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On the Crystal Structure of Ni_5As_2

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The Ni_5As_2 phase has a slight range of homogeneity extending on both sides of the stoichiometric 5 : 2 ratio. The structure is determined from three-dimensional single crystal X-ray data. The phase exhibits a temperature dependent paramagnetic susceptibility which does not obey the Curie-Weiss Law over the temperature interval 80 to 1000 K.

Although a phase of approximate composition Ni_5As_2 was described[1] as early as 1857, some one hundred years elapsed before its existence was confirmed by Hellner.[2] When the present investigation was started the Ni_5As_2 phase was known to exhibit hexagonal symmetry and a slightly temperature dependent range of homogeneity on the Ni-poor side of the stoichiometric composition.[2–4] Since no structure determination had been carried out it was considered of interest to undertake this study. However, at the time when the first draft to a report on our findings was completed, we became aware of a paper by El-Boragy *et al.*[5] which describes the crystal structure of Ni_5As_2.

EXPERIMENTAL

Materials. Samples were prepared from 99.999 + % As (Johnson, Matthey & Co.) and 99.99 + % Ni (The British Drug Houses). (The nickel powder was obtained by hydrogen reduction (600°C) of NiO.)

Preparations. Weighed quantities of the components were heated in evacuated, sealed silica tubes for 4 days at 600°C. The sintered powders were ground and reannealed at temperatures between 700 and 900°C for 15 day periods and, finally, quenched in ice water. Several samples with different initial compositions were prepared on both sides of the 5 : 2 stoichiometric ratio. Single crystals of Ni_5As_2 of rather irregular, flaky shape were found in the sintered samples heated at 750°C.

X-Ray diffraction. X-Ray powder photographs of all samples were taken in a Guinier type camera of 80 mm diameter with monochromatized Cu$K\alpha_1$-radiation using KCl as internal standard.

Three-dimensional single crystal data from the layers $hk0$ to $hk6$ were collected in an integrating Weissenberg camera of 57.3 mm diameter with Zr-filtered Mo$K\alpha$-radiation using the multiple-film technique. The 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. Additional intensity data from the layers $0kl$ to $3kl$ were obtained by the precession technique.

Computations. The computational work, including least squares refinements of the unit cell dimensions, corrections, data reductions, scalings, Patterson- and Fourier-syntheses, full matrix least squares refinements of the structure factors, and evaluations of interatomic distances, was carried out on a CDC 3300 computer using, in most cases, the programmes of Dahl *et al.*[6]

The atomic scattering factors were taken from Hanson *et al.*[7] The extent of the agreement between the observed and calculated structure factor data was judged from the reliability factor:

$$R = \sum||F_o| - |F_c||/\sum|F_o|$$

The unobserved reflections were not included in the calculations of R, and were omitted from the least squares refinements.

Magnetic susceptibilities were measured between 80 and 1000 K by the Faraday method (maximum field ~ 8kØ) using 70 – 100 mg samples.

RESULTS AND DISCUSSION

(i) Composition and homogeneity range. Polycrystalline samples of Ni_5As_2 are easily synthesized by direct reactions of the elements at 700 – 900°C. In order to obtain thermodynamic equilibrium it is necessary to crush the samples during the annealing process.

The unit cell dimensions of the Ni_5As_2 phase decrease as the As content increases over the homogeneity range (extending from 28.09 ± 0.16 to 28.74 ± 0.16 atomic % As). It is thus inferred, in contrast with earlier findings,[3,4] that the homogeneity range extends on both sides of the stoichiometric formula Ni_5As_2.

(ii) Unit cell dimensions and space group. The unit cell dimensions range between $a = 6.815(1)$ Å, $c = 12.512(2)$ Å, $c/a = 1.8360(6)$ at 28.09 atomic % As and $a = 6.813(1)$ Å; $c = 12.502(2)$ Å; $c/a = 1.8350(6)$ at 28.74 atomic % As; $a = 6.815(1)$ Å; $c = 12.506(2)$; $c/a = 1.8351(6)$ being obtained at the stoichiometric composition. These values are reasonably consistent with those reported in the literature.[2,3,5,8]

Although all previous studies agree on the hexagonal symmetry of the Ni_5As_2 phase, there is considerable uncertainty as to the correct choice of space group. According to the X-ray powder diffraction data of Heyding and Calvert[3] indices of the type $h0l$ were found to be systematically absent for $l = 2n + 1$. A later single crystal study by Saini *et al.*[8] could not confirm this, and $P6_322$ was proposed as the space group for Ni_5As_2.

