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Permanent magnetism of intermetallic compounds between light and heavy transition-metal elements

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Abstract

First principle calculations are used to investigate the intrinsic magnetic properties of intermetallic alloys of the type XM_n , where X is a 4d or 5d element and M is Fe or Co. Emphasis is on the hexagonal C14 Laves-phase 1:2 and 1:5 alloys, the latter crystallizing in the CaCu_5 structure. These series are of interest in permanent magnetism from fundamental and practical viewpoints, respectively. In the former, the unit cells form a prototypical motif where a heavy atom with high spin-orbit coupling and magnetocrystalline anisotropy is surrounded by many somewhat smaller M atoms with high magnetization, and the latter are Laves-phase derivatives of renewed interest in permanent magnetism. Our DFT calculations predict magnetic moments, magnetizations and anisotropies, as well as formation energies. The results are analyzed across the 4d and 5d series, especially with respect to hybridization effects between 3d and 4d/5d bands.

1. Introduction

Today's high-performance permanent magnets contain light (3d) transition-metal atoms that largely determine magnetization and Curie temperature and heavy atoms that possess a strong spin-orbit coupling and therefore support high magnetocrystalline anisotropy (MCA).^[1, 2] Rare-earth (4f) atoms are particularly suitable for the latter purpose, but rare-earth markets are threatened by the Chinese raw-materials monopoly and by the increasing domestic market in this rapidly developing country.^[3] This has led to renewed interest in materials where the anisotropy originates from other heavy transition-metal series. Actinide (5f) atoms have potentially very high anisotropies, but their inter-atomic exchange is typically small, leading to low Curie temperatures,^[4] and the elements raise environmental concerns, especially with respect to radiation. This leaves us with the heavy transition-metal (4d and 5d) series. What are the odds that completely new permanent-magnet materials based on 3d–4d or 3d–5d alloys will be discovered or created in the future? The large number of tough requirements (magnetization, Curie temperature, anisotropy, raw-materials prices) suggests that the odds are rather low. Furthermore, these alloys may not be found in the realm of existing structures, and the number of potential ternary or quaternary alloys is astronomical and virtually impossible to treat numerically.

Our approach is to explain complicated structures in terms of simpler structural units or “motifs.” A good example is the yttrium–iron intermetallics, which may be interpreted as both 4f and 4d/5d alloys. YFe₂ is a Laves-phase alloy, where the motif is a large Y atom, surrounded by many Fe atoms. The replacement of a part of the Y atoms by two Fe atoms each, followed by structural reconstruction, yields compositions Y_{p-q}Fe_{2p+2q} or, with $2p = 2m + n$ and $2q = n - 2m$, Y_mFe_n. Examples include YFe₂, YFe₅, Y₂Fe₁₇, and YFe₁₂.^[5] Some of the structures generated by this method are unstable or require additional substitutions for structural stabilization, for example in the form of small particles^[6] or melt spinning^[7]. An example of a very unstable compound is YFe₅, which does not exist in the Y–Fe phase diagram, in contrast to YCo₅ and YCo_{5-x}Fe_x ($x < 1$). Attempts to create YFe₅ typically result in the formation of Y₂Fe₁₇, whose structure is closely related to YFe₅^[8] but shows a different stacking with partial substitution of Fe for Y. Similarly, YFe₁₂ exists but requires small additions of Ti or V to become stable. Naturally, only a few of the stabilized alloys created in this way are suitable as permanent magnets, and some are even nonmagnetic (Pauli paramagnetic). In this paper, we assume that the structures exist in nature or can be produced artificially. It is not our aim to discuss whether and how this structuring could be achieved in practice, or to focus on specific classes of compounds,^[5, 9–13] but to see how the magnetic properties of a certain structure depend on the atomic composition, that is, on the choice of the 3d and 4d/5d atoms. For a list of XM_n with $n = 2$ or 3, see Makino.^[14]

