Magnetism and stability interplay: Correlations in simple BCC-based Fe intermetallic compounds

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ABSTRACT

In this work, we present an ab initio study of a large set of simple, highly symmetrical ordered Fe-compounds (superlattices of the body-centered cubic structure, BCC), in order to analyze the role of the magnetism in the phase stability of these compounds. Our results, confirm that ferromagnetism and compound stability can be related. That is, the highest magnetic moments are observed for the least stable compounds. We also show that compounds have qualitatively different behavior as regards stability, according to whether their nature is ferromagnetic or non-magnetic.

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1. Introduction

Unraveling the laws behind the stability of intermetallic compounds is a recurring topic in Materials Science. It is recognized that both magnetism and chemical order play a role on reaching the observed stability, but investigations were so far restricted to determine in which conditions ferromagnetic or antiferromagnetic alignment will occur.

Chemical (or configurational) and magnetic order are the two most common cooperative phenomena observed in the nature of crystalline materials. In many compounds both phenomena occur simultaneously, showing that some degree of interplay must exist. This interrelation has already been investigated by many researchers, but results have been mainly directed to determine under which conditions ferromagnetic (or antiferromagnetic) alignment takes place (e. g. Ref. [1]). Bieber and coworkers [2,3] explicitly investigated the interaction between magnetic and chemical order in the stability of intermetallic compounds, using an ab initio technique (Generalized Perturbation Method in the Coherent Potential Approximation, CPA-GPM). These works were motivated by an experimental result, namely, the observation that the short-range order (SRO) parameter for diluted Fe−Co and Fe−V compounds shows different behaviors with onset of ferromagnetism, the former exhibiting an increment in ordering while the later presents a depression of ordering. In Refs. [3] and [4], a simple explanation on how magnetic order affects the interactions between clusters of atoms in the CPA reference medium is given, interpreting the experimental results in terms of band structure

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properties.

The investigation of the stability of intermetallic compounds is not as easy as one would think at first. An obvious criterion for the stability of a compound would be the appearance of that particular compound in the experimental phase diagram of a given system. Such criterion is not convenient, however, because the appearance of a phase depends on the stability of all other compounds in that system. A phase may not be experimentally observed simply because there is another compound or a mixture of compounds which is more stable. This approach has been used by Pettifor in his phenomenological stability maps [5,6]. An alternative would be to consider that a given intermetallic structure is made of, at least, two species. Stability against spontaneous dissociation in these species could be considered. It is commonplace that the constituent species of a given compound have quite different crystallographic builds-up, usually much simpler, such as primitive Body-Centered Cubic (BCC). The energy difference between both configurations (inter-metallic compound and dissociated species) may contain, there-fore, a parcel ascribed to this difference in the atomic arrangements.

In the present work we discuss intermetallic compound stability focusing on a set of highly symmetric binary superlattices of the BCC structure. These compounds, namely, the B2−FeX, the B32−FeX and the D0$_3$−Fe$_3$X and FeX$_3$, present cubic symmetry and no internal positional degrees-of-freedom, such that, apart from ordering and the proportional expansion or contraction of the lattice, the atoms are found in the same positions as in the parent BCC lattice. This allows to treat its stability in terms of the competition between the mechanical mixture of the pure species in the BCC structure A2−Fe and A2−X. We define the compound formation energy, $^{f}U_{Fe_{x}X_{y}}^{\Phi}$, as:

$$^{f}U_{Fe_{x}X_{y}}^{\Phi} = \frac{^{0}U_{Fe_{x}X_{y}}^{\Phi} - x\,^{0}U_{Fe}^{A2} - y\,^{0}U_{X}^{A2}}{x + y} \quad (1)$$

