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Abstract

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ON THE NUMBER OF 3*d*-ELECTRONS OF TRANSITION METALS

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The fundamental investigations of Weiss and De Marco ([1,2]), devoted to the x-ray determination of the number of 3*d*-electrons per atom of transition metals in the solid state, lead to the conclusion that there is a profound connection between this number (the electronic structure) and the crystalline structure of the metals. In close-packed metals Cu, Ni, and γ-Fe (face-centered cubic lattice (FCC)) and Co (hexagonal close-packed lattice (HCP)), the majority of the electrons outside the argon shell (which contains 18 electrons) are in atomic 3*d*-states; their spins have two directions (parallel and antiparallel); the number of outer 4*s*-electrons is small (smaller than in the isolated atom). On the contrary, in α-Fe, Cr, and V (body-centered cubic lattice (BCC)) there are few inner 3*d*-electrons (two for α-Fe, zero for the remaining metals); their spins have one direction; the number of outer 4*c* (4*s* and 4*p*)-electrons is large.

Fig. 1. Relation between the electronic structure (n_d) of atoms of transition metals in the solid state and their crystalline structure for the elements of the first long period of the periodic system of elements. The curves are according to equation (1); the dots and crosses are experiment ([1,2,3]) (crosses are from paramagnetic data for strongly dilute solid solutions of Mn and Fe in Al([11])).

The purpose of the present work is to show that the relation under consideration between the structures and the total number n_d of atomic 3*d*-electrons can be expressed by the following relation:

$$n_d = N - \{[(Z/2) - \omega\pi^2\nu^2]^2 + p\}, \tag{1}$$

where the expression in braces gives the number of unoccupied places in the 3*d*-shell of an atom of a transition metal in the solid state, $N = 10$ (the maximum possible number of 3*d*-electrons with two spin directions) for FCC and HCP, $N = 5$ (the maximum possible number of 3*d*-electrons with one spin direction) for BCC, and Z is the atomic number of the element. The numerical coefficient $\omega\pi^2\nu^2$ was calculated by Dyson ([3]), who investigated a model of a ferromagnet, a cubic lattice of identical spins with isotropic exchange coupling between nearest neighbors. Here ν is a geometrical factor

$$\nu = \delta^2 V^{-2/3} = 1;\ 2^{1/3} \text{ and } 3 \cdot 2^{-4/3}. \tag{2}$$

for the simple cubic (SC), FCC, and BCC lattices, respectively; $\vec{\delta}$ is the vector connecting a lattice atom with its nearest neighbors $\left(|\vec{\delta}| = a;\ a\sqrt{3}/2 \text{ and } a/\sqrt{2}\right.$, respectively, where a is the lattice constant in Å), V is the volume of the primitive cell ($V = a^3$; $a^3/4$ and $a^3/2$ for SC, FCC, and BCC, respectively; a^3 is the volume of the unit cell of the cubic lattice. BCC may be regarded as consisting of two simple cubic lattices inserted into one another, and FCC as four). The exact expression for the numerical coefficient ω has the form

$$\omega = 25/32 + 3\langle\cos^4\varphi\rangle/4, \tag{3}$$

where φ is the angle between two lattice vectors $(\vec{\delta}, \vec{\delta}')$ that connect nearest-neighbor atoms, and $\langle\cos^4\varphi\rangle$ denotes the average over all $\vec{\delta}$ and $\vec{\delta}'$; the calculation shows that

$$\omega = 33/32; \quad 15/16 \quad \text{and} \quad 281/288 \tag{4}$$

for the three types of cubic lattice listed. In this case the Dyson coefficient has the following values:

$$\omega\pi^2\gamma^2 = 10.2; \quad 14.7 \quad \text{and} \quad 13.7 \tag{5}$$

for SC, FCC, and BCC, respectively. The quantity p in relation (1) is equal to 0 for FCC and HCP and to 2 for BCC. For HCP the coefficient $\omega\pi^2\gamma^2$, according to our calculations, has the same value as for FCC. In our work ([4]), proceeding from other considerations, the numbers 14.75 for FCC and HCP and 13.75 for BCC were found; these are close to the above-considered values of the Dyson coefficient (14.7 and 13.7, respectively).

Table 1

Number of $3d$-electrons in transition metals

Element (Z)	Crystal structure	Total number of $3d$-electrons in isolated atom	Total number of $3d$-electrons in a metal atom: experiment	Total number of $3d$-electrons in a metal atom: calculated
Cu (29)	FCC	10	9.8 ± 0.3 ([1])	10
Ni (28)	FCC	8	9.7 ± 0.3 ([1])	9.5
Co (27)	HCP	7	8.4 ± 0.3 ([1])	8.6
α-Co (27)	BCC*	7	3 ([2])	3

Element (Z)	Crystal structure	Total number of $3d$-electrons in isolated atom	Total number of $3d$-electrons in a metal atom: experiment	Total number of $3d$-electrons in a metal atom: calculated
γ-Fe (26)	FCC	6	7 ([2])	7.2
α-Fe (26)	BCC	6	2.3 ± 0.3 ([1])	2.5
α-Fe (26)	BCC**	6	3 ([2])	2.5
α-Mn (25)	BCC	5	–	1.6
Cr (24)	BCC	5	0.2 ± 0.4 ([1])	0.2
V (23)	BCC	3	0 ([2])	0
Ti (22)	HCP	2	0 ([2])	0

* Co in an alloy of 30% Fe and 70% Co with a BCC lattice.
** Fe in an alloy of 30% Fe and 70% Co with a BCC lattice.

Table 1 gives data on the numbers of $3d$-electrons calculated from the proposed relation (1) and determined experimentally ([1],[2]). The agreement between these data appears to us satisfactory (see Fig. 1). From Fig. 1 it is seen that $3d$-electrons in atoms of solid metals appear for the first time in Cr (in free atoms, in Sc). The fact that $n_d < 0$ for $Z < 24$ (shown by the dotted line in Fig. 1) means that Sc, Ti, and V have no $3d$-electrons.

Above, in calculating the geometrical factor γ from relation (2) for BCC, only the nearest neighbors of the atom were taken into account. In the present case, however, it is also necessary to take into account neighbors following the nearest ones. If this circumstance is considered, still better agreement is obtained between the calculated and experimental values.

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CITED LITERATURE

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Note: Figure translations are in progress. See original paper for figures.