Our main emphasis is on the 1:2 intermetallics (Laves phases) and 1:5 phases (prototype CaCu₅). Laves phases are dense-packed crystal structures whose unit cells form a prototypical motif where large atoms are surrounded by many small atoms. There are three Laves-phase structures, namely the hexagonal C14 structure (prototype MgZn₂, ABAB stacking), the cubic C15 structure (prototype MgCu₂, ABCABC stacking), and the hexagonal C36 structure (prototype MgNi₂, ABACABAC stacking). There are many rare earth-containing Laves-phase compounds (RFe₂), but the present rationale is to combine the high

spin-orbit coupling and potential anisotropy contribution of the relatively heavy 4d/5d atoms with the high magnetization of the smaller Fe and Co atoms. Note that Laves-phase magnets cannot be used as permanent magnets directly because they tend to have low magnetizations, low Curie temperatures, and—in the cubic structure—low anisotropies. Furthermore, the relatively large fractions of heavy elements make the materials fairly expensive. The present calculations on the Laves phases primarily serve to understand the moment formation in alloys of 3d and 4d/5d elements.

XM_5 intermetallics (prototype CaCu_5) are Laves-phase derivatives that are directly relevant to permanent magnetism. Aside from the well-known permanent magnet SmCo_5 , whose discussion goes beyond the scope of this paper, various rare-earth-free structures with compositions close to 1:5 are presently being considered. The basic idea is to replace Sm and Co by other transition metals^[7], possibly with some changes in stoichiometry. Furthermore, many other structures, such as the above-mentioned 1:12 and 2:17 structures, derive from the 1:5 structures, which is an additional incentive to study 1:5 compounds.

The main purpose of this study is to investigate the magnetic properties of hexagonal 1:2 and 1:5 compounds of Fe and Co with late transition metals using first-principle calculations, from the viewpoint of exploiting them for permanent-magnet applications. One question is the relative ferro- or antiferro-magnetic alignment of the 3d and 4d/5d elements—that is, the applicability of the rule that the coupling of d moments is parallel if they are in the same half of the series and antiparallel if they are in opposite halves.^[15] Quantitatively, we compare the spin and orbital atomic magnetic moments of the alloys, investigate their structural stability and calculate the magnetocrystalline anisotropies for some of the compounds. Note that present-day computational approaches have a variety of objectives, from highly accurate descriptions of specific materials and formation processes to a high-throughput screening of materials. Our approach is unique in the sense that it considers series of alloys that may only partially exist in nature, yielding comprehensive bird’s-eye views on these series and predicting their magnetic properties. Our accompanying heat-of-formation calculations determine whether individual alloys are stable with respect to the elemental metals, which is a necessary (though not sufficient) condition for the creation of these alloys in nature, laboratory, and industry.

2. Scientific background: alloy structures

Figure 1 shows the two main crystal structures investigated in this paper. As outlined above, our focus is on hexagonal Laves-phase compounds XM_2 crystallizing in the C14 structure, figure 1(a), and XM_5 compounds crystallizing in D_{2d} structures, figure 1(b). Both structures are dense-packed, each of the somewhat larger X atoms having many M neighbors. These neighborhoods form the building blocks or motifs of the structures. The hexagonal 1:5 structure, figure 1(b), has the Strukturbericht designation D_{2d} and the prototype CaCu_5 . The XM_5 alloys can be considered as Laves-phase derivatives consisting of alternating XM_3 and M_3 layers. The atomic positions are largely determined by steric considerations, and Laves phases form if the atomic radii have a ratio of about 1.23. In the 1:5 structures, this radius is generally somewhat larger, up to about 1.45. There are three reasons for specifically investigating these hexagonal 1:2 and 1:5 structures.

Figure 1. Crystal structures of (a) hexagonal Laves phase (C14, prototype MgZn₂) and (b) D2_d (prototype CaCu₅) M₁ and M₂ denote different 3d sites (Fe or Co) and X is the 4d/5d element. The numbers of formula units per unit cell are 4 (a) and 1 (b).

First, these structures imply low (noncubic) anisotropy, which is required for permanent-magnet applications. The creation of such anisotropic structures is a challenge in practice. In fact, among the XFe₂ Laves phase, those with Y and Zr crystallize in the cubic C15 structure. The compounds with Sc, Ti, Nb, Hf, Ta, and W exhibit C14 type structure^[16–19], and C15 NbFe₂ is actually Pauli paramagnetic.^[16]

Second, the dense packing may be favorable for the development of the magnetizations, although both the presence of the large X atoms and the trend toward antiferromagnetic exchange coupling in dense-packed Fe systems^[2] has the opposite effect.

