whether diffusing with or against them or present in uniform concentration throughout. These are illustrated by varied experiments with potassium chloride and hydrochloric acid. The general equations (for infinite dilution) are stated and shown to be common to the cases studied by all writers since Arrhenius. Collision effects of diffusing columns modify the results at higher concentrations.

2. Unprecedentedly high rates of diffusion were found for all constituents in experiments where glycine diffused against hydrochloric acid. In the case of chlorine ion in dilute solution, this amounted to as much as a five-fold increase, although the chlorine ion was not reacting.

STANFORD UNIVERSITY, CALIF.

RECEIVED AUGUST 31, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Crystal Structure of NdAl

BY CHARLES W. STILLWELL* AND ELMER E. JUKKOLA

Because of the scarcity of x-ray data for the alloys of the rare earth metals it has been impossible to consider this group in any of the recent attempts to systematize, on the basis of their structure, binary alloys and intermetallic compounds in general. Any information is of value, therefore, which may indicate how alloys of these elements fit into the general scheme, particularly as to whether or not they resemble the better known alloys of other transition elements.

Experimental Part

The first preparation of NdAl was incidental to the preparation of metallic neodymium by the decomposition of neodymium amalgam in an alundum crucible.[1] The brittle, metallic, octahedral crystals formed were found to contain 85–88% neodymium, indicating the compound NdAl (84.4% Nd) with a varying amount of excess neodymium, probably in solid solution. Other specimens were prepared by fusing together the theoretical amounts of the two metals.

The analysis of an average set of diffraction data for the alloy is shown in Table I, appended to which are other data needed for the structure analysis. The diffraction data were obtained by reflecting CuK radiation from the sharp edge of a multicrystalline piece of the metal. The camera employed has been described before.[2] The method is useful to avoid the necessity for powdering, and to permit the protection of the surface of substances easily oxidized. It is accurate to within 0.5%.

TABLE I

DIFFRACTION DATA FOR THE COMPOUND NdAl

Intensity	d_{hkl}	hkl	a_0
m	3.73	100	3.73
s	2.64	110	3.74
s	2.16	111	3.74
s	1.866	200	3.73
s	1.667	210	3.73
vs	1.522	211	3.73
s	1.318	220	3.73
s	1.237	221, 300	3.71
s	1.176	310	3.72
s	1.122	311	3.73
m	1.075	222	3.73
w	1.032	320	3.72
vs	0.997	321	3.73
vw	.932	400	3.73
s	.907	410, 322	3.74
s	.880	411, 330	3.73
vw	.857	331	3.73
m	.834	420	3.73
w	.818	421	3.74
m	.797	332	3.74

Average a_0 = 3.73 ± 0.01 Å.

Molecular weight of NdAl (84.4% Nd) = 171
Analysis of specimen from which above pattern was obtained = 86.5% Nd
Molecular weight of this specimen = 199
Pycnometric density of this specimen = 6.05 at 25°
Number of molecules NdAl per unit cell = 0.97

Discussion

The diffraction data indicate a cesium chloride type of structure. Since the diffracting powers of neodymium and aluminum are so different, it is to be expected that planes containing only aluminum atoms may not produce diffraction lines, and it is the neodymium atoms, lying on a simple cubic lattice, which produce the pattern obtained. Assuming this structure, the body

* Present address, Baker Laboratory, Cornell University, Ithaca, N. Y.

(1) Jukkola, Audrieth and Hopkins, to be published soon.

(2) Stillwell and Robinson, THIS JOURNAL, **55**, 127 (1933).

diagonal of the unit cube (6.47 Å., calculated from a_0 = 3.73Å.) should be equal to the sum of the diameters of one atom of neodymium, 3.65Å.,[3] and one of aluminum, 2.86Å.[4] This check lends further support to the assumption of the cesium chloride type of structure.

