Disorder-induced cubic phase in Fe$_2$-based Heusler alloys.

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Based on first-principles electronic structure calculations, we analyze the chemical and magnetic mechanisms stabilizing the cubic phase in Fe$_2$-based Heusler materials, which were previously predicted to be tetragonal when being chemically ordered. In agreement with recent experimental data, we found that these compounds crystallize within the so-called “inverted” cubic Heusler structure perturbed by a certain portion of the intrinsic chemical disorder. Understanding these mechanisms is a necessary step to guide towards the successful future synthesis of the stable Fe$_2$-based tetragonal phases, which are very promising candidates for the fabrication of rare-earth-free permanent magnets.

Keywords: rare-earth-free, hard magnets, Heusler alloys, chemical disorder

One of the oldest problems within the field of materials science is the search for the inexpensive hard magnets, i.e., for materials retaining their magnetisation after being once magnetized. Their role in the daily life can be hardly overestimated: hard magnets are widely used in automotive applications, telecommunications, data processing, consumer electronics, instrumentation, aerospace and bio-surgical applications. In particular, they play a unique role in renewable energy technologies based on electric generators (e.g., rotors in wind turbines, small hydroelectric systems etc.). However, materials exhibiting outstanding hard-magnetic properties together with high magnetization and high Curie temperature are rather expensive as being based on combinations involving rare-earth elements (e.g., Sm-Co, Nd-Fe-B). Thus, the development of new inexpensive compounds with hard-magnetic properties (i.e., rare-earth-free hard magnets) which can be industrially mass produced is important and highly relevant (for the review see e.g., Ref. [5]). The recent explosion of attention for the tetragonally-distorted magnetic Heusler systems originates at a large extent from this prospective as well.[3]

Indeed, apart of being promising candidates for tunneling magneto-resistance and spin-torque-transfer applications[3,4], this family may also provide materials combining the tetragonal distortion with a large magnetic moment and high Curie temperature, suitable as hard magnets. The group of Fe$_2$YZ-based Heusler compounds (with Y and Z being the transition and the main group element, respectively), theoretically predicted to be tetragonal with a large magnetization (4–5 $\mu_B$/f.u., f.u.=formula unit) would be one of such promising materials sources[5]. In contrary, the subsequent synthesis, XRD and Mössbauer characterization have shown that all these compounds crystallize in the cubic phase[6]. To understand which ingredients can lead to their tetragonal distortion obviously implies an important preliminary step – a detailed understanding of the mechanisms stabilizing their cubic phase. This is the main point of the present study.

Before proceeding to the results, first we would like to introduce the notations extensively used throughout in the text (see Fig. 1). In the most general case any cubic Heusler system corresponds at least to the point-symmetry group No. 216. In order to distinguish between different chemical configurations, we will use the special written notation according to the occupations of the four high-symmetric Wyckoff positions 4a, 4b, 4c and 4d are distinguished by different colors.

![FIG. 1. (color online) The cubic unit cell of the point-symmetry group No. 216 together with its schematic graphical diagram and the corresponding written notation. The high-symmetric Wyckoff positions 4a, 4b, 4c and 4d are distinguished by different colors.](Image)

To clarify the discrepancy between the theoretical predictions from Ref. [6] and the experimental data [5], in the following we will study the relative stability of the cubic and tetragonal phases of the Fe$_2$-based Heusler...
systems by optimizing both structural, magnetic and chemical degrees of freedom based on \textit{ab-initio} density-functional calculations. As a suitable numerical tool which accounts for these factors simultaneously, we use the fully-relativistic Green’s function formalism implemented within the SPR-KKR (Spin-Polarized fully Relativistic Korringa-Kohn-Rostoker) method \cite{8}. The random occupation is described in terms of the CPA (Coherent Potential Approximation) \cite{9}. Despite its mean-field nature (the effective averaging of the short-range order effects) CPA remains the most practical technique which includes the essential features of randomness. In order to ensure that the CPA result is not an artifact of the single-site approximation, we performed additional supercell calculations. It was also found, that the usage of the full potential (i.e., the non-spherical potential) is much more essential for the adequate description than a particular choice of the exchange-correlation potential. For this reason, the presented calculations corresponds to the fully-relativistic and full-potential results employing the local density approximation for the exchange-correlation functional \cite{10}. The calculations for different \(c/a\) ratios are performed for the fixed volume, which was taken from the available experimental data \cite{6}.

