Structural and Magnetic Properties of CoAs

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The CoAs phase has been investigated by X-ray and neutron diffraction, density, magnetic susceptibility, and diffuse reflectance measurements. CoAs adopts the stoichiometric 1:1 composition without any appreciable range of homogeneity. The crystal structure of CoAs (as determined at room temperature from three-dimensional single crystal X-ray data) is essentially of the MnP type. Compared with the symmetry hitherto assumed for the MnP type, the structure of CoAs lacks a mirror plane. The least squares refined Guinier photographic data gave the following unit cell dimensions: $a = 5.2867(11)$ Å, $b = 5.8682(14)$ Å, $c = 3.4892(8)$ Å. (Standard deviations are appended in brackets.) The unit cell contains 4Co and 4As in position 4(a) of space group $Pna2_1$ with $x = 0.0023(10)$, $y = 0.2000(5)$, $z = 1/4$ for Co and $x = 0.1996(7)$, $y = 0.5869(3)$, $z = 0.2716(22)$ for As. Both kinds of atoms exhibit anisotropic thermal vibrations at room temperature. The crystal structure remains essentially unchanged between room and liquid helium temperatures with approximately constant values for the x and y parameters. CoAs shows no evidence of magnetic ordering at liquid helium temperature. The temperature dependence of the magnetic susceptibility of CoAs exhibits a Curie-Weiss Law relationship above 490°K, with $\theta = -230 \pm 40$°K and $\mu_P = 1.15 \pm 0.05$ B.M./Co atom. An anomalous temperature variation of the magnetic susceptibility below 490°K is suggested as being due to a temperature dependent population of two different spin states.

Fylking[1] reported some 35 years ago that CoAs and a number of other transition metal mono-pnictides are isostructural with MnP; the latter structure being nowadays recognized as the prototype for this class of compounds. His powder X-ray diffraction data and the associated unit cell dimensions and positional parameters clearly support the assertion that the structure of CoAs is of the regular MnP type (neglecting a space group ambiguity, *vide infra*). However, more recently Ventriglia[2] has maintained that CoAs takes an idealized MnP type structure, *viz.* fixed positional parameters for the atoms which concur with those of the NiAs type structure in the ortho-hexagonal setting, while no such limitation is imposed on the axial proportions. This possible, but nevertheless improbable special position of CoAs in the relationship between the NiAs and MnP type structures called

for a definitive redetermination by a single crystal technique and the use of modern computing and correction methods.

A further reason for a thorough reexamination of the crystal structure of CoAs stems from the fact that the (formally) MnP type structure of FeAs is shown to lack the mirror plane characteristic of the space group *Pnma* currently assumed for the prototype structure.[3] Clearly, this space group ambiguity, *i.e.* *Pna2₁* versus *Pnma* (b and c interchanged), cannot be eliminated on the basis of systematic extinctions in diffraction data.

Magnetic data for CoAs are almost completely lacking in the literature (*cf.* Ref. 4). In view of the interesting magnetic properties recently found for the isostructural compound CrAs,[5,6] the scope of the present study also includes this aspect of CoAs.

EXPERIMENTAL

Materials. The pure elements used in this study were 99.99 + % Co (Johnson, Matthey & Co., Ltd.; turnings from rods) and 99.999 + % As (Fluka AG).

Preparations. Polycrystalline samples for the powder X-ray and neutron diffraction, density, and magnetic susceptibility measurements were prepared by heating weighed quantities of the components in evacuated and sealed silica tubes at 850°C for 10 days. After careful grinding, the samples were reannealed at 850°C for another 10 days and finally cooled to room temperature over a period of 3 days. Several samples with different initial compositions were prepared, on both sides of the 1:1 stoichiometric ratio.

Single crystals of CoAs were formed by chemical transport reactions, using iodine (~ 1 mg/ml capsule volume) as the transport agent. A good yield of suitable crystals was obtained by applying a temperature gradient of ~1.5°C/mm along a ~ 200 mm long (evacuated and sealed) silica capsule, with the hot end containing powdered CoAs at 850°C. These conditions produced a considerable number of crystals at the cold end of the capsule after 7 days.