where $^{0}U^{\Phi}$ are the total energies of compound Φ and x, y take care of the stoichiometry. This furnishes not only a stability criterion ($^{f}U_{Fe_{x}X_{y}}^{\Phi} < 0$), but also a quantitative measure of this stability. Apart from the eventual difference of reference state, this quantity is equivalent to the thermodynamic formation energy [7]. Further, we chose X among the early transition metals, imposing the condition that its ground state is non magnetic, namely X = Ti, V, Zr, Nb, Mo, Hf, Ta and W. Finally we restrain our analysis to collinear ferro-magnetism. With these simplifications practically all conditions (the exception is the lattice volume, since the lattice parameter is characteristic of each compound) are kept constant within the same compound, allowing to separate the influence of different distributions of species in the lattice in the formation energies. Experimentally only the B2−FeTi compound is observed as a stable phase in the respective binary system [8]. Also, both systems Fe-Zr and Fe-Hf show other, more stable, compounds with different stoichiometries [9,10]. It is interesting to observe that, in these two cases, the B2-compound is almost in the limit to become stable in the respective systems [9]. Both systems are known for their glass forming abilities. The usual criteria for screening glass forming al-loys require seeking systems in which the formation energy of the liquid phase is strongly negative [11]. The presence of a metastable B2 phase is consistent with a negative formation energy in the liquid state, since the nearest neighborhoods are similar in both cases, resulting, probably, in a strong SRO parameter in the liquid [12]. With such a specific list of systems, we cannot rely on existing systems to perform our analysis, so ab initio calculations are used as an experimental tool, in the same sense as calorimetric measure-ments would be used, to probe these compounds.

To sum up, the BCC structures, even when not observed exper-imentally, were chosen due to their highly symmetric lattices, that gives us a controlled scenario to analyze stability and the correla-tion with magnetism.

2. Methodology

2.1. Electronic structure calculations

First principles electronic-structure calculations were carried out with the full-potential linear augmented-plane-wave method using the Wien2k code [13] in the framework of Density Functional Theory [14]. The exchange-correlation potential was treated using the Wu-Cohen [15] parametrization of the generalized-gradient approximation [14]. The muffin-tin radius (R_{MT}) used for all ele-ments was 0.105 nm, and the product of R_{MT} and the maximum wave vector included in the interstitial region (K_{max}) was $R_{MT} \times K_{max} = 9$. Integration in the reciprocal space was performed using the tetrahedron method, taking 20 000 $k-points$ in the First Brillouin Zone. All calculations have been performed in order to ensure a ΔE in the formation energy smaller than 10^{-2} eV. We have considered the following set of cubic crystal structures in the cal-culations: A2 (BCC) for all pure elements (Fe and X), B2 (FeX), B32 (FeX), and D0$_3$ (both FeX$_3$ and Fe$_3$X). See Fig. 1.

3. Results and discussion

3.1. Compound formation energies

Fig. 2 shows the compound formation energies (^{f}U) plotted against the total magnetic moment per unit cell (M_{Tot}) for the investigated compounds. For the compounds which possess mag-netic moment, a clear trend is observed, in which the compound stability decreases (i.e. its formation energy becomes less negative) with increasing magnetic moment, with a roughly linear correla-tion among compounds with the same structure. The only excep-tions to this behavior are the B32−FeNb and B32−FeTa compounds. These have similar formation energies to that observed for the B32−FeZr and B32−FeHf, while they present magnetic moments
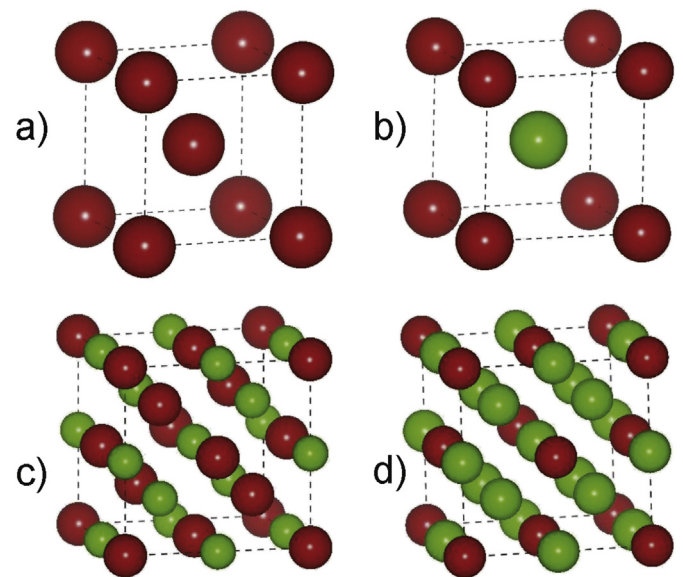