Third, these structures may serve as a model system to systematically investigate the effect of “nonmagnetic” 4d and 5d elements on the magnetism of Fe-series elements. This includes both off-stoichiometric compositions with substitutional disorder, such as Fe-rich ZrFe₂,^[20] and alloys that are not Laves-phase derivatives in a strict sense but contain similar motifs. A well-known example is Nd₂Fe₁₄B^[21], which is not a 1:5 derivative but contains stacking of 3d and mixed 3d/4f layers similar to SmCo₅. In section 5.2 we discuss one example of such a structure, namely HfCo₇.

3. Computational details

Our first-principle calculations involve an accurate frozen core projector augmented plane-wave (PAW) method within the framework of density functional theory, as implemented in the Vienna *ab initio* simulation package (VASP).^[22, 23] We employ PAW pseudopotentials, with exchange and correlation described by Perdew, Burke, and Ernzerhof (PBE), using a generalized gradient approximation (GGA).^[24] The kinetic energy cutoff for the plane-wave basis set was taken to be 300 eV. The equilibrium ferromagnetic spin polarized structures for C14 and D2_d phase were obtained by relaxing the unit cell using the conjugate gradient method. In this process, the positions of atoms are kept as those of standard C14 and D2_d phases. The lattice constants estimated from spin polarized calculations using a high convergence limit of 10^{−4} eV are presented in table 1. We used 72 *k*-points to relax the unit cell and 144 *k*-points for the spin polarized calculations in the irreducible part of the

Brillouin zone, using the Monkhorst-Pack scheme.^[31] The use of a high convergence limit is advantageous in reducing the computational cost. However, to check the accuracy of this approach, we also performed the structural relaxations with a low convergence limit of 10^{-6} eV, and this analysis yields lattice constants very similar to those shown in table 1. In addition, some of the compounds, such as YCo₅ and XFe₂ (X = Nb, Hf, Ta, W) have already been synthesized^[25–30], and the calculated lattice constants are in good agreement with the corresponding experimental values with a deviation of only 0.02–1.3%, as shown in table 1.

Table 1. The experimental^[25–30] and calculated lattice constants of alloys crystallizing in the hexagonal C14 Laves and D2_d (1:5) phases. The lattice constants c are found to obey $c/a = 1.6329$ for C14 phase alloys and $c/a = 0.792$ for D2_d alloys.

X	a (Å)			
	XFe ₂	XCo ₂	XFe ₅	XCo ₅
Y	5.155	5.087	4.993	4.941
Y ^{exp}				4.927
Zr	4.979	4.899	4.895	4.841
Nb	4.807	4.774	4.786	4.722
Nb ^{exp}	4.830			
Mo	4.683	4.696	4.735	4.682
Mo ^{exp}	4.744			
Tc	4.645	4.662	4.729	4.774
Ru	4.652	4.670	4.732	4.684
Rh	4.697	4.703	4.776	4.782
Pd	4.802	4.744	4.819	4.811
Lu	5.177	4.999	4.931	4.876
Hf	4.967	4.852	4.867	4.827
Hf ^{exp}	4.974			
Ta	4.825	4.744	4.770	4.706
Ta ^{exp}	4.859			
W	4.735	4.692	4.724	4.702
W ^{exp}	4.736			
Re	4.691	4.618	4.711	4.665
Os	4.672	4.603	4.714	4.665
Ir	4.653	4.702	4.756	4.768
Pt	4.650	4.744	4.804	4.801

The magnetocrystalline anisotropy calculations require a better energy resolution and a very fine mesh in k -space. We use a mesh containing 3375 k -points for all the anisotropy calculations in this paper. The anisotropy is calculated using the energy difference method—that is, the anisotropy energy is the difference in energy between two self-

consistent calculations for two different directions with an energy convergence criterion of 10^{-7} eV.

4. Results

4.1. Moment and magnetization

Figure 2 shows the calculated magnetizations of different types of atoms in the XFe_2 and XCo_2 Laves phases. In general, the magnetization depends on the filling of the bands and on the interatomic distances. The relative orientation of the spin moment of the 4d/5d elements changes from antiparallel (antiferromagnetic) to parallel (ferromagnetic) near the middle of the 4d/5d series, as expected.^[15] Due to hybridization, the M moments (Fe and Co moments) decrease across the first halves of the 4d and 5d series. This decrease is more pronounced for the M_1 sites, which are closer to the X or 4d/5d atoms.