On the basis of the present Weissenberg data it was very difficult to decide whether indices of the type $h0l$ for $l = 2n + 1$ were absent or of low intensity, and because of this uncertainty, space group $P6_322$ was assumed in the preliminary structure analysis.

Numerous trial structures based on the (001) Patterson-synthesis were tested, but all were unfruitful. However, the precession data which were subsequently collected unequivocally showed that reflections of the type $h0l$ for $l = 2n + 1$ are extinguished, hereby eliminating space group $P6_322$. A $N(z),z$-plot demonstrated that the (001) projection is centro-symmetric. The most probable space group is thus $P6_3cm$.

(iii) Refinement of the structure. On account of the Patterson-synthesis a set of positional parameters were deduced according to space group $P6_3cm$. Apart from some problems associated with absorption corrections the least

squares refinements proceeded fairly normally and were terminated at $R = 0.095$. The final positional and thermal parameters are listed in Table 1. The value of one temperature factor is negative and another one takes a rather high positive value, indicating that the applied absorption correction is still somewhat unsatisfactory.

Table 1. Positional and thermal parameters for Ni_5As_2 according to $P6_3cm$.

Atom	Position	x	y	z	B(Å^2)
Ni(I)	2*a*	0	0	0.9478(38)	−0.15(18)
Ni(II)	4*b*	1/3	2/3	0.0768(56)	0.58(28)
Ni(III)	6*c*	0.2460(15)	0	0.0891(44)	0.43(16)
Ni(IV)	6*c*	0.6228(17)	0	0.1942(40)	0.22(14)
Ni(V)	6*c*	0.3043(20)	0	0.3057(36)	0.66(19)
Ni(VI)	6*c*	0.6212(37)	0	0.4027(59)	1.68(39)
As(I)	6*c*	0.6669(19)	0	0.9931(31)	0.60(12)
As(II)	4*b*	1/3	2/3	0.2745(35)	0.47(18)
As(III)	2*a*	0	0	0.2260(29)	0.46(26)

A similar solution for the structure of Ni_5As_2 is obtained in the independent study by El-Boragy *et al.*[5] The two investigations concur on $P6_3cm$ being the correct space group. However, considerable discrepancy is to be found between some of the values for the positional parameters. The determination of El-Boragy *et al.*[5] was based on Weissenberg data from the layers 0*kl*, 1*kl*, and 2*kl* and their refinements were terminated at $R = 0.15$. Due to the relatively high R-value we subjected their structure factor data to further least squares refinements. However, regardless of the choice of input parameters their original values for the variable parameters were obtained. There is accordingly a real discrepancy between the two studies and although the origin of this remains unknown the following considerations appear to be relevant:

(1) The two structure determinations of Ni_5As_2 are carried out at room temperature, which thus excludes temperature variation as a cause for the different values of the positional parameters.

(2) Both studies utilized crystals prepared from elements of high purity. This excludes any hypothetical difference in impurity content as the origin of the different positional parameters.

(3) Structural parameters will generally vary within a homogeneity range. If the crystals of the two studies are of different composition, this will cause a variation in the positional parameters.

(4) Another and perhaps more likely explanation may be to connect the discrepancy with the fact that El-Boragy *et al.* did not correct their intensity data for absorption.

