing (▲) and decreasing (●) temperature. The analytical expressions for $\chi(T)$ are:

α-Rh_2As: $\chi \times 10^6 = -0.348 + 0.000101T$; 90 K$<T<$880 K.

β-Rh_2As: $\chi \times 10^6 = 0.1285 + 0.000010T$; 90 K$<T<\sim$600 K and $T>$880 K.

repeated on other samples confirm the reproducibility of the curve. Above $\sim$60 K Co_2As is in a paramagnetic state, and the $\chi^{-1}(T)$-curve satisfies the Curie-Weiss Law ($\chi^{-1} = C^{-1}(T-\theta)$) for $T > \sim 300$ K. At 725±5 K there is a hysteresis-less discontinuity in $\chi^{-1}(T)$. Although Heyding and Calvert [7] report that Co_2As exists in two modifications, they did not establish the transition temperature properly. They give 490 − 502°C as the range for the transition on heating and 388 − 402°C on cooling, implying that the phase change is associated with an appreciable hysteresis. Neither of these temperature intervals coincide with the discontinuity in the $\chi^{-1}(T)$-curve which defines 725 ± 5 K as the transformation temperature for α-$Co_2As \rightarrow$ β-Co_2As. (The temperature of the discontinuity is independent on whether the measurements are performed by heating or cooling the samples.) The reversible nature of the transition is consistent with a close similarity in atomic arrangement of the two modifications as proposed by Heyding and Calvert.[7] Support for this suggestion is provided by the inability to obtain high enough quenching rates to isolate even trace amounts of β-Co_2As at room temperature.

The slope of the $\chi^{-1}(T)$-curve yields a paramagnetic moment $\mu_P = \sqrt{8C_{mol}} =$ 2.26 ± 0.06 B.M/Co-atom for α-Co_2As and $\mu_P = 2.24 \pm 0.06$ B.M./Co-atom for β-Co_2As. This corresponds to the spin quantum number $2S_{Co} = 1.47 \pm 0.05$ and $2S_{Co} =$ 1.45 ± 0.05 for α- and β-Co_2As, respectively, according to the "spin-only" approximation ($\mu = 2\sqrt{S(S+1)}$). Hence, within the experimental error, the two modifications have the same number of unpaired electrons per metal atom. Extrapolation of the linear sections to $\chi^{-1} = 0$ gives θ-values of − 680 ± 50 and − 430 ± 50 K for α- and β-Co_2As, respectively. The shape of the $\chi^{-1}(T)$-curve resembles a parabola below ~ 300 K, strongly suggesting a paramagnetic → ferrimagnetic transition at ~ 60 K. This implies that the magnetic ordering in Co_2As cannot be of the simple antiferromagnetic type as found in Cr_2As and Fe_2As.[5,10,13,14,16–19] A low temperature neutron diffraction study of Co_2As is in progress.

Magnetic susceptibility measurements of Rh_2As were made on samples slowly cooled or quenched from 900°C. The results (Fig. 2) exhibit excellent reproducibility and consistency between the two kinds of heat treated samples. The quenched samples contain the high temperature modification, β-Rh_2As, as the single phase which is seen to exhibit a nearly temperature independent paramagnetism. Fig. 2 demonstrates that β-Rh_2As can be maintained in a metastable state below ~ 600 K. At this temperature the atomic mobilities become large enough to facilitate the transition from β- to α-Rh_2As. The magnetic susceptibility of α-Rh_2As remains negative (*viz.* diamagnetism) after a further slow temperature cycling and has an approximately constant value below 880 ± 10 K. Similar results were obtained for α-Rh_2As from the slowly cooled samples.

On the basis of Fig. 2, the reversible transition between the two modifications of Rh_2As occurs at 880 ± 10 K. Quesnel and Heyding[12] give 650 − 700°C as the transformation temperature.

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