X-Ray diffraction. All samples were crushed, and X-ray powder photographs were taken in a Guinier type camera of 80 mm diameter with monochromatized CuKα₁-radiation ($\lambda = 1.54050$ Å) using KCl ($a = 6.2919$ Å[7]) as internal standard.

Single crystal X-ray photographs were taken in an integrating Weissenberg camera of 57.3 mm diameter with Zr-filtered MoKα-radiation using the multiple-film technique. Three-dimensional data consisting of 419 independent reflections (of which 102 had zero intensity) were collected from the layers 0kl to 4kl and their intensities were measured microphotometrically except for the weakest reflections which were estimated visually by comparison with a standard scale. The intensities were corrected for the combined Lorentz and polarization factors, and for absorption (the crystal shape being approximately spherical with $\mu R = 2.7$) and secondary extinction. (No correction for dispersion was carried out.)

Neutron diffraction. Powder neutron diffraction data were collected at liquid helium, liquid nitrogen, and room temperatures, using cylindrical sample holders of aluminium or vanadium. Neutrons of wavelength 1.863 Å were obtained from the reactor JEEP II. The integrated intensities from the neutron diffraction diagrams were converted to $jF_o{}^2$ by multiplication with L^{-1}.

Computations. The computational work on the X-ray data, including least squares refinements of the unit cell dimensions, corrections, data reductions, scalings, and full matrix least squares refinements of the structure factors, and calculations of interatomic distances and angles, was performed on a CDC 3300 computer using in most cases the programmes devised by Dahl *et al.*[8]

The atomic scattering factors used in the calculations of F_c-values were taken from Hanson *et al.*[9] The extent of the agreement between the observed and calculated structure factor data is judged from the average and weighted reliability factors:

$$R = \sum ||F_o| - |F_c|| / \sum |F_o|$$
$$R^* = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{\frac{1}{2}}$$

where w denotes the weight factor. The unobserved reflections are not included in the calculations of R and R^*, and are omitted from the least squares refinements. (The observed and calculated structure factor data are available from the authors upon request).

The nuclear scattering lengths ($b_{Co} = 0.25 \times 10^{-12}$ cm, $b_{As} = 0.64 \times 10^{-12}$ cm) were taken from the table published by *The Neutron Diffraction Commission*.[10] A least squares profile refinement programme written by Rietveld[11] was applied in the final fitting of the variable crystallographic parameters to the observed intensity data.

Throughout this paper the calculated standard deviations are given in parentheses after the corresponding parameter values, only the last digit (or the two last digits) being presented.

The magnetic susceptibilities of stoichiometric CoAs samples were measured between 90 and 900°K by the Faraday method (maximum field ~ 8000 Ø) using $50-60$ mg samples.

Diffuse reflectance measurements were made in the range $2\,400-20\,000$ Å in a Cary 14 dual-beam spectrophotometer with diffuse reflectance accessory, using $MgCO_3$ as a standard. The integrating sphere was coated with MgO.

Density measurements were carried out pycnometrically at 25.00°C with kerosene as displacement liquid. To remove gases adsorbed by the sample (weighing ~ 2 g), the pycnometer was filled with kerosene under vacuum.

RESULTS AND DISCUSSION

(i) *Homogeneity range, composition, and unit cell dimensions.* The unit cell dimensions of the CoAs phase, as determined from Guinier photographs taken at room temperature, were found to be constant within experimental error for samples with different initial proportions. This finding immediately suggested that the CoAs phase has no appreciable range of homogeneity, and this was confirmed by application of the disappearing phase principle to Guinier photographs of samples with different nominal composition. The composition estimated according to the latter technique is $CoAs_{1.00 \pm 0.02}$ with the uncertainty in the determination indicated by the limits of error. The formula CoAs was also confirmed by comparing the pycnometrically measured density ($d_{pycn.} = 8.17$ g cm^{-3}) with that calculated from the unit cell dimensions and a cell content of 4 CoAs-groups ($Z_c = 3.98$).