(iv) Discussion of the structure. The atomic arrangement of the Ni_5As_2 structure is shown in Fig. 1 and using the same projection axis, the immediate environment of the different atoms is illustrated in Fig. 2. Interatomic distances (< 4 Å) are listed in Table 2, and the coordination numbers together with the average values of the Ni – Ni and Ni – As distances around each kind of atoms

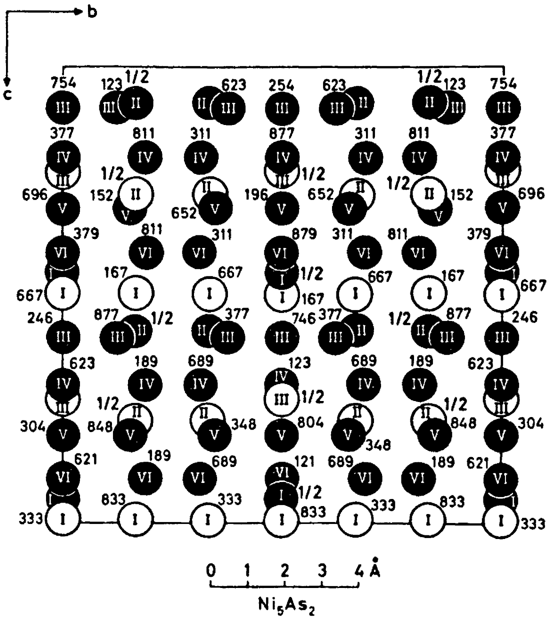

Fig. 1. The structure of Ni_5As_2 projected along [100] of the ortho-hexagonal unit cell. The filled and open circles represent Ni and As, respectively.

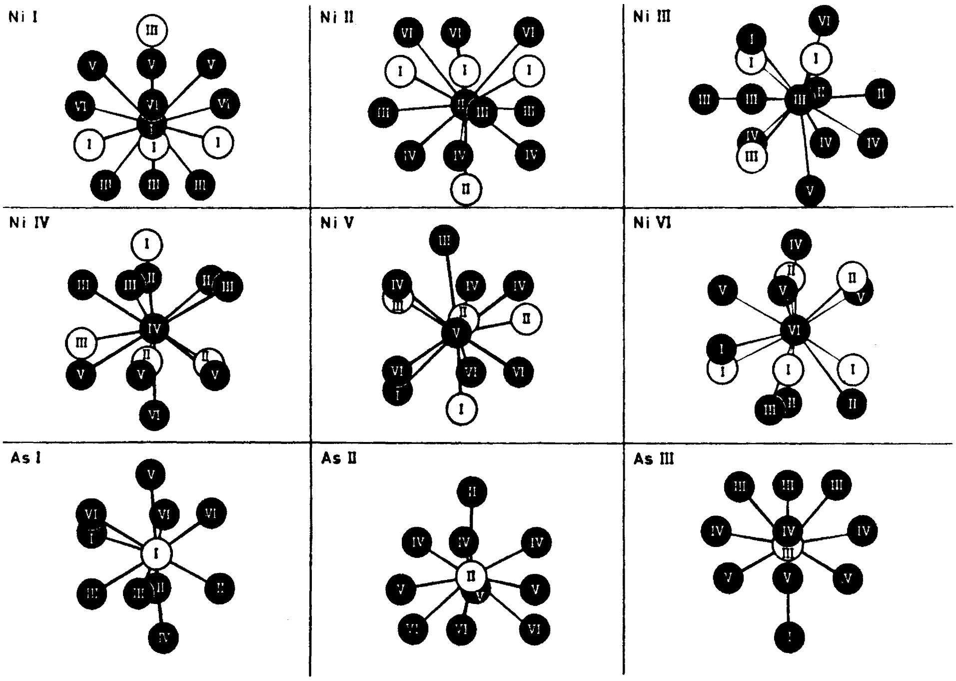

Fig. 2. The coordination polyhedra of the Ni_5As_2 structure projected along [100] of the ortho-hexagonal unit cell. The filled and open circles represent Ni and As, respectively.

Table 2. Interatomic distances (< 4 Å) in Ni_5As_2.

