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Ferromagnetism, Antiferromagnetism and Superconductivity in Periodic Table of D.I. Mendeleev

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Abstract. Definite regularity in the distribution of ferromagnetic, antiferromagnetic and superconducting elements is observed in the periodic table starting with the 4-th period. These trends were explained by distinction of degree of division of the d (f)- or p-orbitals of neighboring atoms in the crystal. We calculated also the radii of the external d (f)- and p-orbitals and the nearest to them orbitals with the Slater's method. It is demonstrated that in the superconducting crystals the d-shells approach the nucleus of neighboring atoms are much closely those for ferromagnetic or antiferromagnetic crystals.

Introduction

The nature of superconductivity (SC), antiferromagnetism (AFM) and ferromagnetism (FM) is only partly clear at present, in spite of numerous researches in this area. At the same time, the clear regularity of arrangement of superconductors, antiferromagnetics and ferromagnetics in the periodical table is amazing. The distributions of elements showing SC, AF and FM in the periodical table is analyzed in this article. It seems plausible that this analysis may allow a unified consideration of these phenomena. In the present paper the radii of external *d-, f-* and *p*-shells and the shells nearest to them, calculated by us with the Slater's method [1], are submitted. Comparison of radii of external *d-, f-* and *p*-shells with the inter-atomic distances in crystals is permitted to reveal the connection of FM, AFM and SC with the division degree of these shells in crystals. Recently a distribution of the elements with indicated types of ordering was viewed in our short article [2]. This consideration was based on supposition that indicated types of ordering are connected with the filling of the *d-, f-* and *p*-shells of atoms.

Elements allocation in the periodic table of D.I. Mendeleev

Fig. 1 shows the periodic table. Let us examine how one type of ordering is substituted for another when moving from left to right along the 4-th period of the table. When the number of 3*d*-electrons n equals 1 (Sc), SC appears both in thin films and in bulk samples under pressure. SC takes place at $n = 2$ (Ti) and 3 (V) in bulk samples. The Cr bulk samples with $n = 5$ show AFM, SC also occurs in thin films. Then follow antiferromagnetic Mn ($n = 5$) and the ferromagnets Fe ($n = 6$), Co ($n = 7$) and Ni ($n = 8$), in which the indicated types of ordering take place in bulk samples. It is necessary to note that α-Fe, having a b.c.c. structure, is a ferromagnet while γ-Fe with f.c.c. structure is an antiferromagnet. Under a pressure of ~15 GPa, α-Fe undergoes a structural transition from b.c.c. to f.c.c. that is accompanied by a FM-SC transition; at the same time SC is observed between 15 and 30 GPa [3]. Cu ($n = 10$), which follows Ni, shows none of the 3 types of ordering. However, in the Cu compounds, where Cu is bi- or trivalent (n = 9, 8 respectively), high-temperature SC is observed. Moving along this period, superconductors again occur: Zn (bulk form; the configuration of electrons is $3d^{10}4s^2$); Ga, Ge (under pressure in thin films); As, Se (only under pressure), in which the 4*p*-orbital is sequentially filled with the maximum number of electrons equal to 4. Thus, the following tendency exists in the 3-d period: SC occurs only when the number of 3*d*-electrons is small ($1 \le n \le 3$) or, vice versa, large ($8 \le n \le 10$). It should be note that elements at a boundary between different types of ordering possess both types at once: bulk Cr with a b.c.c. lattice is antiferromagnetic but, in thin films, it is a superconductor; Fe with a b.c.c. lattice is a ferromagnet and γ-Fe is an antiferromagnetic. Furthermore, in the 4-th period SC begins to manifest only under pressure and in thin films (Sc) and ends at Se, only under pressure.

