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A Determination of the Crystal Structure of CdNi

By J. K. Critchley

Department of Chemistry, Brunel College, London, England

and J. W. Jeffery

Department of Crystallography, Birkbeck College, London, England

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CdNi is a defect structure, the cubic unit cell ($a=11{\cdot}39$ Å) containing 48Cd+44Ni+4 vacancies. Laue and Weissenberg photographs gave the space group as *Fd*3*m*. The Cd atoms lie on the 48 special positions (*f*) with parameter 0·429, 32Ni on (*e*) with parameter 0·204 and 16Ni on (*c*) (origin at centre of symmetry). The best agreement was obtained if the 4 vacancies were divided equally among all the Ni positions. Least-squares refinement gave a final *R* value of 6%. Cd atoms were 14-coordinated; Ni atoms 12-coordinated, with normal interatomic distances.

The compound CdNi was first reported by Lihl & Buhl (1955) and was shown to exist over the composition range 47·0 to 48·5 at.% Ni. A complete phase diagram for the system is given by Critchley & Lott (1963) who investigated the structure of the compound by the powder method, showing it to be face centred cubic with a lattice parameter of 11·39 ± 0·01 Å.

Single crystals of the cadmium-saturated compound were obtained by prolonged annealing of an alloy in the solid-plus-liquid phase field. The crystals were then extracted from the cadmium-rich matrix by electrolysis. A single crystal was ground to a sphere, etched lightly, its diameter measured, and the sphere then oriented by means of a Laue photograph. A second photograph along the [100] direction showed the crystal to belong to the Laue group *m*3*m*: this, together with a knowledge of systematic absences from the Weissenberg record, determines the space group as *Fd*3*m*.

The density of the compound was found to be 8·95 ± 0·02 g.cm^{-3}. From the lattice parameter the total weight per unit cell is found to be 7964 atomic mass units. The presence of forty-eight cadmium atoms would account for 5395 mass units; the difference divided by the atomic mass of nickel gives 43·8 ± 0·2 as being the number of nickel atoms per unit cell. However, from the composition of the crystal, forty-eight cadmium atoms should be associated with 44·4 (±0·3*) nickel atoms. This would give a calculated density of 8·99 g.cm^{-3}. The values of *F* given in Table 3 were obtained on the basis of forty-four nickel atoms plus four vacant lattice sites being present in the unit cell.

Zero and second layer Weissenberg photographs about the *c* axis were taken with the use of the equi-inclination setting and copper radiation. Data for the first layer photograph were not evaluated as the intensity values for it could not have been brought to a common basis with those for even layer lines, there being no common reflextions. Peak intensities were measured with a micro-densitometer, with an estimated accuracy of about eight per cent. The relative intensities were corrected for absorption and the Lorentz-polarization factor.

Two sets of forty eight atoms may be distributed between the equipoints (sets of equivalent positions) in the fifteen possible ways listed in Table 1. The notation used is from *International Tables for X-ray Crystallography* (1952).

Table 1. *Arrangements of atoms among the equipoints*

Arrangements	Cadmium atoms	Nickel atoms
1	48(*f*)	48(*f*)
2	48(*f*)	16(*c*)+16(*d*)+8(*a*)+8(*b*)
3	48(*f*)	32(*e*)+16(*c*)
4	48(*f*)	32(*e*)+16(*d*)
5	48(*f*)	32(*e*)+8(*a*)+8(*b*)
6	16(*c*)+16(*d*)+8(*a*)+8(*b*)	48(*f*)
7	32(*e*)+16(*c*)	48(*f*)
8	32(*e*)+16(*d*)	48(*f*)
9	32(*e*)+8(*a*)+8(*b*)	48(*f*)
10	32(*e*)+16(*c*)	32(*e*)+16(*d*)
11	32(*e*)+16(*d*)	32(*e*)+16(*c*)
12	32(*e*)+16(*c*)	32(*e*)+8(*a*)+8(*b*)
13	32(*e*)+8(*a*)+8(*b*)	32(*e*)+16(*c*)
14	32(*e*)+16(*d*)	32(*e*)+8(*a*)+8(*b*)
15	32(*e*)+8(*a*)+8(*b*)	32(*e*)+16(*d*)

Of the possible arrangements numbers 1, 2 and 6 may be eliminated because they give rise to special absences not observed in the diffraction record. For numbers 12 to 15 the most favourable case has 3Cd and 6Ni atoms on the cube diagonal of 19·7 Å. Taking the diameter of Cd as 3·0 Å, this leaves less than 2 Å each for the Ni atoms (normal diameter 2·5 Å). These arrangements can therefore be eliminated. The arrangements 3, 7 and 10 are equivalent respectively to 4, 8