In order to explain the mechanism which keeps the \(\text{Fe}_2\)-based systems cubic, throughout the discussion we will focus on the \(\text{Fe}_2\text{CuGa}\) system, because as we found, all basic conclusions valid for this system can be transferred without restrictions onto other compounds in this series (i.e., \(\text{Fe}_2\text{CuAl}, \text{Fe}_2\text{NiGa}, \text{Fe}_2\text{NiGe}\) and \(\text{Fe}_2\text{CoGe}\) synthesized experimentally \cite{6}.

The main outcome of the present study is summarized in Fig. 2 which represents the dependency of the total energy on \(c/a\) ratio for various alloy configurations. The ordered “regular” Heusler structure in cubic phase turns out to be unstable (indicated by the corresponding energy curve maximum at \(c/a = 1\), black line in Fig. 2 (a)), whereas at about \(c/a = 1.54\) the system falls into the relatively deep energy minimum. For the fixed chemical order (i.e., \(\text{CuGa}/\text{FeFe}\)) the tetragonal distortion is the only mechanism which can relax the instability of the cubic phase, since the magnetic degrees of freedom are already in use (for more detailed description of tetragonal distortion mechanisms, see e.g. \cite{2,3}). As it follows, the gradual transition towards the “inverted” Heusler structure, realized by random chemical Cu-Fe inter-layer exchange starts gradually to develop an energy minimum for the cubic phase. Although the configurations with intermediate Cu-Fe site occupations (e.g., \([\text{Cu}_{0.5}\text{Fe}_{0.5}]\text{Ga}/[\text{Cu}_{0.5}\text{Fe}_{0.5}]\text{Fe}\) exhibit an energy minima for both tetragonal and cubic phases, the limiting ordered system \((x = 1\), i.e. the fully “inverted” \(\text{FeGa}/\text{FeCu}\)) is stable only within the cubic phase (Fig. 2 (a) or (b), red curve). Despite the large energy difference (about \(-170 \text{ meV/f.u.}\)) between the cubic “regular” and “inverted” phases, the deepest absolute energy minimum is found for the tetragonally-distorted “regular” configuration (see Fig. 2(a)), which is by about 20 meV/f.u. more stable compared to the “inverted” cubic configuration. Thus, for the ordered systems our results agrees with the former calculations \cite{3}. This means, that the mechanisms stabilizing the cubic phase involve degrees of freedom which where neglected so far, e.g. the chemical disorder \cite{6}.

