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Phase formation in $L1_0$ magnets

Ralph Skomski
University of Nebraska-Lincoln, rskomski2@unl.edu

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R. Skomski[a)]

Department of Physics and Astronomy, University of Nebraska, Lincoln, Nebraska 68588
and Nebraska Center for Materials and Nanoscience, University of Nebraska, Lincoln, Nebraska 68588

Structural and magnetic properties of substituted $L1_0$ compounds are investigated. Focus is on $L1_0$ structures of the general type ABC_2, where each second layer of the original structure is replaced by a checkerboard of A and B atoms. At low temperatures, $L1_0$ compounds with ABC_2 stoichiometry will segregate into AC and AB $L1_0$ phases, forming an ordered ABC_2 compound or exhibit a transition into a more complicated structure. The ordering has a strong impact on the magnetism of the alloys, especially on the anisotropy. The hypothetical new ternary compounds are of potential interest in various areas of magnetism, including magnetic recording and permanent magnetism. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2711801]

I. INTRODUCTION

The search for new intermetallic compounds, such as CoPt,[1,2] $Nd_2Fe_{14}B$,[3] and $SmCo_5$,[4] has been a long standing task in magnetism. Examples are permanent magnets, where new phases have contributed to the energy-product increase from about 1 kJ/m³ in 1900 to more than 400 kJ/m³,[5] and recording media.[6] However, the range of magnetic phases with appreciable magnetization, anisotropy, and Curie temperature is limited. This is one reason for the recent emphasis on nanostructuring,[7–10] but exploring new magnetic phases remains an important research direction and has attracted renewed interest. Examples are the attempt to exploit the different crystal fields acting on the $4f$ and $4g$ sites in the 2:14:1 structure to improve the magnetic anisotropy in $Nd_2Fe_{14}B$ magnets[11] and the search for new materials for magnetic recording,[12] where one exploits the strong layer anisotropies[5] of some $3d$-based magnets.

The challenge is to exploit the typically very small[13] and difficult-to-predict free-energy differences between competing ordered and disordered structures to ensure that the atoms are on the "correct" sites. For example, $ErFe_{15}Co_2$ (Ref. 14) shows that this is, in principle, possible. Otherwise, one is forced to rely on nonequilibrium structures, such as strongly strained FeCo thin films.[12] In any case, it is interesting to know which phases may be formed, how they could be stabilized, and what magnetic properties would result.

This paper focuses on $L1_0$ magnets. This interesting class of magnetic materials includes magnets such as the tetragonal intermetallics PtFe and PtCo discovered by Graf and Kussmann[15] and Jellinghaus,[1] respectively. These materials consist of iron-series ($3d$) transition metals, such as Fe and Co, and heavy transition metals, such as rare-earth ($4f$), palladium-series ($4d$) and platinum-series elements. Both $3d$ and $4d/5d$ substitutions are presently considered in magnetic recording, where one tries to improve the writability at room temperature and above (heat-assisted magnetic recording or HAMR).[6]

II. STRUCTURE AND PHASE FORMATION

Traditional binary $L1_0$ or CuAu(I) magnets, such as PtFe and PtCo, are layered fcc derivates. Figure 1(c) shows that they consist of alternating A and B layers, where A and B are $3d$ and $4d/5d$ atoms, or vice versa. However, the most general $L1_0$ structure, Fig. 1(d), has the composition ABC_2 and consists of alternating layers of C atoms and checkerboard patterns of A and B atoms.[16] Other scenarios include but are not restricted to superlattices of the type $ACBC$, more complicated stackings, parallel monatomic wires of A and B atoms in each layer, and segregated A and B patches with or without interlayer correlations. These ABC_2-type compounds $(A,B,C=Pt,Pd,Rh,Ir,Fe,Co,Ni,Mn,Pd,…)$ are largely unexplored, although many combinations are
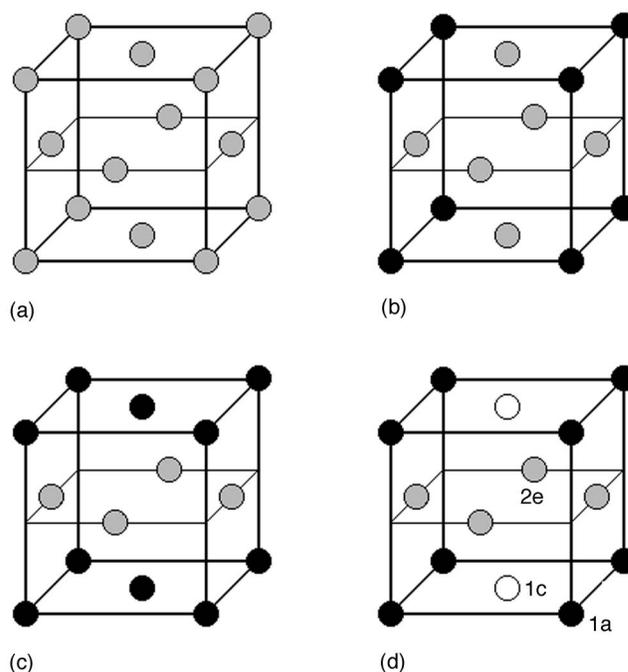