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* This error is an estimate on general grounds, since no details are given in the paper by Lihl & Buhl (1955).

and 11, and the latter need not therefore be considered further. For reflexions with $h+k+l=4n+2$, atoms in the 48(*f*) position cannot contribute to the intensity. The 11 reflexions of this type have an average F_{obs} of 173 compared with 383 for the 9 reflexions for which $h+k+l=4n$ (h, k, $l\neq0$), indicating that one set of atoms lies on the 48(*f*) equipoint. Hence arrangements 10 to 15, for which such a systematic intensity difference would not obtain, may also be eliminated.

The above considerations may be summed up as showing that one type of atom lies on the 48(*f*) equipoint and the other set on the 32(*e*) plus either 16(*c*) or [(8(*a*)+8(*b*)] equipoints.

For reflexions with $h, k=4n$, $l=4n+2$ only the 32(*e*) equipoint can contribute to the intensities and with h, k and $l=4n+2$ only the 32(*e*) and 16(*c*) equipoints. For the first group of reflexions values of the structure amplitudes were calculated as a function of the variable parameter for the 32(*e*) equipoints, the origin being taken at the centre of symmetry. Comparing the values with the relative intensities a value for x between 0·20 and 0·21 or the anti-symmetrical value 0·29 to 0·30 was obtained. Considering the second group of reflexions the intensities could only be accounted for with the 16(*c*) equipoint in conjunction with a parameter value of about 0·20 for the 32(*e*) equipoint. The (*c*)–(*e*) and (*e*)–(*e*) interatomic distances are only about 2·5 Å, too small to accommodate Cd atoms, and therefore Ni atoms must be at these sites.

Using the above information, a scale factor, and temperature factors for the nickel atoms were obtained. The distribution of the vacant lattice sites between the 32(*e*) and 16(*c*) equipoints was then investigated. For reflexions with $h+k+l=4n+2$, *i.e.* those discussed above, structure factors were calculated for the following distributions of vacant lattice sites between the two equipoints: (*a*) associated with 32(*e*) only; (*b*) associated with 16(*c*) only; (*c*) a *pro rata* distribution. The residuals obtained were 14%; 13% and 8% respectively. A *pro rata* distribution was therefore taken as being the best approximation. Using the information so far obtained, values of the structure factor for a number of the remaining reflexions were calculated as a function of the variable parameter of the cadmium atoms on the 48(*f*) equipoint, from $x=0{\cdot}3$ to $0{\cdot}5$· This covered the range of parameter allowable from packing considerations. A value of x of about 0·43 was obtained. A seven-cycle least-squares refinement was then carried out by computer. The refined values of atom positions and temperature factors are given in Table 2. Table 3 gives the calculated and observed structure factors with a residual, R, of 6%. Table 4 gives the inter-atomic distances for the structure together with the coordinations.

Table 2. *Final atomic parameters and temperature factors*

Atom	Equipoint	parameter	Temp. factor B
Cd	48(*f*)	$0{\cdot}428_8 \pm 0{\cdot}000_3$	1·50 Å^2
Ni	32(*e*)	$0{\cdot}203_8 \pm 0{\cdot}000_3$	1·58
Ni	16(*c*)	—	1·68

The structure found for CdNi is similar to that of Ti$_2$Ni (*Strukturbericht* type *E*9$_3$). The alloy chemistry of this group of intermetallic compounds has been discussed by Nevitt (1962). The main factor controlling their occurrence is the relative size of the A and B atoms, an average value of 1·19 being found for binary phases. Nickel atoms in both phases occupy the 32(*e*) positions with C.N.12, but in Ti$_2$Ni the 16(*c*) sites (also C.N.12) are filled by Ti atoms where as in CdNi these are occupied by Ni. Deviation from A$_2$B stoichoimetry is observed in only two binary phases, but occurs widely in ternary phases with oxygen as the third constituent (occupying 16(*d*) positions), the presence of which appears to stabilize the phase by acting as an electron acceptor. Of the known *E*9$_3$ compounds CdNi is the only one having an A element not drawn from the transition metals of groups III to VI; the significance of this in terms of the electronic structure of these phases has yet to be evaluated.