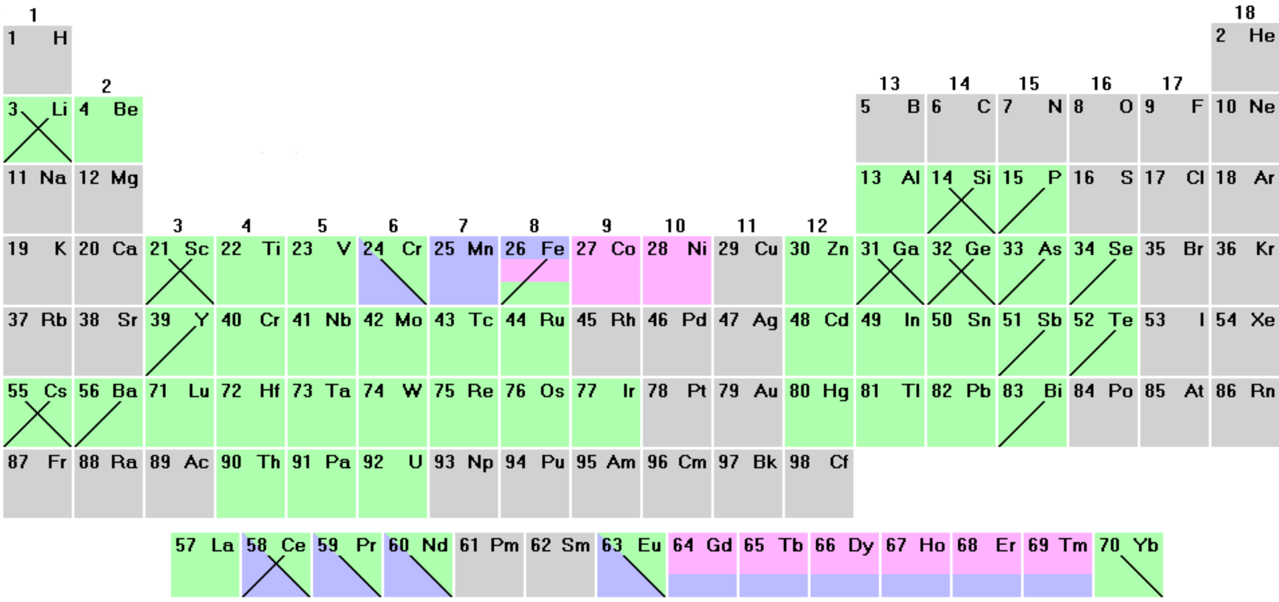

Fig. 1. The periodic Table of D.I. Mendeleev. Ferromagnets, antiferromagnetics and superconductors are coloured Red, Blue and Green, respectively. The signs / and \ indicate superconductivity under pressure and in thin films respectively.

Similar trends are observed in other periods. The 5-th and 6-th periods, in which the 4*d*- and 5*d*-orbitals, respectively, are filled, contain much more superconductors than the 4-th period but contain no FM or AFM elements those manifesting no ordering elements occupy their places. A second area in the periodic table, where AFM and FM are to be observed, is the group of lanthanides. Here, the 4*f*-orbital is filled with the number of *f*-electrons *k*. Thus, some basic trends for the existence of SC, FM, AFM areas are found. Mention should be made of the phenomenon of lanthanide contraction and *d*-compression, implying that an increase in number of electrons in the *d*- and *f*-shells results in a decrease in their radii. FM occurs for the elements, in which the 3*d*-shell is more than half-filled, or for those having a 4*f*-shell, in which the sum $k+n \ge 8$, that is, for the elements with the smallest radii. AFM is observed in the elements, in which the 3*d*- or 4*f*-shell is precisely half-filled. Furthermore, for 4*f*-elements a combination of SC and AFM occurs at $2 \le k \le 4$ and a mixture of AFM and FM occurs at $k+n \ge 8$. SC is observed for 3*d*-elements with a less than half-filled 3*d*-shell ($1 \le n \le 3$) and with a completely filled 3*d*-shell, at the same time the 4*p*-orbital is filled up to 4 and the 4*s*-orbital is completely filled. For lanthanides SC takes place only under pressure and in thin films with a less than half-filled 4*f*-shell ($1 \le k \le 4$) and for one element, Yb, with the completely filled 4*f*- and 6*s*-orbitals. That is, the 3*d*- and 4*f*-shells of SC elements are compressed less than in ferromagnets. As *d*-shells move away from the nucleus, the region of existence of SC expands. So, for the 4*d*- and 5*d*-elements SC occurs at $1 \le n \le 7$. This is due to the fact that the 4*d* and 5*d* wave functions are damped out at a distance from the nucleus longer than the 3*d* wave functions and consequently having a wide overlap with neighboring atoms. For heavier elements, where the 6*d*- and 5*f*-orbitals are filled, SC occurs only for $2 \le n+k \le 4$. Further, SC is observed for the elements, in which the 3*p*-, 4*p*-, 5*p*- and 6*p*-orbitals are not completely filled and contain no more than 4 electrons. Thus, SC occurs for elements with no more than 0.7-filled *d*- and *p*-orbitals and 0.5-filled *f*-orbitals. SC occurs for the elements with completely filled *d*-, *f*- and *s*-orbitals (Zn, Cd, Hg, Yb) too.