Figure 2. The average magnetizations of the atoms in the C14 Laves phase.

For Mo, Tc, and Ru, the coupling remains antiferromagnetic, but the decreasing overlap of the 3d and 4d/5d wave functions due to increase in the bond length results in an increase in the net moments of the M_1 Fe atoms. The magnetizations of Fe and Co in the compounds with Rh and Pd have a ferromagnetic coupling. The 5d series show nearly the same trends as the 4d series, although the magnetization is somewhat lower. The reason is that 5d wave functions extend farther away from the nucleus and overlap with the wave functions of 3d (Fe, Co) elements more intensively.

Figure 3 shows the variation of magnetic moment of different types of atoms in the XCo_5 and XFe_5 compounds. Across the series, antiferromagnetic coupling causes the magnetization contribution of the heavy atoms to be negative up to Mo and W in the 4d and 5d series, respectively, and then positive. For XFe_5 , the decrease extends up to Tc, because the decreasing lattice constants result in an enhanced overlap between the 3d wave functions of Fe with the 5d wave function of the heavy atoms.

Figure 3. The average magnetizations of the atoms in the 1:5 or D2d phase.

4.2. Magnetocrystalline anisotropy

Table 2 shows the spin and orbital moments and the magnetic anisotropy energies for C14 XFe₂ Laves-phase alloys. From the table we see that the SOC creates a small dependence of the spin moment on the magnetization direction, which is well known from magnetic materials such as hcp Co.^[32] The orbital moment and the anisotropy energy exhibit a much more pronounced directional dependence than the spin moment because they are direct consequences of the SOC, as opposed to the higher-order correction to the spin moment.^[33]

Table 2. Anisotropy, spin, and orbital moment of C14-ordered XFe₂ across the 5d series. Based on $a = 4.7 \text{ \AA}$, $1 \mu_B$ per unit cell is about $55 \text{ kA m}^{-1} = 55 \text{ emu cm}^{-3}$ (or $0.08 \text{ T} = 0.8 \text{ kG}$) and 1 meV per unit cell is about 1.0 MJ m^{-3} .

Alloy	a (Å)	Anisotropy energy (meV/unit cell)			Spin moment (μ_B /unit cell)			Orbital moment (μ_B /unit cell)		
		E_z	E_x	E_y	m_z	m_x	m_y	m_z	m_x	m_y
TaFe ₂	4.825	0	-1.383	-1.39	4.899	4.989	4.949	0.357	0.567	0.563
WFe ₂	4.735	0	-2.83	-2.83	6.793	7.08	7.08	0.292	0.473	0.478
ReFe ₂	4.690	0	-2.369	-2.328	9.116	9.112	9.113	0.085	0.16	0.16
OsFe ₂	4.671	0	1.876	1.922	11.88	11.857	11.857	-0.066	-0.009	-0.009
IrFe ₂	4.653	0	0.126	0.139	14.856	14.841	14.841	-0.019	-0.033	-0.033
PtFe ₂	4.649	0	-5.034	-5.019	18.71	18.696	18.696	0.361	0.417	0.417
AuFe ₂	4.652	0	1.407	1.395	16.851	16.87	16.87	0.2	0.24	0.24

As contrasted to rare-earth anisotropies, there exist no simple rules predicting the anisotropies of itinerant transition-metal magnets as a function of the number of d electrons across different structures. This is because rare-earth anisotropy is governed by simple parameters (Stevens coefficients and crystal field),^[2] whereas the anisotropy of itinerant transition metals is determined by a subtle k -space integration [34].

From table 2 we also see a symmetry breaking between the x and y directions. This may reflect the sixth-order anisotropy contribution $K'3 \sin^6 \theta \cos(6\phi)$ ^[2, 33] expected in hexagonal compounds but is more likely a numerical error of the order of 2%. A possible exception is osmium, where the energy difference between the x and y directions is 0.046 meV per unit cell, or about 0.05 MJ m⁻³.

