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The zero-magnetization Heusler ferrimagnet

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An unusual zero-moment half-metallic state has been predicted in stoichiometric Heusler compounds with 24 valence electrons, where, unlike an antiferromagnet, the two sublattices are chemically or crystallographically inequivalent. We have examined the following candidate materials: Cr_2FeGe, Cr_2CoGa, Fe_2VGa, and Mn_3Ga with various annealing and milling treatments. The Fe_2VGa compound is identified as a weak itinerant ferromagnet, but both cubic Mn_3Ga and perfectly ordered Cr_2CoGa are potential zero-magnetization ferrimagnets. © 2013 American Institute of Physics. [http://dx.doi.org/10.1063/1.4794744]

An interesting proposed addition to the family of magnetic materials is the zero-moment half-metallic ferrimagnet, also known as the half-metallic antiferromagnet, or zero-moment half metal.[1] This is a metallic material with a spin gap in one of the two spin subbands, so that there are only ↑ or ↓ electrons at the Fermi level. Such a half-metal could be magnetically ordered with zero net moment. It differs from a conventional ferrimagnet, such as $GdCo_3$ at its compensation point,[2] in that the magnetization vanishes over a wide range of temperature, not at just one temperature where the magnetization of the Gd and Co sublattices cancel due to their different temperature dependences.

Generally, a stoichiometric half-metal will have a spin moment which is an integral number of Bohr magnetons. All the bands are either full or empty for the spin state showing a gap in the density of states, for example, ↑. Since the total electron count in the unit cell is an integer, it follows that the number of ↓ electrons is also an integer, and so is the difference of ↑ and ↓. Hence, the spin moment of the unit cell is an integer, which may be 0, 1, 2… Bohr magnetons. The argument is valid at zero temperature and neglects spin-orbit coupling, which mixes ↑ and ↓ states and introduces an orbital contribution to the moment.

The case of interest here is $0\,\mu_B$, where the two magnetic sublattices have different chemical compositions or reside on different crystallographic sites. The Heusler compounds are a large family of ordered cubic alloys with general formula X_2YZ,[1,3] where the atoms occupy four interpenetrating fcc sublattices. There are three sites in the unit cell (Figure 1(a)), 4a, 4b, and 8c. A wide variety of occupancy schemes is possible, including Y, Z, 2X (Cu_2MnAl-type); Y, X, XZ (CuHg_2Ti-type); and random (2X, Y, Z)/4, (2X, Y, Z)/4, (2X, Y, Z)/2 (W-type). These are known as the $L2_1$, XA, and bcc structures, respectively. The electronic structure and magnetic properties are sensitive to the site distribution of the atoms. Even a small concentration of antisite defects in the $L2_1$ structure, for example, can modify the magnetic moment and Fermi-level spin polarization of the phase.[4–6]

A Slater-Pauling plot for a series of $L2_1$ Heusler compounds shows that the moment per unit cell is linear in electron count, with slope -1.[1] The moment disappears when there are 24 electrons per formula, or an average of six per atom.

Two tetragonal variants are the $D0_{22}$ (Ni_2MnSn or Al_3Ti-type) structure, which has a severely distorted version of the $L2_1$ cubic cell, with $c/a \approx 1.25$, and $L1_0$, (AuCu–type) which is a further-deformed variant with $c/a \approx \sqrt{2}$ having X and YZ on alternate planes. In both unit cells, the a parameter is $a(L2_1)/\sqrt{2}$. The disorder in the $L1_0$ structure means that $c = c(L2_1)/2$. The cell is close to cubic with $c/a \approx 1.01$.

Here, we have made several Heusler compounds with 24 electrons. We discuss their magnetic and electronic properties, in relation to the ideal zero-moment half metal.

All alloys were made by arc-melting the constituents several times. The Mn_3Ga ingots were annealed in sealed quartz tubes two weeks at temperatures in the range of 400–450 °C, and the other three compounds were annealed for 5 days at 800 °C. The ingots were then crushed or ball milled in a high-energy mill. All samples were characterized by X-ray diffraction and magnetization measurements in a 5 T SQUID magnetometer. The iron-containing compounds were further characterized by ^{57}Fe Mossbauer spectroscopy.