Explanation of Superconductors, Ferromagnets and Antiferromagnetics Allocation in the Periodic Table of D.I. Mendeleev

FM and AFM in elements are connected with the presence in these incompletely filled *d*- and *f*-shells, that are petal-shaped and are favorably overlapped with neighboring atoms in crystals. The form of the *p*-shells is similar. It is well known that atoms must be sufficiently separated to facilitate the FM interaction. Only in this case the exchange integral become positive. At smaller distances between atoms negative exchange interactions prevail and AFM order occurs in the crystal [4]. We compared the radii *r* of the *d*- and *p*-shells, calculated by the Slater method [1], with the inter-atomic distances in the elemental crystals *b*, taken from Ref. [5]. Thus shows that in SC crystals the *d*-shells approach the nucleus of neighboring atoms are considerably closer than those of FM or AFM crystals. For example, in the 4-th period the difference b - r for superconductors is within the limits 1.52 – 1.62 Å whereas this difference for antiferromagnetics equals to 1.63 Å for Cr and 1.65 Å for Mn. For ferromagnets, it is substantially greater: from 1.72 Å for Fe to 1.86 Å for Ni. Fig. 2 shows that in some superconductors of the 5-th period the 4*d*-shell of each atom approaches the deeper $4p^6$-shell of neighboring atoms (Zr, Nb, Mo) and are disposed between the $4p^6$- and $4d^1$-shells. Penetration of external 6*p*-orbitals inside the neighboring atoms is also observed in crystals of some superconducting elements located at the end of the period. Thus, the $5p^n$-shells are disposed between the deeper $5s^1$ and $5s^2$-shells of neighboring atoms (for In and Sn). In the 6-th period for a number of superconductors the external 5*d*-shells of each atom penetrate inside the neighboring atom disposing between deeper $5p^6$- and $5d^1$-shells of neighboring atoms (Lu, Hf, Ta, W). The $6p^1$-shell of Tl is disposed in neighboring atoms between deeper $6s^1$- and $5d^{10}$-shells of neighboring atoms. Hence in these superconductors the electron in the external *d*(*p*) shell is situated in neighboring atom in a stronger electrical field than in its own. In this case, the separation of spin and charge for the electron is possible and the charges without spin become bosons. Although, in some superconductors the external *d*-/*p*-orbitals do not penetrate inside the external *d*-/*p*-orbitals of neighboring atoms, they approach them sufficiently closely. In this case the external *d*-/*p*-orbitals are apparently subjected to the influence of the electrical field of neighboring atoms.

That is, the electrons in these orbitals are situated near neighboring atoms in an electrical field different from its own and the separation of spin and charge for the electron is also possible. Spins that have magnetic moments are ordered antiparallel in pairs. Magnetic field transfers this pair in a parallel state and a magnetic flux component along of magnetic field from the pair is equal to one fluxon (quant of magnetic flux).