4.3. Energy of formation

So far, we have systematically investigated the magnetism of a series of intermetallic compounds of Fe and Co with heavy transition metals. In all cases, we have assumed that the compounds actually exist, either as equilibrium phases^[1, 14] or as artificially stabilized structures. However, as outlined in the introduction, many of these compounds do not form easily. To address this question, we have calculated the formation energies of the compounds—that is, the energy change accompanying the formation of the alloys from the metallic elements. This does not necessarily yield the ground state because other structures, such as cubic Laves-phase compounds, may have lower energies, but very high formation energies are a safe indication that a structure is difficult or impossible to stabilize.

Figure 4 shows the formation energies for all compounds investigated in section 4.1.2. Alloying with 4d elements yields the following stable hexagonal 1:2 compounds: ZrFe₂, NbFe₂, TcFe₂, ZrCo₂, and NbCo₂. For the 5d series, the stable compounds are HfFe₂, TaFe₂, HfCo₂, TaCo₂, PtFe₂, and PtCo₂. Some other hexagonal 1:2 compounds, such as MoFe₂, PdFe₂, WFe₂, and ReFe₂, have nearly zero formation energies, which indicate that these alloys are marginally stable. This is essentially in agreement with the above-mentioned experimental situation. For example, WFe₂ is an equilibrium phase in the Fe–W phase diagram. Among the 1:5 alloys, the only stable compounds are YFe₅, ZrFe₅, HfFe₅, YCo₅, ZrCo₅, and HfCo₅. These findings are consistent with experiment,^[1, 14] for example with respect to MoFe₂ and WFe₂.^[14] On the other hand, figure 4 does not allow an actual prediction of the phases. For example, YFe₅ does not exist in equilibrium but segregates into Y₆Fe₂₃ and Y₂Fe₁₇.^[1, 2]

Figure 4. Formation energy per atom in XM₂ and XM₅ phase compounds where M is Fe or Co and X is a heavy late transition-metal atom.

5. Discussion

5.1. Density of states

The magnetization trends in figures 2 and 3 are a direct consequence of the interatomic hybridization. This mechanism and the resulting moments are best rationalized in terms of local (or site-projected) partial d-densities of states (DOS). Figure 5 shows these DOS for some of the compounds of section 4, namely ZrFe_2 , ZrCo_2 , WFe_2 , ZrCo_5 , HfCo_5 , and WCo_5 . For two bands with centers of gravity E_1 and E_2 , the degree of hybridization roughly scales as $1/(E_1 - E_2)$. For the early 4d and 5d elements, there is not much overlap between the 4d/5d and 3d bands, and the electronic structure and magnetism of the alloys is basically 3d-like, with relatively small perturbations from the 4d/5d elements. However, with increasing atomic number, the 4d and 5d bands become narrower and approach the 3d bands of Fe and Co. Figure 5 shows that the corresponding mixing has a strong effect on the electronic structure. As shown in figures 5(a) and (b), the d-DOS for X atom become narrow as one goes from Zr in (a) to W in (b). Similar effects can also be seen in the 1:5 series, figures 5(d) and (e).

Figure 5. Local and site-averaged d-densities of states (DOS) for some of the alloys discussed in section 4. (a)–(c) Crystallizing in C14 Laves phase and (d)–(f) crystallizing in D2d phase.

5.2. Rare-earth-free Co-based 1:7 alloys

It is instructive to compare the above results with more complicated structures, such as HfCo_7 .^[35] This alloy has recently attracted some attention because it is Co rich and promises an appreciable magnetization in combination with a very high Curie temperature.^[7, 36] X-ray diffraction (XRD) data on rapidly quenched (melt-spun) HfCo_7 indicate an orthorhombic unit cell with lattice parameters of $a = 4.718 \text{ \AA}$; $b = 4.278 \text{ \AA}$, and $c = 8.07 \text{ \AA}$ and two formula units per unit cell.^[7] Note that this structure is unrelated to the Sm–Co-type 1:7 (or “disordered 1:5”) structure. Figure 6 shows the corresponding unit cell, with atomic positions obtained after numerical^[37] relaxation.

An interesting feature of HfCo_7 is that its formation requires rapid quenching^[7] or other nonequilibrium methods. This is because, in the phase diagram, it is stable only from 1050 to 1245°C. If the quenching rate is very high, then the structure is basically amorphous. The structure of figure 6, with a Laves-like motif, requires a fairly well-defined cooling rate, whereas slow cooling leads to the segregation of elemental Co. This trend is also seen in our numerical simulation. Without the constraint of experimental lattice parameters a , b , and c , the numerical relaxation of the atoms causes a deformation of the unit cell, indicating that figure 6 does not reflect the structural ground state.