Least squares refinements of the Guinier photographic data gave: $a = 5.2867(11)$ Å, $b = 5.8682(14)$ Å, $c = 3.4892(8)$ Å for the orthorhombic unit cell of CoAs at room temperature (using a setting based on space group $Pna2_1$, *vide infra*) in close agreement with the corresponding values: $a = 5.2850(16)$ Å, $b = 5.8699(7)$ Å, $c = 3.4923(8)$ Å determined from the neutron diffraction data. The present results are reasonably consistent with those reported by Fylking[1] and Heyding and Calvert.[12]

(ii) *Space group and refinement of the structure.* The systematic extinctions in the diffraction data are of the type $0kl$ absent when $k+l = 2n+1$ and $h0l$ absent when $h = 2n+1$ implying that the possible space groups are limited to $Pna2_1$ and $Pnma$ (cf. the introduction).

A three-dimensional Fourier synthesis based on the positional parameters reported by Ventriglia[2] demonstrated unequivocally that his proposal is inconsistent with the present experimental data and gave, on the other hand, shifts towards the positional parameters found by Fylking.[1] The latter set of parameters was accordingly chosen as input for the subsequent least squares refinements. A determination of possible deviations of the CoAs structure from the symmetry of space group $Pnma$ requires that the calculations must

be performed in terms of a description based on the alternative space group $Pna2_1$. According to the latter space group both kinds of atom reside in position $4(a)$ x,y,z; $\bar{x},\bar{y},\frac{1}{2}+z$; $\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}+z$; $\frac{1}{2}+x,\frac{1}{2}-y,z$. Since only the difference between the z-parameters of Co and As is a relevant parameter in this problem, that of Co is equated to $1/4$ in the refinements of the positional and thermal parameters. (The choice $z_{Co}=1/4$ conveniently allows direct comparison of the two space groups.)

Analogous refinement models to those tried for the isostructural compound FeAs[3] were considered, including the possibility of anisotropic as well as isotropic thermal motion of the atoms. In the cases where anisotropic temperature factors were allowed, the first refinement cycles were performed according to the complete expression

$$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)].$$

However, as in the case of FeAs, the calculations showed that the parameters β_{ij} with $i \neq j$ were almost identical zero and considerably smaller than the corresponding standard deviations for both kinds of atom. The restriction $\beta_{12} = \beta_{13} = \beta_{23} = 0$, which fixes the principle axes of the vibration ellipsoids to coincide with the crystallographic axes, was therefore introduced in the final calculations. The least squares refinements of the structure factor data were continued until no shifts were produced in all variables of each model.

Using the Hamilton[13] test in judgements between the various models it was found that our unrestrained model specified by the following parameters: $x = 0.0023(10)$, $y = 0.2000(5)$, $z = 1/4$, $\beta_{11} = 0.0086(22)$, $\beta_{22} = 0.0007(4)$, $\beta_{33} = 0.0084(12)$ for Co and $x = 0.1996(7)$, $y = 0.5869(3)$, $z = 0.2716(22)$, $\beta_{11} = 0.0107(17)$, $\beta_{22} = 0.0000(3)$, $\beta_{33} = 0.0061(8)$ for As according to space group $Pna2_1$ is superior to all the others at a significance level < 0.005. Except for y_{As} the positional parameters for CoAs show a striking similarity with those found for FeAs, whereas the thermal parameters differ considerably. In FeAs[3] the As and Fe atoms show isotropic and moderate anisotropic thermal motions, respectively, at room temperature, whereas both kinds of atom vibrate strongly anisotropically in CoAs where the vibration amplitudes along [010] are particularly small.