We have synthesized the 24-electron compounds Cr_2FeGe, Cr_2CoGa, Mn_3Ga, and Fe_2VGa. The annealed samples of Cr_2CoGa and Fe_2VGa exhibited a cubic Heusler structure, in accord with the previous reports,[7,8] but it is difficult to decide the atomic distribution from the x-ray powder diffraction pattern.[1] However, Cr_2FeGe was found to be tetragonal, although electronic structure calculations for the XA structure find it to be a zero moment half metal.[9] Mn_3Ga had the tetragonal $D0_{22}$ structure.[10] After ball milling, the Mn_3Ga became almost cubic (tetragonal, with a c/a ratio 1.016 and a crystallite size of about 18 nm. Lattice parameters for all the samples are included in Table I.

The magnetization curves for the alloys are shown in Fig. 2. The curves for unmilled Mn_3Ga are sensitive to annealing treatment and show large anisotropy and hysteresis, with a saturation magnetization (inferred by doubling the extrapolated remanence) of up to $1.2\,\mu_B$ per formula unit. A little Mn

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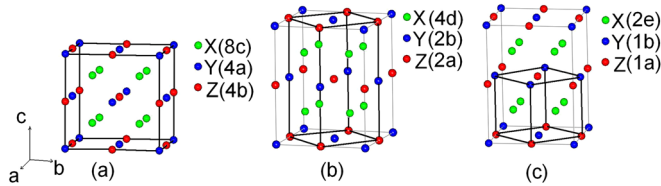
FIG. 1. Unit cells of the (a) cubic L2$_1$, (b), (c) tetragonal D0$_{22}$ and L1$_0$ structures, showing the unit cell of each compound in a black outline. In the L10 structure, Y and Z are disordered on one site. The density of the three structures is conserved in the figure.

is exsolved on annealing. The Curie temperature for this tetragonal ferrimagnet is in excess of $500\,^\circ$C.[1] The moments for all the others are much smaller, $0.07\,\mu_B$ for Fe$_2$VGa, $0.25\,\mu_B$ for Cr$_2$CoGa, and $0.71\,\mu_B$ for Cr$_2$FeGe. That of Fe$_2$VGa shows little temperature dependence but those of Cr$_2$CoGa and Cr$_2$FeGe are roughly doubled at 4 K.

Mössbauer spectra of the iron-containing alloys are shown in Fig. 3. The Fe$_2$VGa shows a single broadened absorption line in agreement with previous work.[11] It is best fitted with a very small hyperfine field of 0.76 T at room temperature. Previous studies of this compound have attributed its weak ferromagnetic moment to antisite defects in the L2$_1$ structure. It is puzzling that such a small number of antisite moments (which are not detected in the spectrum) could lead to high-temperature ferromagnetism. The compound, which has a semimetallic electronic structure, with a pseudogap at the Fermi level,[7,12–14] is possibly a weak itinerant ferromagnet.

The Cr$_2$FeGe exhibits broadened magnetic hyperfine splitting, for only 25% of the iron at 20 K is 22.5 T. The average hyperfine field corresponds to an iron moment of $1.5\,\mu_B$. The room temperature value is 14.5 T, corresponding to an iron moment of $1.0\,\mu_B$ and the compound is then close to its magnetic ordering temperature. The remaining 75% of the iron is in a non cubic site with a quadrupole splitting of 0.55 mm/s. Since the measured room-temperature moment of $0.71\,\mu_B$/f.u is almost three times greater than the iron contribution ($0.25\,\mu_B$), we deduce that there is an average Cr moment of $0.23\,\mu_B$/atom.