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Table 3. *Calculated and observed structure factors for* CdNi

hkl	F_{calc}	F_{obs}	*hkl*	F_{calc}	F_{obs}	*hkl*	F_{calc}	F_{obs}
004	783	750	08,12	289	255	24,12	36	51
008	373	387	0,10,10	586	551	24,14	133	109
00,12	468	486	224	816	824	266	204	183
026	60	n.o.*	226	288	294	268	288	292
02,10	424	417	228	1035	1049	26,10	108	93
02,14	117	114	22,10	374	354	26,12	299	338
044	1089	1077	22,12	474	505	288	137	151
048	36	n.o.	22,14	187	145	28,10	183	183
04,12	169	199	244	353	364	28,12	34	23
066	1096	1079	246	39	n.o.	2,10,10	53	46
06,10	593	607	248	225	204			
08,8	22	n.o.	24,10	106	146			

* not observed.

Table 4. *Coordination*

Central atom	Coordinating atoms		Distances (±0·005)	Sum of atomic radii*
Cd(*f*)	4Ni(*e*)		2·86 Å	2·73 Å
	2Ni(*c*)	14	2·86	2·73
	4Cd(*f*)		2·97	2·98
	4Cd(*f*)		3·16	2·98
Ni(*c*)	6Cd(*f*)	12	2·86	2·73
	6Ni(*e*)		2·44	2·49
Ni(*e*)	3Ni(*e*)		2·54	2·49
	3Ni(*c*)	12	2·44	2·49
	6Cd(*f*)		2·86	2·73

* *International Tables for X-ray Crystallography* (1962).

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The Crystal Structure of Guanidinium Chloride

By D. J. Haas,* D. R. Harris and H. H. Mills†

Roswell Park Memorial Institute, Buffalo, New York, U.S.A.

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Guanidinium chloride, $C(NH_2)_3{}^+Cl^-$, crystallizes in the orthorhombic system with the space group *Pbca* and lattice constants:

$$a=9{\cdot}18_4,\quad b=13{\cdot}03_9,\quad c=7{\cdot}76_5\ \text{Å}\quad (\text{all } \pm 0{\cdot}005\ \text{Å})$$

The crystal structure was solved by the heavy-atom method and refined by block-diagonal least-squares methods; the final R value is 0·062. The crystal structure consists of chloride ions coordinated by six nitrogen atoms of three different guanidium ions, two of which are nearly coplanar. The hydrogen bonds between the guanidium and chloride ions appear to be non-linear. The average carbon–nitrogen and chloride–nitrogen distances for the six coordinating nitrogen atoms are 1·323 and 3·303 Å respectively. The guanidinium ion is planar and has the molecular symmetry C_{3v}.

Introduction

The crystal structure of guanidinium chloride, $C(NH_2)_3^+Cl^-$, was determined in order to identify any structural similarities with those of the guanidinium chloride-*N*,*N*-dimethylacetamide complex (Haas, Harris & Mills, 1965). Even though the crystal structure of guanidinium chloride itself has never been determined, the structures of guanidinium bromide and iodide (Theilacker, 1935) and several other crystals containing the guanidinium ion and derivatives of guanidine have been published (Bryden, 1957).

Experimental

Crystals of pure guanidinium chloride were washed with acetone in order to round all corners and edges. A crystal in the shape of a prolate spheroid with dimensions 0·09 × 0·25 mm was chosen for the analysis. The space group and lattice constants were redetermined (Theilacker, 1931) and are given in Table 1.

Table 1. *Crystal data*

		(Theilacker, 1931)
Space group:	*Pbca*	*Pbca*
Lattice constants:	$a=9{\cdot}18_4$ (±0·005 Å)	9·22
	$b=13{\cdot}03_9$ (±0·005 Å)	13·06
	$c=7{\cdot}76_5$ (±0·005 Å)	7·76
ϱobs:	1·35 g.cm^{-3}	1·35 g.cm^{-3}
ϱcalc: ($z=8$)	1·365	

Three-dimensional intensities were collected (for $2\theta \leq 150°$) on the General Electric XRD 5 with the Single Crystal Orienter using Cu $K\alpha$ radiation 'monochromatized' by Ni–Co balanced filters. No absorption correction was applied and the intensities were converted to $|F|^2$ in the usual way. A total of 960 intensities were collected of which 287 were less than the minimum observable intensity. These reflections were not considered further in the analysis.

Determination of the crystal structure

The crystal structure was solved by the heavy-atom method. The coordinates obtained for the chloride ion from the three Harker lines of the three-dimensional

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* Present address: U.S. Naval Research Laboratory, Washington, D.C., U.S.A.

† Present address: Chemistry Department, University of Glasgow, Glasgow, Scotland.