Fig. 1. Cubic crystal structures a) A2, b) B2, c) B32 and d) D0$_3$. Red and green spheres represent distinct species. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
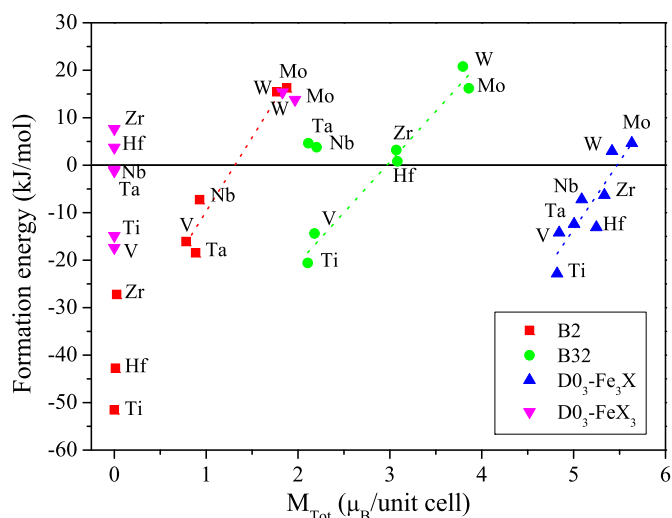
Fig. 2. Correlation between total magnetic moment and formation energies for the investigated compounds (μ_B is the Bohr magneton).

similar to B32—FeV and B32—FeTi.

The case of compounds with no magnetic moment is more complex. Let us consider, for instance, compounds B2—FeTi, B2—FeZr and B2—FeHf. Among these, the B2—FeTi is the most stable. This fact is to be expected, since Titanium is, like iron, a 3d element. This means that the d electron bands are located around the same energy levels in both species, increasing hybridization and, consequently, favoring formation of this compound. The next most stable compound is B2—FeHf (5d), and not B2—FeZr (4d). This behavior can be understood from the fact that, due to scalar-relativistic effects, the 4d band is located below that of the isoelectronic 3d element, but the 5d band is again higher in energy, compared with 4d. This effect brings a general trend in properties that go mostly like 3d-5d-4d. This picture is also confirmed for the D0$_3$—FeX$_3$ cases. We observe that the most stable compound is always the one in which the X atom is a 3d transition metal (D0$_3$—FeTi$_3$ and D0$_3$—FeV$_3$) and the least stable is always the one in which X is a 4d transition metal (D0$_3$—FeZr$_3$ and D0$_3$—FeNb$_3$). In an intermediate place, one founds D0$_3$—FeHf$_3$ and D0$_3$—FeTa$_3$ for each group.

One factor which is long recognized to play a role in intermetallic compound stabilization is the so called "atomic size mismatch factor" [16], which has been previously correlated with important properties of intermetallic phases [17,18]. Nevertheless, the question is how to define the "atom size" in an intermetallic alloy. As the investigated compounds are highly symmetric, a simple hard spheres model can be used to postulate an apparent atomic radius for each compound. Since the compact directions are, in all cases, the <111> directions, and assuming the "spheres" touch along this direction, we introduce the apparent X atom size mismatch, ρ as:

$$\rho = \frac{r_X - r_{Fe}}{r_{Fe}} = \alpha \frac{r_{1nn}^{\Phi} - r_{1nn}^{A2-Fe}}{r_{1nn}^{A2-Fe}} \tag{2}$$