The single crystal results referred to above may be compared with those obtained from a powder sample by means of the neutron diffraction technique. The small number of reflections accessible by this method, necessitated the simplifying assumption of isotropic temperature factors in the profile refinement procedure despite the fact that models based on this assumption were rejected for the single crystal X-ray data (vide supra). The attempted profile refinements in terms of a model based on space group $Pna2_1$ gave no convergence in the calculations and this failure is clearly a consequence of the small number of reflections available with $l \neq 0$. However, with both z-parameters fixed, i.e. $z_{Co} = z_{As} = 1/4$, the powder neutron diffraction data gave positional parameters: $x = 0.0043(20)$, $y = 0.1998(17)$ for Co and $x = 0.1996(6)$, $y = 0.5877(9)$ for As in excellent agreement with the values obtained from the single crystal X-ray data (vide supra).

The fact that the neutron diffraction technique is capable of providing satisfactorily accurate values for the x and y parameters, and thus an adequate

overall description of the structure, and good average values for the inter-atomic distances, is in accordance with previous experience.[14,15] However, three-dimensional single crystal data are needed in order to obtain information on those details of the structure which are connected with the parameter z_{As}.

The results of the powder neutron diffraction measurements at liquid helium and liquid nitrogen temperatures show that the crystal structure remains the same as at room temperature. The values of x and y derived from these data agree, within standard deviations, with those given above.

(iii) *Interatomic distances and angles.* Important interatomic distances and angles calculated from the unit cell dimensions (Guinier data) and the best positional parameters (single crystal X-ray data) are listed in Table 1. The shortest interatomic distances definitely represent bonding distances, the

Table 1. Interatomic distances and angles in the crystal structure of CoAs.

Interatomic distances (Å)

Type		CoAs
Bonding interatomic distances	Co − As(1)	2.324(5)
	Co − As(1)	2.343(7)
	Co − As(1)	2.390(7)
	Co − As(1)	2.453(7)
	Co − As(1)	2.497(7)
	Co − As(1)	2.500(5)
Possible bonding interatomic distances	Co − Co(2)	2.708(8)
	Co − Co(2)	2.925(4)
	As − As(2)	2.922(8)
Shortest interatomic distances neglected as bonding	Co − As	3.747(4)
	Co − Co	3.489(1)
	As − As	3.264(5)

Interatomic angles (°)

Type	CoAs	Type	CoAs
As − Co − As(1)	72.31(18)	Co − As − Co(1)	68.18(17)
As − Co − As(1)	74.15(18)	Co − As − Co(1)	69.79(24)
As − Co − As(1)	82.49(19)	Co − As − Co(1)	74.59(18)
As − Co − As(1)	87.19(20)	Co − As − Co(1)	76.69(18)
As − Co − As(1)	87.48(20)	Co − As − Co(1)	91.09(17)
As − Co − As(1)	89.89(21)	Co − As − Co(1)	93.34(14)
As − Co − As(1)	91.09(26)	Co − As − Co(1)	105.02(24)
As − Co − As(1)	92.62(22)	Co − As − Co(1)	108.43(24)
As − Co − As(1)	93.34(24)	Co − Co − Co(1)	73.24(9)
As − Co − As(1)	95.51(23)	Co − Co − Co(2)	99.54(18)
As − Co − As(1)	102.61(19)	Co − Co − Co(2)	100.49(18)
As − Co − As(1)	106.00(19)	Co − Co − Co(1)	154.97(16)
Co − As − Co(1)	66.32(23)	As − As − As(1)	73.32(20)

values showing reasonable conformity with the corresponding expected value for a single Co − As bond. The situation with respect to the category designated as possible bonding interatomic distances, is still as uncertain as when the FeAs paper [3] was completed. In fact, most of our discussion of the crystal structure of FeAs is also pertinent to the case of CoAs and needs no repetition.