Electron count alone is in sufficient to guarantee that the zero-moment composition will be a half-metal. In order to achieve the requisite ferrimagnetic order it is necessary that there is antiferromagnetic coupling between the sublattice moments. Without this coupling, the zero-moment state will be achieved by hybridization and band broadening, which
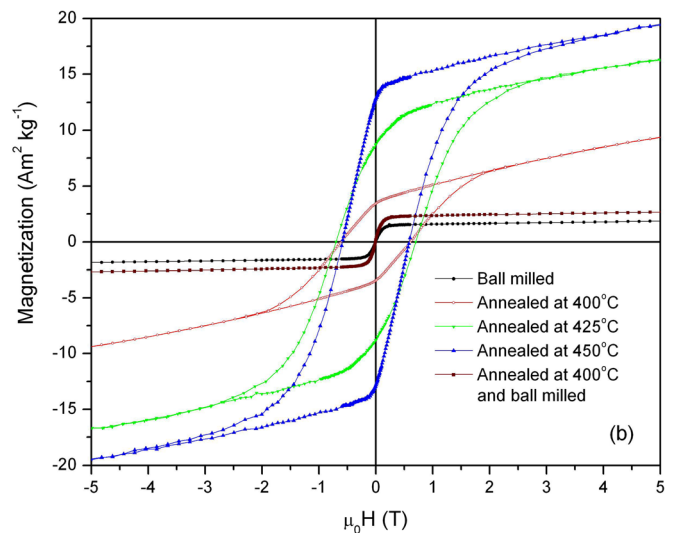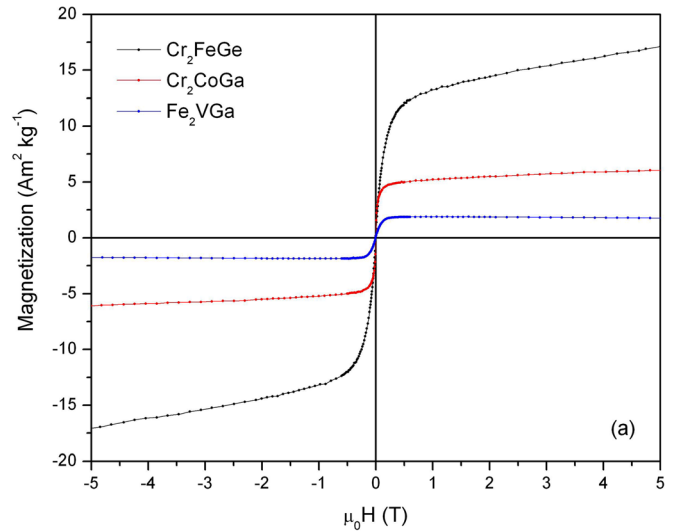

FIG. 2. Room-temperature magnetization curves for (a) three 24-electron compounds. (b) Mn$_3$Ga after different annealing and milling treatments.

reduce the atomic moments themselves to zero, rather than their resultant. There can be a gap in the density of states of both spins, resulting in a nonmetal, rather than a half-metal. Fe$_2$VGa is a case in point, although we raised the possibility that the tiny ferromagnetic moment of $0.035\,\mu_B$ per iron might be distributed over all the iron, and not concentrated on a few antisite defects. Using the conversion factor of $15\,T/\mu_B$ for metallic iron, the 0.76 T hyperfine field corresponds to an atomic moment of $0.05\,\mu_B$.

TABLE I. Magnetization and lattice parameters of the samples investigated.

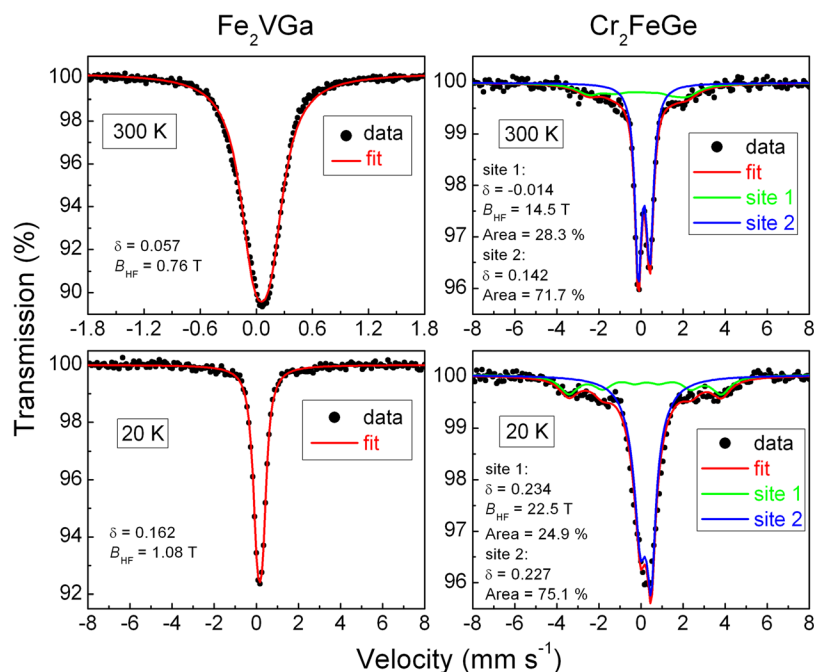| Sample	Treatment	T$_a$ ($^\circ$C)	M$_s$ (Am^{2}kg^{-1})	M$_s$ (μ_B/f.u)	a (pm)	c (pm)
Cr$_2$FeGe	Annealed	800	17.0	0.71	462.9	1241.4
Cr$_2$CoGa	Annealed	800	6.0	0.25	579.7	…
Fe$_2$VGa	Annealed	800	1.7	0.07	578.0	…
	Ball milled	…	1.8	0.07	377.0	383.6
	Annealed	400	9.5	0.40	390.6	713.1
Mn$_3$Ga	Annealed	425	25.0	1.05	390.3	711.0
	Annealed	450	28.5	1.20	390.2	710.7
	Annealed+ ball milled	400	2.7	0.11	375.8	382.2