where r_{1nn}^{Φ} is the nearest neighbor distance in the compound Φ and α is a geometric factor, characteristic of each structure (α = 1 for B2 and B32, α = 2 for D0$_3$-Fe$_3$X and α = $\frac{2}{3}$ for D0$_3$-FeX$_3$). Fig. 3(a) shows the formation energies as a function of ρ only for the non magnetic compounds: a correlation within a given group (compounds joined by lines), and in the expected way (stability decreases with increasing misfit) can be observed. When the same analysis is performed in the magnetic compounds (Fig. 3(b)) no correlation
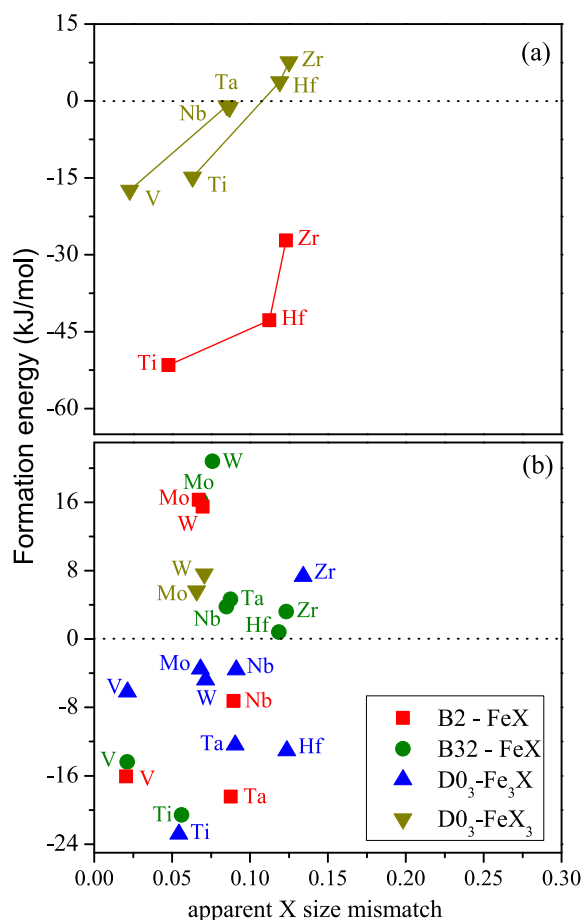

Fig. 3. Correlation between compound formation energy and the apparent X atom size mismatch (defined in the main text) for (a) non magnetic and (b) magnetic compounds. In case (a), they are joined according to their groups in the periodic table.

can be discerned showing that, here again, the onset of magnetism "switches off" a correlation.

Since iron atoms are the principal species which polarizes, one would, in principle, expect some kind of correlation between the formation energies and the iron magnetic moments (m_{Fe}), see
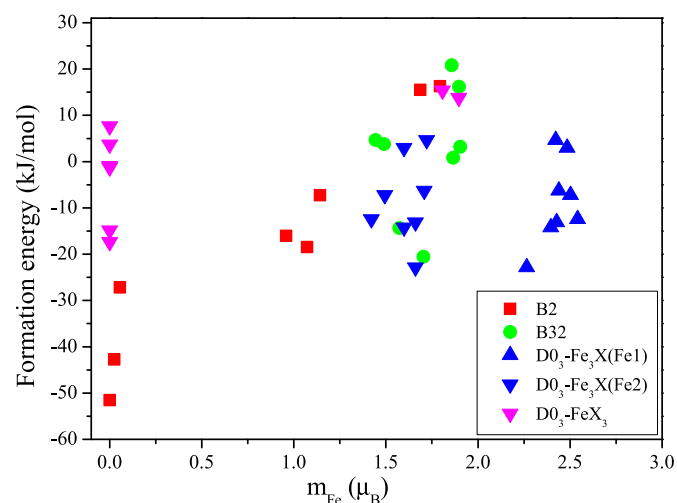

Fig. 4. Correlation between iron magnetic moment and formation energies for the investigated compounds.

Fig. 4. This idea must be abandoned when analyzing thoroughly our model. The change in variable (from total magnetic moment to iron magnetic moment) does not affect the compounds which possess no magnetic moment. The remaining compounds, however, are divided roughly into two categories: those with only one iron site per unit cell, (namely the magnetic B2, B32 and $D0_3$-FeX_3 compounds) where a correlation between iron magnetic moment and formation energy can be defined, and the $D0_3$-Fe_3X compounds with two iron sites per unit cell. It is clear that, having two different iron magnetic moments (m_{Fe}) per compound, one cannot define a unique correlation between the formation energies and m_{Fe}. One interesting observation can be made, however, the second iron site on these compounds behaves similar to the iron site on the B32 compounds, with similar m_{Fe} values, see Fig. 4.

3.2. Effect of the iron neighborhoods

The magnetic moment of iron is determined by its neighborhood. This can be better appreciated by consideration of Fig. 5, which presents the iron magnetic moment as a function of the number of X nearest neighbors. The Fe1 site in $D0_3$-Fe_3X is surrounded by eight iron atoms, hence it resembles the environment in α−Fe (A2 Fe), which presents a magnetic moment of 2.2 μ_B [19] (2.17 μ_B, according to our calculations). In the remaining cases, the nearest neighborhood of iron is composed either by 4 Fe and 4 X atoms (in the Fe2 site in $D0_3$-Fe_3X and in the B32−FeX compound) or by 8 X atoms (in B2−FeX and in the iron site of $D0_3$-FeX_3).