The axial ratio b/c (or an equivalent quantity depending on the setting of the unit cell) has been introduced by Pfisterer and Schubert [16] to define two subclasses within the MnP type structure, corresponding to $b/c > \sqrt{3}$ and $b/c < \sqrt{3}$. The close correspondence between the interatomic distances and angles in the crystal structures of FeAs and CoAs, which belong to different subclasses ($b/c = 1.787$ for FeAs and $b/c = 1.682$ for CoAs), definitely demonstrates that this subclassification is not rooted in any other distinct structural dissimilarity. This observation together with the fact that the isostructural compound CrAs [6] converts from one subclass to the other near the Néel temperature without being subjected to appreciable changes in the atomic arrangement, leads one to conclude that very little significance may be attached to Schubert's [17] considerations on the MnP phases.

The most accurate structure determinations of MnP phases have hitherto been carried out for CrP,[18] MnP,[18] FeP,[18] CoP,[18] CrAs,[6] MnAs,[19] FeAs,[3] and now CoAs. It is interesting to note that the average metal − pnigogen bond distance varies considerably less within the phosphide series (Cr − P: 2.381 Å; Mn − P: 2.358 Å; Fe − P: 2.308 Å; Co − P: 2.304 Å) than among the arsenides (Cr − As: 2.511 Å; Mn − As: 2.56_8 Å at 55°C; Fe − As: 2.436 Å; Co − As: 2.418 Å). The most apparent inference from these data is that the electron configuration associated with the metal atoms varies relatively more for the arsenides than the phosphides (*cf.*, e.g., Refs. 20, 21).

The maximum in the metal-arsenic bond distance reached at MnAs is a point of special interest in this connection, since this observation appears to shed some light on the anomalous magnetic susceptibility curve of this compound (*vide infra*).

MnAs adopts the MnP type structure between 316 and 393°K, whereas the NiAs type structure prevails above and below this temperature range (*cf.* Refs. 4, 19, 22, 23, and in particular Ref. 24, which also includes an up to date review of the field). The transformations in MnAs are of some special interest in that that at 393°K appears to occur homogeneously, *i.e.* essentially a second order transformation, with the cell distortion and the atomic displacements relative to the NiAs type structure increasing progressively on cooling to 316°K, where there is a first order transformation back to the NiAs type structure and an accompanying onset of ferromagnetism.[19,22-24] The high temperature phase with NiAs type structure exhibits a normal Curie-Weiss Law relationship throughout its existence range.[22] Now that it has been definitely shown that MnAs is not antiferromagnetic in the region where it takes the MnP type structure,[19,25] there occurs a considerable problem in accounting for the increasing magnetic susceptibility with increasing temperature, which appeared so characteristic of an antiferromagnetic state at one time.[26] In our opinion it seems very probable that this phenomenon results from the pairing of d electrons in (formally) covalent bond formation. The implied accompanying loss of spin moment accounts for the observed reduction from ∼ 4 unpaired electrons per Mn atom in the genuine paramagnetic state above 393°K to an extrapolated value of ∼ 3.4 unpaired electrons per Mn atom in the ferromagnetic state at 0°K. The maximum value of the metal-arsenic bond distance for MnAs among the MnP phases is consistent with this view, since this compound thus would obtain a much larger number (∼ 3.4 − ∼ 4) of unpaired electrons than any of the other MnP phases under consideration. The present interpretation of the magnetic susceptibility anomaly in MnAs is much simpler, and differs also in other essential details from that proposed by Goodenough and Kafalas.[27]

(iv) *Magnetic properties*. The reciprocal magnetic susceptibility *versus* temperature curve for CoAs is shown in Fig. 1.