It is important to note, that the huge energy decrease (about \(-170 \text{ meV/f.u.}\)) gained by going from the “regular” cubic to the “inverted” cubic configuration (the largest energy scale in the diagram on Fig. 2) is most likely of the magnetic origin. The latter is due to the optimization of the magnetic exchange coupling within the Fe sublattice, since the nearest magnetic neighbors (i.e., the Fe atoms from the adjacent layers within “inverted” cubic \(\text{FeGa}/\text{FeCu}\)) are sitting closer to one another compared to the “regular” cubic \(\text{CuGa}/\text{FeFe}\) setup, in which they are in-plane. For this reason, by searching for the more stable configurations, we start from the “inverse” cubic system and perturb it by in-plane chemical disorder (i.e., by conserving the total amount of Cu and Ga within adjacent layers). Hence, there are two important in-plane disorder scenarios: random in-plane mixtures of \(\text{FeGa}\), and that of \(\text{Fe-Cu}\).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{(color online) Total energy of \(\text{Fe}_2\text{CuGa}\) Heusler alloy calculated as a function of \(c/a\) ratio for various distributions of Fe and Cu (indicated by the box-like diagram; green, yellow and white colored areas correspond to the Fe, Cu and Ga occupations, respectively). (a) Thick black and red curves correspond to \(\text{CuGa}/\text{FeFe}\) (“regular”) and \(\text{FeGa}/\text{CuFe}\) (“inverted”) configurations, respectively. Thinner violet line shows the intermediate \([\text{Cu}_{0.5}\text{Fe}_{0.5}]\text{Ga}/[\text{Cu}_{0.5}\text{Fe}_{0.5}]\text{Fe}\) case between “regular” and “inverted”. The absolute energy minimum of the “regular” (\(\text{CuGa}/\text{FeFe}\)) tetragonal phase is taken as a reference. (b) Solid red curve represents the same “inverted” configuration as on the left panel, whereas the solid blue line shows the most stable configuration: \(\text{FeGa}/[\text{Cu}_{0.5}\text{Fe}_{0.5}],[\text{Cu}_{0.5}\text{Fe}_{0.5}]\), obtained from the ordered “inverted” by mixing Fe and Cu randomly in-plane. The dashed red and blue lines correspond to the distributions derived from the previous two configurations via additional in-plane random spread of Ga and Fe: \([\text{Fe}_{0.5}\text{Ga}_{0.5}],[\text{Fe}_{0.5}\text{Ga}_{0.5}]/\text{CuFe}\) (red dashed) and \([\text{Fe}_{0.5}\text{Ga}_{0.5}],[\text{Fe}_{0.5}\text{Ga}_{0.5}]/[\text{Cu}_{0.5}\text{Fe}_{0.5}], [\text{Cu}_{0.5}\text{Fe}_{0.5}]\) (blue dashed). The absolute energy minimum of the “inverted” (\(\text{FeGa}/\text{CuFe}\)) phase is taken as a reference.}
\end{figure}
We found, that the random in-plane spread of Ga and Fe (case \([Fe_{0.5}Ga_{0.5}][Fe_{0.5}Ga_{0.5}]/CuFe\), red dashed line in Fig. 2(b)) leads to the increase of the total energy (compared to the “inverted” configuration, FeGa/CuFe) by about 150 meV. In contrast, the random in-plane spread of Cu and Fe (case FeGa/[Cu_{0.5}Fe_{0.5}][Cu_{0.5}Fe_{0.5}], solid blue line in Fig. 2(b)) leads to an energy gain of about −40 meV (again, compared to the “inverted” case, FeGa/CuFe). The key observation is, that this −40 meV energy gain is enough to stabilize the cubic structure (in FeGa/[Cu_{0.5}Fe_{0.5}][Cu_{0.5}Fe_{0.5} configuration), which finally becomes more stable than the tetragonal “regular” ordered CuGa/FeFe by about \(40 − 20 = 20\) meV/f.u., in agreement with experiment.

Our results show, that these two effects (Fe-Ga and Fe-Cu in-plane random mixtures) are rather independent on one another: i.e. disregarding the particular arrangement of atoms within the adjacent layer, the energy changed by 150, 40 or 150 ± 40 meV while going from one distribution to another within all four cases. The large increase in energy by 150 meV in the first case is mainly due to the distinct nature of Fe and Ga. So, within the fixed square lattice it is unfavorable to form separate clusters of Fe and Ga, since each atomic sort would prefer to create its own lattice within a cluster which will be rather different from another. For this reason, any perturbation of the perfect chemical order in Fe-Ga layers will increase the total energy. This issue, however, is not critical for the second case: the separation of Fe and Cu within the given lattice does not cost so much energy, since both atom types are much more similar. To ensure that the −40 meV energy gain in this case is not just an artifact of the single-site nature of the CPA, we have performed supercell calculations by systematically increasing the number of Fe-Cu in-plane swaps, mimicking Fe-Cu disorder. This has shown that by increasing the degree of Fe-Cu separation the total energy is indeed reduced by around −40 meV.

The subsequent calculations of the magnetic energy exchange coupling constants \(J_{ij}\) (Fig. 3) of the classical Heisenberg model \((H = −\sum_{i>j}J_{ij}\hat{e}_i\cdot\hat{e}_j\), where \(\hat{e}_i\) is the unity vector along the magnetization directions on local sites \(i\) and \(j\) revealed the magnetic origin of both stabilization mechanisms responsible for the atomic rearrangement from the “regular” into the “inverted” phase and for the chemical disorder within the Fe-Cu layers. Namely, the strong Fe-Fe inter-layer coupling \((J_{\text{inter-layer}} ≈ 25\) meV between the adjacent Fe-Ga and Fe-Cu layers) keeps the whole system ferromagnetic. This is in agreement with the high Curie temperature (798 K) measured in Ref. 6. Although the in-plane couplings appear to be an order of magnitude weaker, still, as we mentioned, their optimization plays a crucial role in the stabilization of the cubic phase. In the ordered “inverted” configuration (FeGa/FeCu) the nearest in-plane Fe atoms tend to couple antiferromagnetically \((J_{\text{in-plane}} = −1.4\) meV). This interaction works against the overwhelming ferromagnetic order already set by the strong inter-layer coupling. Thus, the magnetic energy can be further reduced by bringing the Fe atoms closer together as shown in Fig. 3(b), so that they couple ferromagnetically \((J_{\text{in-plane}} ≈ 5.2\) meV). Put in practical terms, this effect favors the formation of random Fe clusters within the Fe-Cu planes, which—in contrast to the ordered case—can be more adequately described by the chemical disorder picture, i.e. by implying the FeGa/[Fe_{0.5}Cu_{0.5}][Fe_{0.5}Cu_{0.5}] configuration.