Figure 6. Structure of $(\text{HfCo}_7)_2$ unit cell after relaxation.

5.3. Lowest-order nonuniaxial anisotropy

In lowest order, hexagonal and tetragonal crystals are uniaxial, that is, the preferential magnetization direction is along the c -axis (easy-axis anisotropy, $K_1 > 0$) or in the a – b plane (easy plane anisotropy, $K_1 < 0$). The in-plane anisotropy discussed in the previous section does not affect this basic picture, because it is a higher-order effect and often very small. However, for crystals with very low symmetry, such as orthorhombic crystals, the magnetocrystalline anisotropy energy is in lowest order:^[2]

$$\frac{E}{V_{\text{atom}}} = K_0 + K_1 \sin^2 \theta + K'_1 \sin^2 \theta \cos 2\varphi, \quad (1)$$

where K_1 and K'_1 are anisotropy constants. Writing equation (1) for the three principal directions yields

$$\frac{E_{001}}{V_{\text{cell}}} = K_0 \quad (\theta = 0^\circ, \varphi = 0^\circ) \quad (2a)$$

$$\frac{E_{100}}{V_{\text{cell}}} = K_0 + K_1 + K'_1 \quad (\theta = 90^\circ, \varphi = 0^\circ) \quad (2b)$$

$$\frac{E_{010}}{V_{\text{cell}}} = K_0 + K_1 - K'_1 \quad (\theta = 90^\circ, \varphi = 90^\circ). \quad (2c)$$

Solving equation (2), we obtain

$$K_0 = \frac{E_{001}}{V_{\text{cell}}} \quad (3a)$$

$$K_1 = \frac{1}{2V_{\text{cell}}} (E_{100} + E_{010} - 2E_{001}) \quad (3b)$$

$$K'_1 = \frac{1}{2V_{\text{cell}}} (E_{100} - E_{010}). \quad (3c)$$

Specifically, the HfCo₇ structure of figure 6 is characterized by the unit-cell energies $E_{100} = 0.00$ meV/unit cell, $E_{010} = 3.347$ meV/unit cell; $E_{001} = 3.55$ meV/unit cell. Using equation (3), this yields the anisotropy constants $K_1 = -1.853$ and $K'_1 = -1.646$ MJ m⁻³. If the magnet was uniaxial, a negative K_1 would mean easy plane anisotropy and low coercivity, but for orthorhombic magnets, this is not the case. Unless the two lowest of the three energy values E_{100} , E_{010} , and E_{001} are degenerate, orthorhombic magnets are always suitable for coercivity development, even if K_1 is negative. In the present case, the effective anisotropy, determined by the energies of the lowest-lying and first excited states is 3.5 MJ m⁻³, somewhat larger than the experimental room-temperature estimate of 1.4 MJ m⁻³.^[7] The calculated magnetization is 1.14 T, including a negative orbital-moment contribution of 0.043 T, compared to the room-temperature experimental value of 0.89 T.

6. Conclusions

In summary, we have used first-principle calculations to investigate how the magnetic moments, magnetizations, and anisotropies of Fe and Co are affected by alloying with heavy transition metals. Our emphasis has been on dense-packed hexagonal 1:2 and 1:5 alloys. The moments and magnetizations follow the trends expected from band-filling arguments, with unfavorably reduced magnetizations for the cheap early 4d and 5d elements. These magnetization trends are likely to remain operative for similar structures and stoichiometries. There is also the trend that the alloys do not form easily if the 3d or 5d element is near the beginning of the second half of the series. By contrast, anisotropy trends are less predictable, and both their signs and their magnitudes exhibit drastic changes as a function of stoichiometry and crystal structure. However, a general condition for magnetic anisotropy in alloys rich in light transition metals is an anisotropic arrangement of motifs where heavy atoms are surrounded by many 3d atoms. The materials-specific clarification of this

structure-property relationship is a challenge for future research. An interesting case is crystals with orthorhombic structure, such as HfCo_7 , where large anisotropy energies and coercivities can be expected even if K_1 is negative. This alloy also illustrates how metastable structures can be exploited in permanent magnetism.

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