Excellent reproducibility has been found between a number of different samples. Field strength dependent susceptibilities were not observed and the results shown in Fig. 1 represent mean values obtained at several different field strengths. The data are uncorrected for induced diamagnetism since reliable corrections are not easily estimated.
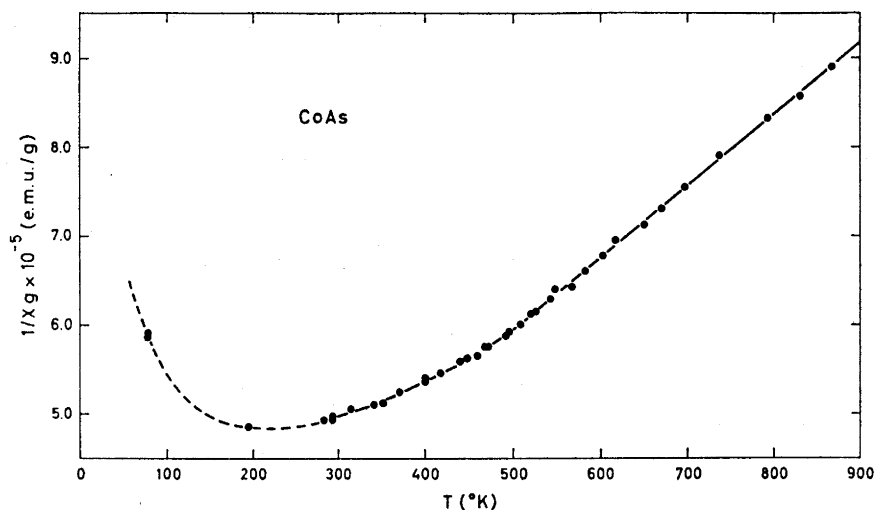

Fig. 1. Reciprocal of the magnetic susceptibility of CoAs as a function of temperature

The high temperature portion $(T > 490°K)$ of the $\chi^{-1}(T)$-curve is consistent with an analytical description of the Curie-Weiss Law type, *i.e.* $\chi^{-1} = C^{-1}(T - \theta)$ with $\theta = -230 \pm 40°K$ and $\mu_P = \sqrt{8C_{mol}} = 1.15 \pm 0.05$ B.M./Co atom. The equivalent spin quantum number according to the "spin only" approximation $(\mu = g\sqrt{S(S+1)}$ with $g = 2)$ is $S = 0.26 \pm 0.02$.

Below 490°K the $\chi^{-1}(T)$-curve shows a positive deviation from the Curie-Weiss Law relationship and it passes through a broad minimum at $225 \pm 50°K$. The most obvious inference of this behaviour, that a transformation involving ordering of magnetic moments (corresponding to $2S = 0.52 \pm 0.04$ unpaired electrons per Co atom, *vide supra*) occurs below 490°K is, however, inadmissable on the basis of the neutron diffraction data. The neutron diffraction patterns at liquid helium, liquid nitrogen, and room temperatures definitely show no purely magnetic reflections, and any contributions of magnetic origin to the nuclear reflections must be small. A small magnetic contribution to the nuclear peaks is difficult to detect, but we estimate that any possible ordered moment in CoAs must be less than 0.1 B.M.

In the light of these findings, the $\chi^{-1}(T)$-curve (Fig. 1) shows an anomalous temperature dependence below 490°K. A more detailed understanding of this behaviour appears to require data over and above those available at present,

but it is nevertheless tempting to indicate a possible explanation. It is conceivable that the anomalous shape of the $\chi^{-1}(T)$-curve below 490°K results from a thermal distribution of electrons between states which differ in their magnetic description, *e.g.* a transfer of electrons from a spin-paired configuration in essentially non-bonding t_{2g} orbitals to unpaired states in anti-bonding orbitals. Jaccarino *et al.*[28] have recently presented a simple quantitative model which satisfactorily accounts for a similar χ-T relationship for FeSi. We have tried to adjust their model to the case of CoAs, but it has proved impossible to obtain a reasonable agreement with the *whole* $\chi^{-1}(T)$-curve in Fig. 1 for *one set* of values for the variable parameters. However, the problem merits attention and will be investigated further.

Finally we record that CoAs exhibits a metallic type of conduction. The diffuse reflectance of CoAs decreases uniformly from 2 400 to 20 000 Å, with no observed absorption edge or other anomalies.

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