The considerations presented above can be further supported by comparing the electronic structures as shown on Fig. 4. The instability of the electronic subsystem is typically related to the strength of the DOS peaks in the vicinity of the Fermi energy. In case of the “regular” CuGa/FeFe cubic system, a huge instability peak at \(E_F\) (total DOS\((E_F) ≈ 6.1\) sta./eV) is produced by the van-Hove singularity in the minority-spin channel at W-point of the Brillouin zone (Fig. 4(a)). By replacing Cu from

FIG. 3. (color online) Comparison of the magnetic exchange coupling in the “inverted” FeGa/FeCu (a) and in the most stable FeGa/[Fe_{0.5}Cu_{0.5}][Fe_{0.5}Cu_{0.5}] (b) configurations. The atoms are arranged within Fe-Ga and Fe-Cu layers marked by light- and dark-blue horizontal planes, respectively. Fe, Cu and Ga atoms are shown as green, yellow and white spheres, respectively. Magnetic moments are shown by arrows. The bond thickness reflects the strength of the exchange interaction. The in-plane Fe-Fe interactions are dominating: \(J_{\text{in-plane}} ≈ 25\) meV (thick green bonds). The in-plane interactions are negligibly small, except those in Fe-Cu planes. Case (b) illustrates the typical distinction from the ordered “inverted” structure: the random in-plane swap of one Fe and one Cu atoms which brings two Fe atoms closer to one another within the Cu-Fe plane. This alters the nearest in-plane Fe-Fe exchange from antiferromagnetic \((J_{\text{in-plane}} = −1.4\) meV, thin red bond) in case (a) to ferromagnetic \((J_{\text{in-plane}} = 5.2\) meV, thin green bond) in case (b).
ASR benefit from the in-plane magnetic optimization, and therefore it is by 40 meV/f.u. lower in energy compared to the “inverted” FeGa/CuFe system. We would like to point out, that very similar stabilization mechanisms characterized by comparable energy scales can take place in other Fe$_2$-based cubic Heusler compounds. For example, for Fe$_2$CuAl and Fe$_2$NiGe the inter-plane exchange energy optimization (i.e. by going from the “regular” to the “inverted” cubic phase) gains $-367$ and $-168$ meV/f.u., whereas the in-plane optimization (due to Fe-Y in-plane disorder) contributes with $-27$ and $-40$ meV/f.u., respectively to the energy. Thus the stabilization mechanisms presented in this letter are rather general within the group of Fe$_2$YZ materials.

To conclude, we emphasize that the presented analysis explains the stability of the cubic phase in Fe$_2$YZ Heusler compounds, and provides a clear exaplantion for the discrepancy between experimental results and theory. The actual stabilizing mechanism appears to be the chemical disorder, which optimizes the magnetic exchange coupling within Fe-Y layers of the initially ordered FeZ/FeY cubic phase. At the same time, the FeZ layers remain chemically ordered due to a large difference (i.e. atomic radius, valency, electronegativity etc.) between Fe and the main-group element Z. Thus, the most stable configurations can be written as FeZ/[Fe$_{0.5}$Y$_{0.5}$]$_{[Fe_{0.5}Cu_{0.5}]}$ in general, the important prerogative enabling the chemical disorder is the “inverted” ordered structure: as we have seen, the effect of the rearrangement from YZ/FeFe into FeZ/YFe within the cubic phase is comparably efficient to the tetragonal distortion in YZ/FeFe. On the other hand, the first scenario allows to further optimize the system by chemical disorder, whereas the second one does not.

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