FIG. 3. Mössbauer spectra of Fe_2VGa and Cr_2FeGe at room temperature and 20 K.

TABLE II. Interatomic distances in the $D0_{22}$ structure, in pm. The lattice parameters are $a = 390$ pm, $c = 710$ pm.

	2a	2b	4d
2a	390/450	276/355	264
2b	276/355	390/450	264
4d	264	264	276/355

Antiferromagnetic direct exchange in metals is most common for atoms with seven valence electrons and a half-full d shell, $4s^2 3d^5$. In other words, for Mn, but Cr and Fe may also exhibit antiferromagnetic interactions in metals. The interatomic distance is quite critical. If it is too short, the d band becomes too broad to support a moment. If it is too long, the direct exchange is weakened and indirect, ferromagnetic coupling becomes dominant. In the case of Mn, the Mn atoms with the shortest bonds (<250 pm) tend to be non-magnetic, Mn with bond lengths from 250 to 280 pm has a small moment, which tends to couple antiferromagnetically, while Mn with a bond length >290 pm tends to have a large moment, which couples ferromagnetically. This is only a rough rule of thumb, and ignores what ever else may be in the compound. Nevertheless, it is interesting to look at the interatomic distances in the cubic $L2_1$ structure where the $4a$ site is occupied by nonmagnetic Ga. For $a_0 = 600$ pm $4b$-$8c$ (260 pm) coupling is antiferromagnetic, but the $4b$-$4b$ (424 pm) and $8c$-$8c$ (300 pm) interactions are weakly ferromagnetic.

A heavily distorted variant of the cubic structure is the tetragonal $D0_{22}$ structure of Mn_3Ga, which has c/a ≈ 1.29. Table II shows how the distances change, while conserving the cell volume.[4] The $2b$-$4d$ antiferromagnetic interaction is still the dominant coupling, while $4d$-$4d$ may now be close to zero. Note the $D0_{22}$ cell has $Z = 2$, whereas the $L2_1$ cell has $Z = 4$. In the $L1_0$ structure with the same density having

unit cell parameters very close to those of milled Mn_3Ga, $a = 376$ and $c = 382$ pm, the interatomic distances are 266 pm and 268 pm; both are antiferromagnetic, so the magnetic structure will depend sensitively on the site occupancy of the nonmagnetic Ga.

We have shown that several of the 24-electron Heusler compounds exhibit a very small net magnetic moment when they have a cubic or near-cubic structure. However, the example of Fe_2VGa illustrates that this does not necessarily imply they are close to zero-moment ferrimagnetism. We suggest that Fe_2VGa is actually an itinerant electron ferromagnet. Alloys with Mn or Cr are most likely to exhibit antiferromagnetic interactions, and we find that a metastable, near-cubic variant of Mn_3Ga has a very net small moment, but the atomic moment of the Mn is likely to be of order $2\,\mu_B$, as in the $D0_{22}$ structure. The other promising candidate is cubic Cr_2CoGa, with improved atomic order. In both cases, it is necessary to confirm by XMCD or neutron diffraction that the Mn or Co/Cr moments are much greater than a few tenths of a Bohr magneton in order to be certain they are the zero-magnetization ferrimagnets we seek.

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