As already observed, the Fe1 environment shows the higher moments, with a small dispersion. Decreasing the number of Fe atoms in the nearest neighbor coordination shell to four, results in a decrease of the local moment and an increase in the dispersion. For the environments with zero iron nearest neighbors the dispersion is so high that virtually all possible values of iron magnetic moments are obtained. In particular for the B2 iron environments, we observe that the magnetic moment depends on the group to which X belongs in the periodic table, with Mo and W inducing moments which are similar to the pure iron environment, Nb, Ta and V belonging to the intermediate group (as in the environment with four iron nearest neighbors) and Ti, Zr and Hf presenting only residual moments. These results are in line with the Slater-Pauling
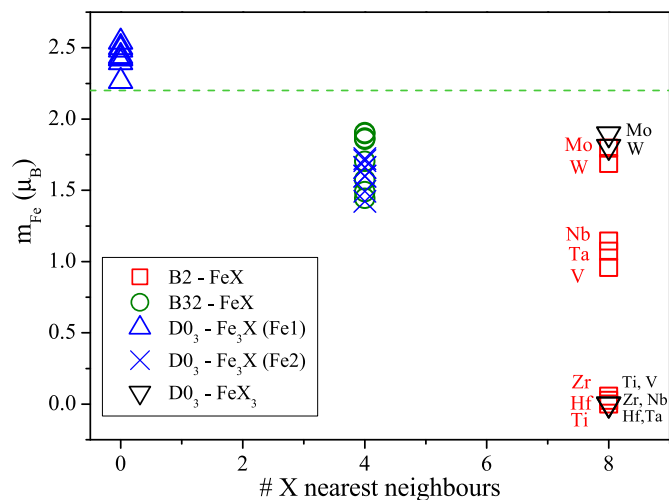

Fig. 5. Iron magnetic moments in the investigated compounds as a function of the number of X atoms in the nearest-neighbor coordination shell. The green (dashed) line represents the experimental magnetic moment of iron [19]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

behavior [24,25]. As the present results show, the compound formation energies correlate with the total magnetization rather than with the magnetic moment of iron and the larger the magnetic moment, the less stable is the compound. In the framework of the covalent magnetism of alloys [26,27], from a simple molecular orbital scheme, this behavior can be associated with the fact that the increase in the magnetic moments corresponds to a filling of more anti-bonding states in the majority spin channel, reducing the stability. This fact is simpler to be noticed by inspecting the projected density of states (not shown) into the case of the B2 compounds. Furthermore, we recover an idea expressed in Ref. [20] almost 100 years ago, where the formation of an ordered intermetallic compound can be understood as a competition, in which Fe−X pairs replaces Fe−Fe and X−X pairs, schematically in the form

$$2\delta_{Fe-X} \leftrightarrows \delta_{Fe-Fe} + \delta_{X-X}. \qquad (3)$$

here δ takes account of the different stoichiometries. As the authors warn, this idea is too simplistic, but it allows us to draw a simple model that explains the observed correlation. In fact, the above mentioned competition, in the case of a non-magnetic compound, involves the formation of a non-magnetic (virtual) Fe−Fe pair. Pure iron, however, is ferromagnetic and the formation of a paramagnetic Fe−Fe pair requires paying an energy "penalty". In this sense, the compound becomes more stable not because the Fe−X pairs become stronger, but because the Fe−Fe pairs become weaker. This effect is amplified by the X−X pairs, since they also change from a natural paramagnetic state to a (virtual) polarized state. This model also explains why the formation energies do not correlate with the local magnetic moment, but with the total magnetic moment, since the new Fe−Fe pair is virtual and must be formed in the environment defined by the total compound magnetization. In this way, the "mean field" idea is validated, since it can successfully explain the stability trends in these compounds.

The present results are limited to the cases here investigated, there is, however, no reason to believe they are restricted to iron compounds or to the simple structures here investigated. Iron compounds based on the Face centered cubic (FCC) structure would deserve to be investigated, but FCC Fe has a small magnetic moment (and is antiferromagnetic [21,22]) and some of these structures present internal degrees of freedom for relaxation which result in larger changes of the crystal symmetry, introducing new variables in the calculation (for example, the equiatomic L1$_0$ structure, although presenting the atoms approximately in the same positions as in the corresponding disordered FCC lattice, is slightly tetragonal). Hexagonal close-packed cobalt (1.71 μ_B) [23] would surely be more appropriate for a test.