FIG. 1. $L1_0$ and related structures: (a) fcc, (b) $L1_2$ or Cu_3Au, (c) binary $L1_0$, and (c) ternary $L1_0$.
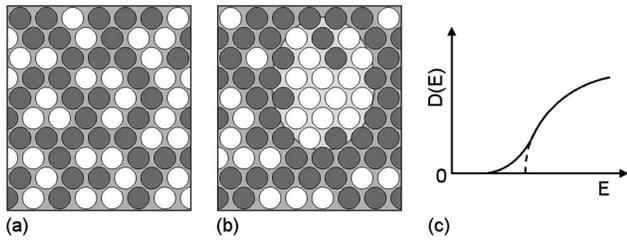
a)Electronic mail: rskomski@neb.rr.com

FIG. 2. Cluster localization: (a) random clusters, (b) cluster localization, and (c) schematic density of states (DOS) for CPA (dahed line) and cluster corrected (solid line).

probably unstable or form solid solutions in the A-B plane. However, the magnetic recording community is well aware of the potential usefulness of atomic substitutions, and in-plane phase segregation has been investigated for $FePt_{1-x}Pd_x$ (Ref. 17 and $Fe_{1-x}Co_xPt$.[18]

From bulk A-B alloys it is known that the relative strengths of the A-A, A-B, and B-B interactions determine whether the structure forms a solid solution, undergoes spinodal decomposition into A and B phases, or forms an ordered compound. These transitions are reasonably well described by the Gorsky-Bragg-Williams approximation.[19] In fact, at sufficiently low temperature, any $L1_0$ compound with an ABC_2 composition will segregate into AC and AB $L1_0$ phases, form an ordered ABC_2 compound or exhibit a transition into a more complicated structure.

The small energy differences and the large number of atoms and competing configurations (both spin and structure) complicate first-principles calculations. Calculations based on the coherent-potential approximation (CPA)[17,18] yield valuable insight into phase formation but suffers from an effect known as cluster localization.[20] As illustrated in Fig. 2(b), the single-site character of the CPA underestimates the energy gain due to hopping in clusters of A or B atoms. This leads to a qualitatively incorrect density of states (DOS) at the band edge, Fig. 2(c), and overestimates the energy of structures with pronounced clustering.

In broad terms, the phase-formation energy depends on the electronic structure of the involved atoms (numbers of $3d$ and $4d/5d$ atoms) and, via elastic interactions, on the relative sizes of the involved atoms. For a given band structure, a large size difference favors segregation. As a crude rule, the corresponding contribution to the binding energy U scales as $G\Delta v^2/V_{at}$, where G is the shear modulus, Δv is the volume difference, and V_{at} is the atomic volume.

The degree of $L1_0$ ordering depends on the annealing temperature. Assuming that short-range diffusion is the main consideration, one can model the local environment as a standard two-level system,[21] as illustrated in Fig. 3. The situation is similar to the AA, AB, and BB bonds considered in the Gorski-Bragg-Williams approximation, except that we focus on the local dynamics. A master-equation analysis of Fig. 3 yields finite-temperature dynamics of the order parameter $0 \leq S \leq 1$,

$$\frac{dS}{dt} = \Gamma(T)[S_{eq}(T) - S]. \tag{1}$$

Here $\Gamma = 2\Gamma_0 \exp(-E_a/k_BT) \cosh(U/2k_BT)$, $U = E_0 - E_1$, and $E_a = \frac{1}{2}(E_b - E_0) + \frac{1}{2}(E_b - E_1)$. The attempt frequency Γ_0
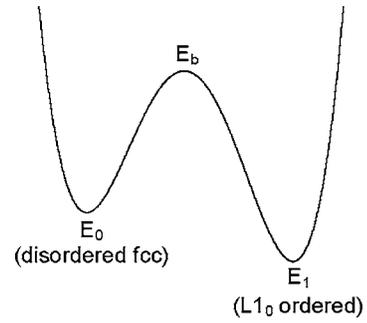

FIG. 3. Energy level scheme for the model.

$\approx 10^{13}$ Hz for typical metallic diffusion processes, and the equilibrium value,

$$S_{eq} = \frac{1 - \exp(-U/k_BT)}{1 + \exp(-U/k_BT)}, \tag{2}$$

varies between 0 (random fcc solid solution) and 1 (perfect $L1_0$ order). This order parameter can be defined for the in-plane ordering in ABC_2 alloys. Typical energies U are comparable to or smaller than 0.1 eV, whereas activation energies E_a are of order 1 eV. As in other areas of metallurgy, low temperatures may improve S_{eq} but yield generally very long equilibration times $1/\Gamma$.