The diffraction patterns for the series of compounds CuZn, AgZn and AuZn illustrate very clearly the effect on diffraction data of a large difference in the atomic numbers of the two elements of the compound.[5] CuZn, in which both atomic varieties have about the same diffracting power, produces a body-centered cubic pattern; AgZn produces a simple cubic pattern in which the additional lines characteristic of the simple cubic are very weak; AuZn produces a simple cubic pattern in which all lines approximate their normal intensities. All three compounds have the cesium chloride type of structure characteristic of many β-phase alloys.

It is evident that the cesium chloride type of structure for NdAl is consistent with all available data and the structure is the same as that of β-brass.

It was first pointed out by Hume-Rothery[6] that in all of the β-phases the ratio of valence electrons to atoms is as 3:2. Recently it has been found that the same structure is also common in alloys of the transition elements (FeAl, CoAl, NiAl). It is not surprising, therefore, to find this β-brass structure for NdAl. Westgren has suggested[7] that in order to make these β-phases fit the 3:2 rule, the valence of the transition element must be assumed to be zero. He cites several reasons why this is a legitimate assumption. It is, for example, significant that Ekman[8] prepared the alloys Co_5Zn_{21}, Ni_5Zn_{21}, Pt_5Zn_{21} and Pd_5Zn_{21}, all of which should have the structure of γ-brass, the ratio of valence electrons to atoms being as 21:13 if the valence of the transition element is assumed to be zero. He found the γ-brass structure in every case.

Summary

The compound NdAl has the cesium chloride type of structure, the structure of β-brass. a_0 = 3.73 ± 0.01 Å. As is the case with other β-phase alloys of the transition elements (CoAl, NiAl, FeAl), the ratio of the number of valence electrons to the number of atoms is as 3:2 if the valence of the transition element is assumed to be zero.

---

[3] Quill, *Z. anorg. allgem. Chem.*, **208**, 273 (1932).

[4] Wyckoff, "The Structure of Crystals," second edition, The Chemical Catalog Co., New York, 1931, p. 192.

[5] Westgren and Phragmen, *Phil. Mag.*, [6] **50**, 331 (1925).

[6] Hume-Rothery, *J. Inst. Metals*, **35**, 295 (1926).

[7] Westgren, *J. Franklin Inst.*, **212**, 577 (1931).

[8] Ekman, *Z. physik. Chem.*, **B12**, 157 (1931).

URBANA, ILLINOIS RECEIVED SEPTEMBER 5, 1933

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Phenanthroline-Ferrous Ion. II. Oxidation Potentials at High Acidities and the Determination of Vanadium[1]

BY GEORGE H. WALDEN, JR., LOUIS P. HAMMETT AND SYLVAN M. EDMONDS

Our investigation of the utility of the new oxidimetric indicator, phenanthroline ferrous ion,[2] has led us by way of a determination of relative oxidation potentials in strong sulfuric acid solutions to oxidimetric methods, both accurate and rapid, for the determination of vanadium and of iron in the presence of each other and of other commonly interfering elements. The present paper deals with the potential measurements and with the determination of vanadium; a subsequent one will describe a direct method, using a silver reductor for the determination of iron in the presence of vanadium and titanium.

Of the numerous methods which have been proposed for the oxidimetric determination of vanadium, those which depend upon a titration of quadrivalent vanadium with an oxidizing agent require the inconvenience of a titration in warm solutions.[3,4] If permanganate is used the presence of chromium renders the end-point fleeting; if ceric sulfate is used, an electrometric titration has been necessary.[4] Those methods which

---

[1] This article is based upon part of a dissertation submitted by Sylvan M. Edmonds to the Faculty of Pure Science of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, May, 1933. The material was presented at the Washington meeting of the American Chemical Society, March, 1933.

[2] Walden, Hammett and Chapman, THIS JOURNAL, **53**, 3908 (1931); **55**, 2649 (1933).

[3] U. S. Bureau of Mines Bull. 212 (1923).

[4] Furman, THIS JOURNAL, **50**, 1675 (1928).