4. Conclusions

The *ab-initio* study of the bcc Fe-X model compounds presented here support that ferromagnetism and compound stability are related: the highest total magnetic moments are found in the least stable compounds. The implications of the present results are found both in the case of equilibrium and non-equilibrium situations. Reference states are usually considered necessary, but brings no additional information to a thermodynamic calculation. They are just integration constants when solving the differential equation of states. While this is true for equilibrium situations, it is not necessarily so for non-equilibrium. This offers an insight that could be used to explain some phenomena related to the kinetics of phase transitions, mainly those that can be explained by local equilibria at the interface between phases. That is, it makes more sense to use a virtual state for the reference state of a component when trying to describe a phase transformation, since it is what the material

"feels" when proceeding towards equilibrium. This is a major change in paradigm in thermodynamics and could lead to the solution of several paradoxes of thermodynamic calculations.

References

[1] J.B. Staunton, Rep. Prog. Phys. 57 (1994) 1289—1344.
[2] A. Bieber, F. Gautier, Acta Metall. 34 (1986) 2291.
[3] A. Bieber, F. Gautier, J. Magn. Magn. Mater. 99 (1991) 293.
[4] V. Pierron-Bohnes, M.C. Cadeville, A. Bieber, F. Gautier, J. Magn. Magn. Mater. 54—57 (1986) 1027.
[5] D.G. Pettifor, J. Phys, C Solid State Phys. 19 (1986) 285—313.
[6] D.G. Pettifor, J. Chem, Soc. Faraday Trans. 86 (1990) 1209—1213.
[7] C.H.P. Lupis, Chemical Thermodynamics of Materials, Prentice Hall, 1983.
[8] L.T.F. Eleno, C.G. Schön, J. Balum, G. Inden, Z. Met. 95 (2004) 464—468.
[9] K. Mahdouk, J.-C. Gachon, J. Phase Equilibria 17 (1996) 218—227.
[10] F. Stein, G. Sauthoff, M. Palm, J. Phase Equilibria 480 (2002).
[11] C. Suryanarayanna, A. Inoue, Int. Mater. Rev. 58 (2013) 131—166.
[12] M. Palumbo, L. Battezzati, CALPHAD 32 (2008) 295—314.
[13] P. Blaha, K. Schwarz, G. Madsen, D. Kvasnicka, J. Luitz, WIEN2k: an Augmented Plane Wave Plus Local Orbitals Program for Calculating Crystal Properties, Vienna University of Technology, Inst. Physical and Theoretical Chemistry, Getreidemarkt 9/156, A-1060 Vienna, Austria, 2008.
[14] R.M. Martin, Electronic Structure: Basic Theory and Practical Methods, Cambridge, 2008.
[15] Z. Wu, R.E. Cohen, Phys. Rev. B 73 (2006) 235116.
[16] W. Hume-Rothery, G.W. Mabbott, K.M. Channel Evans, Philos. Trans. R. Soc. Lond. A 233 (1934) 1—97.
[17] L. Anthony, B. Fultz, Acta Metall. Mater. 43 (1995) 3885—3891.
[18] F. Stein, A. Schneider, G. Frommeyer, Intermetallics 11 (2003) 71—82.
[19] N.W. Ashcroft, N.D. Mermin, Solid State Physics, Cengage, 1976.
[20] G. Borelius, C.H. Johansson, J.O. Linde, Ann. Phys. 391 (1928) 291—318.
[21] S.C. Abrahams, L. Guttman, J.S. Kasper, Phys. Rev. 127 (1962) 2052—2055.
[22] C. Paduani, Mater. Sci. Eng. B 121 (2005) 9—11.
[23] R.M. Moon, Phys. Rev. 136 (1964) A195—A202.
[24] J.C. Slater, Phys. Rev. 49 (1936) 931—937.
[25] L. Pauling, Phys. Rev. 54 (1938) 899—904.
[26] G.S. Rohrer, Structure and Bonding in Crystalline Materials, Cambridge University Press, 2004.
[27] P. Mohn, Magnetism in the Solid State, Springe-Verlag, 2003.