Type	Distance (Å)	Type	Distance (Å)
Ni(I) – 3 Ni(III)	2.436(55)	Ni(I) – 3 As(I)	2.341(20)
– 3 Ni(V)	2.733(43)	– As(III)	2.777(53)
– 3 Ni(VI)	2.643(33)	– As(III)	3.480(53)
Ni(II) – 3 Ni(III)	2.626(8)	Ni(II) – 3 As(I)	2.502(17)
– 3 Ni(IV)	2.595(27)	– As(II)	2.477(44)
– 3 Ni(VI)	3.047(51)	– As(II)	3.779(44)
– 3 Ni(II)	3.936		
– 3 Ni(V)	3.724(36)		
Ni(III) – Ni(I)	2.436(55)	Ni(III) – 2 As(I)	2.366(23)
– 2 Ni(II)	2.626(8)	– As(III)	2.398(44)
– 2 Ni(III)	2.905(19)	– As(I)	3.110(28)
– 2 Ni(IV)	2.616(22)	– 2 As(II)	3.503(33)
– Ni(IV)	2.887(24)		
– Ni(V)	2.740(37)		
– Ni(VI)	2.498(51)		
Ni(IV) – 2 Ni(II)	2.596(27)	Ni(IV) – As(I)	2.532(44)
– 2 Ni(III)	2.616(23)	– 2 As(II)	2.364(21)
– Ni(III)	2.887(24)	– As(III)	2.602(15)
– Ni(V)	2.581(28)		
– 2 Ni(V)	2.744(21)		
– Ni(VI)	2.613(61)		
– 4 Ni(IV)	3.705(9)		
Ni(V) – Ni(I)	2.733(43)	Ni(V) – As(I)	2.354(39)
– Ni(III)	2.740(37)	– 2 As(II)	2.409(11)
– Ni(IV)	2.581(28)	– As(III)	2.302(13)
– 2 Ni(IV)	2.744(21)		
– Ni(VI)	2.480(39)		
– 2 Ni(VI)	2.664(32)		
– 2 Ni(II)	3.724(36)		
– 2 Ni(V)	3.593(27)		
Ni(VI) – Ni(I)	2.643(33)	Ni(VI) – As(I)	2.265(36)
– 2 Ni(II)	3.047(51)	– 2 As(I)	2.691(29)
– Ni(III)	2.498(51)	– 2 As(II)	2.671(43)
– Ni(IV)	2.613(61)	– As(III)	3.402(54)
– Ni(V)	2.480(39)		
– 2 Ni(V)	2.664(32)		
– 4 Ni(VI)	3.697(18)		
As(I) – Ni(I)	2.341(20)	As(I) – 2 As(I)	3.934(26)
– 2 Ni(II)	2.502(17)	– 4 As(I)	3.937(13)
– 2 Ni(III)	2.366(23)	– 2 As(II)	3.556(27)
– Ni(IV)	2.532(44)	– As(III)	3.693(34)
– Ni(V)	2.354(39)		
– Ni(VI)	2.265(36)		
– 2 Ni(VI)	2.691(29)		
– Ni(III)	3.110(28)		
As(II) – Ni(II)	2.477(44)	As(II) – 3 As(I)	3.556(27)
– 3 Ni(IV)	2.364(21)	– 3 As(II)	3.936
– 3 Ni(V)	2.409(11)	– 3 As(III)	3.983(6)

Table 2. Continued.

As(II) – 3 Ni(VI)	2.671(43)		
– Ni(II)	3.779(44)		
– 3 Ni(III)	3.503(33)		
As(III) – Ni(I)	2.777(53)	As(III) – 3 As(I)	3.693(34)
– 3 Ni(III)	2.398(45)	– 6 As(II)	3.983(6)
– 3 Ni(IV)	2.602(15)		
– 3 Ni(V)	2.302(27)		
– Ni(I)	3.480(53)		
– 3 Ni(VI)	3.402(54)		

Table 3. The coordination numbers together with the average values of the Ni – Ni and Ni – As distances around the different atoms in Ni_5As_2. (CN(Ni) is the number of nearest Ni neighbours, CN(As) the number of nearest As neighbours, d_m the average distance in Å, R_{Ni} Goldschmidt Ni radius CN12, and r_{As} is the covalent (CN = 4) radius for As.)