It is interesting, as can be seen from Fig. 1, that SC for a number of elements occurs only in thin films (Cr, Ga, Ge, Si, Sc, Nd, Eu and so on) or under pressure (Y, Sb, Te and so on). It is obvious that, under pressure, neighboring atoms approach each other more closely (distance *b* diminishes). It has been proposed that, at high pressures, $s \rightarrow d$ electron transfer occurs, for example, in the trivalent rare earths Sc, Y and Lu and in nonmetals such as Te, I etc.[6,7]. In thin films compression of the crystalline lattice occurs by connection with substrate.

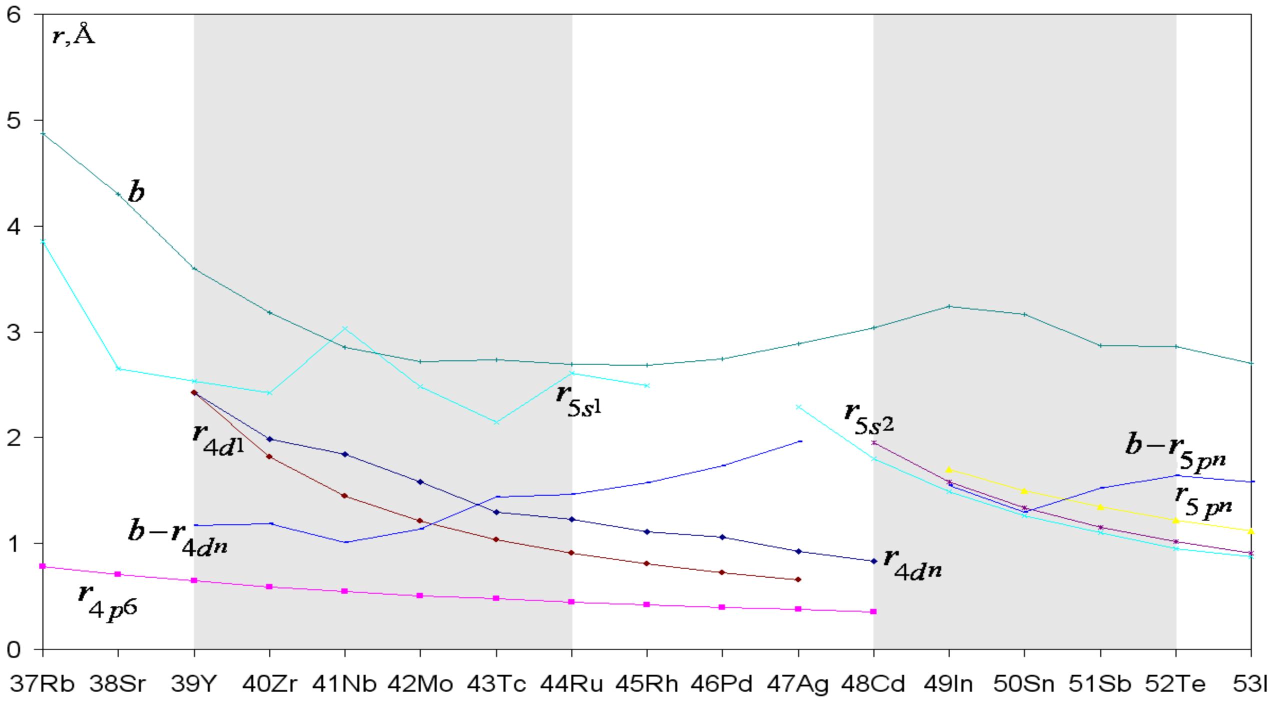

Fig. 2**.** The 5-th period of the periodic table. The figure shows the dependence on atomic number of the radii of various external shells of atoms. Here $r_{5p}{}^{n}$ and $r_{4d}{}^{n}$ are, respectively, the radii of the external 5*p*- and 4*d* – shells of the atom. The differences $b - r_{4d}{}^{n}$ and $b - r_{5p}{}^{n}$ indicate the degree of penetration of the external *d*(*p*) orbitals in the neighboring atom. Regions of superconducting elements are darkened.

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