III. MAGNETIC PROPERTIES

The structural versatility of the compounds translates into a broad range of spin structures (Fig. 4). The simultaneous presence of ferromagnetic (FM) and antiferromagnetic (AFM) interactions leads to a competition between various types of magnetic order, including ferromagnetism, different types of antiferromagnetism, and noncollinear spin structures, even in binary $L1_0$ compounds. For example, spin structures of various $L1_0$ alloys with the composition MT (M=Rh,Pd,Ir,Pt; T=Mn,Fe,Co,Ni) have recently been investigated by self-consistent spin-polarized linear muffin-tin orbital atomic-sphere approximation (LMTO-ASA) calculations.[22] Fe and Co favor ferromagnetism, although AFM order may be possible in some Fe-containing compounds. The Ni compounds are paramagnetic, with the ex-
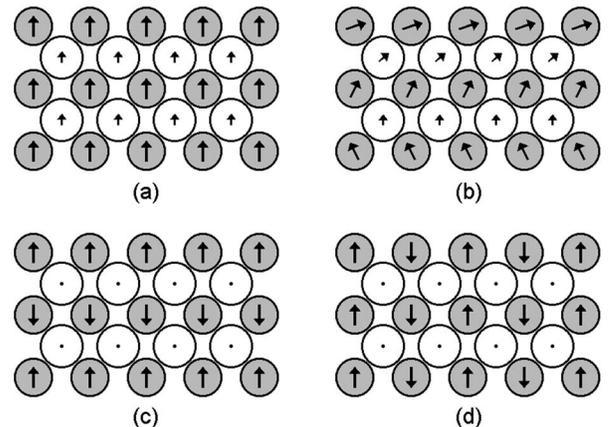

FIG. 4. Some $L1_0$ spin structures: (a) ferromagnetism, [(b)–(d)] antiferromagnetism. The dark and bright spheres are $3d$ and $4d/5d$ atoms, respectively.

ception of the ferromagnetic NiPd. The manganese-containing alloys are AFM, reflecting the well-known general trend toward antiferromagnetism for half-filled $3d$ shells. In addition to the AFM interlayer coupling, Mn spins exhibit a strong AFM intralayer interaction.

Chemical disorder further complicates the picture.[23] First-principle calculations on FePt (Ref. 24) predict an AFM ground state, in seeming contrast to experiment. These two findings may be reconciled by taking into account that a relatively small concentration of strongly ferromagnetic Fe bridges may suffice to compensate a weak antiferromagnetic bulk interlayer coupling.[16]

The high *anisotropy* of some $L1_0$ magnets, of order 5 MJ/m^3, is essentially of the $4d/5d$ single-ion type and involves crystal-field (CF) interaction and spin-orbit coupling. However, the mechanism is different from the usually considered Callen-and-Callen single-ion anisotropy.[25,26] Unlike Néel-type pair interactions,[27] CF interactions are not limited to magnetic neighbors (Fig. 4). The contribution due to nonmagnetic neighbors is often huge, as exemplified by $Sm_2Fe_{17}N_3$, where the nonmagnetic nitrogen changes the room-temperature anisotropy from -0.8 (Sm_2Fe_{17}) to 8.6 MJ/m^3.[5]

Let us consider the anisotropy of an ABC_2 alloy where A and B are heavy transition-metal atoms. In a crude approximation, the C or $3d$ atoms create a stable magnetic moment in the A and B atoms, so that we can approximate the anisotropy as a sum[28] over individual crystal-field contributions

$$K = \tfrac{1}{2}K_0(3\cos^2\theta - 1), \tag{4}$$

where θ is the coordination angle with respect to the c axis. For neighbors in the a-b plane, $\theta = 0$ and the anisotropy is a sum over all A-A, A-B, B-A, and B-B pairs. Denoting the average number of j atoms surrounding an i atom as n_{ij}, we obtain $n_{AB} = n_{BB} = 4S$ and $n_{AA} = n_{BB} = 4(1-S)$, where the layer order parameter n_p has been mentioned in Sec. II. Summation over all terms $-\tfrac{1}{2}K_{ij}n_{ij}$ yields the anisotropy,

$$K = -2(K_{AB} + K_{BA})S - 2(K_{AA} + K_{BB})(1-S). \tag{5}$$

This equation shows the strong dependence of the anisotropy on the order parameter S in the A-B plane, even for exactly obeyed ABC_2 stoichiometry.

IV. CONCLUSIONS

In summary, we have investigated some structural and magnetic properties of a largely unexplored class of $L1_0$-type alloys with nominal composition ABC_2 and a variety of A-B ordering scenarios. These compounds might be of interest in magnetic recording and in permanent magnetism. There are no simple models for the prediction of the degree of $L1_0$ ordering, but the main criteria are differences in atomic sizes and band filling. At low temperatures, $L1_0$ compounds with ABC_2 composition will segregate into AC and AB $L1_0$ phases, form an ordered ABC_2 compound, or exhibit a transition into a more complicated structure. However, the corresponding reaction may be very slow. The ordering has a strong impact on the magnetism of the alloys, especially on the anisotropy.

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