Central atom	CN(Ni)	d_m(Å)	$d_m/2R_{Ni}$	CN(As)	d_m(Å)	$d_m-(R_{Ni}+r_{As})$(Å)
Ni(I)	9	2.604	1.05	4	2.449	+0.03
Ni(II)	9	2.756	1.11	4	2.496	+0.08
Ni(III)	10	2.686	1.08	3	2.377	–0.04
Ni(IV)	9	2.666	1.08	4	2.466	+0.05
Ni(V)	8	2.669	1.08	4	2.369	–0.05
Ni(VI)	8	2.707	1.09	5	2.598	+0.18
As(I)	10	2.461				+0.04
As(II)	10	2.481				+0.06
As(III)	10	2.468				+0.05

are summarized in Table 3. Each of the six different kinds of Ni atoms is surrounded by 8 – 10 other Ni atoms at distances ranging from 2.44 to 3.05 Å, and 3 – 5 As atoms at distances between 2.27 and 2.78 Å, so that each Ni atom has a total of 12 – 13 close neighbours. The coordination numbers of the three different kinds of As atoms are constant and equal to 10 Ni. The Ni – Ni distances which are classified as non-bonding exceed 3.59 Å, while the corresponding non-bonding Ni – As distances are greater than 3.11 Å. As seen from Table 3 the average Ni – Ni distance is smallest around Ni(I) and largest around Ni(II), the two averages differing only 5.8 %. A considerable larger degree of individual variation is found for the average Ni – As distance. The average Ni(VI) – As distance is 9.7 % greater than the average Ni(V) – As distance which represents the extremes in this case. The weighted average Ni – Ni distance in Ni_5As_2 is 2.67 Å which exceeds Goldschmidts[9] value for the Ni diameter (2.48 Å for CN = 12) by 7.7 %. The mean Ni – As distance is 2.456 Å which is 0.04 Å larger than the sum of the metal radius for nickel (1.24 Å [9]) and the tetrahedral covalent radius for arsenic (1.18 Å [9]). There are no As – As distances shorter than 3.55 Å, and As has accordingly only Ni as nearest neighbours.

The structure of Ni_5As_2 is rather complicated and the coordination polyhedra are so irregular (Fig. 2) that it is difficult to describe them in normal terms. The structure is in fact among the most complicated for the metal rich pnictides. Apart from the isostructural Pd_5Sb_2 it is difficult to find any relationship connecting it with other structures.

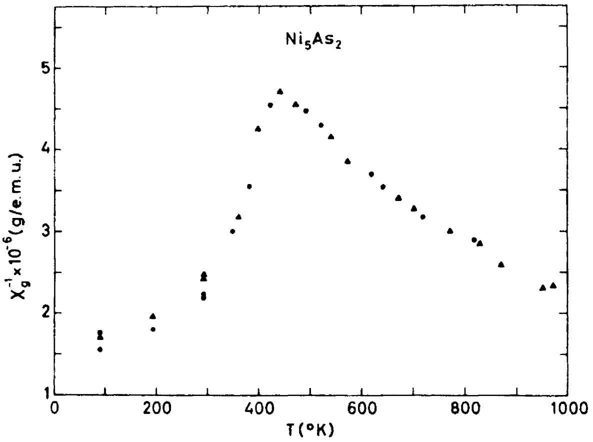

Fig. 3. Reciprocal of the magnetic susceptibility of Ni_5As_2 as function of increasing (▲) and decreasing (●) temperature.

Magnetic properties. Magnetic susceptibility measurements of Ni_5As_2 were made on samples quenched from 900°C. The results (Fig. 3) exhibit excellent reproducibility between a number of different samples. Field strength dependent susceptibilities were not observed and the results shown in Fig. 3 represent mean values obtained at several different field strengths. (The data are uncorrected for induced diamagnetism since reliable corrections are not easily estimated.) The $\chi^{-1}(T)$-curve does not follow the Curie-Weiss Law in any temperature range. Apart from a gross classification as paramagnetic it is impossible on account of the present data to establish the detailed magnetic behaviour of Ni_5As_2. In order to rectify this situation a neutron diffraction study of Ni_5As_2 is currently being undertaken.

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