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Electronic structure and magnetism for $FeSi_{(1-x)}Ge_x$ from supercell calculations

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Abstract

Recent studies of $FeSi_{(1-x)}Ge_x$, which found a transition from an insulating to a magnetic metallic state near $x = 0.25$, have revived the discussion about the role of strong correlation in these systems. Here are spin-polarized band calculations made for 64-atom supercells of $FeSi_{(1-x)}Ge_x$ for different x and different volumes for large x. The results show that the small band gap in FeSi is closed for $x \geqslant 0.3$, because of both substitutional disorder and increased volume. Ferromagnetism appears near this composition and becomes enforced for increasing x. The x-dependence of the electronic specific heat can be understood from the exchange splitting of the density-of-states near the gap. Strong volume dependencies for the properties of FeGe suggest experiments using pressure instead of x for investigations of the gap.
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1. Introduction

The unusual properties of the cubic compound ε-FeSi, investigated early by Jaccarino et al. [1], continue to be the subject of many theoretical and experimental studies [2–15]. Band calculations based on the local density approximation (LDA) [16], showing that FeSi is a very narrow band gap semiconductor with a gap of about 6 mRy [9–15], can explain many observed low-temperature properties. The sharpness of the density-of-states (DOS) below the gap is observed as a dispersionless feature in the spectra of angular resolved photoemission [4] taken at low temperature, T. Optical measurements reveal that the gap is gradually filled at higher T, and an unusual feature appears to be that the spectral weight is not conserved [5,6]. The problem is also to understand why the material behaves as a metal with large magnetic susceptibility $\chi(T)$ at higher T. Electronic

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excitations within the band structure (determined at $T = 0$), described by the Fermi–Dirac function, are not able to explain such T-dependent properties [1,2]. Many theories, mostly based on some form of strong correlation, have been proposed for an explanation of the unusual T-dependence [7,8,10,11]. On the other hand, electronic structure calculations within the LDA can explain the T-dependent properties when the effect of thermal disorder is included [13]. The filling of the gap is an effect of structural disorder for T larger than about 150 K, and the material behaves as a Stoner enhanced paramagnet above this temperature [13].

Different dopings of FeSi or other compositions like FeGe, MnSi, etc. lead to a large variety of properties, and metallic magnetism is often found [17]. The LDA approach has been used to analyze thermoelectric properties in doped FeSi [18]. Recent studies [19,20] focused on Ge substitutions on Si sites, in which the evolution of the gap and other properties were followed continuously between the isoelectronic FeSi and FeGe systems. Pure FeGe is metallic and magnetic with a long-range spiral spin alignment, and the saturation moment is about 1 μ_B per Fe [19,21,22]. The alloy $FeSi_{(1-x)}Ge_x$ shows a transition from an insulating state to a metallic ferromagnetic one near $x = 0.25$, with enforced magnetism at larger x [19]. Some, but not all properties are interpreted in terms of the Kondo insulator model with a Hubbard U as parameter [19]. In order to pursue the search for the alternative solution based on LDA band structures, we study here the evolution of the gap and the magnetic moment as function of Ge substitutions with special attention to the effect of substitutional disorder. Methods like the virtual crystal approximation, which interpolate potential parameters between the pure constituents, are insufficient to study the effect of disorder. Therefore, we use supercells with different site occupations for the band calculations of the $FeSi_{(1-x)}Ge_x$ alloys.

2. Method of calculation

The bandstructure for the ordered material can be described by the use of a supercell, although it is a more complicated calculation than for the normal cell. The bands of the normal cell are folded back into the smaller Brillouin Zone of the supercell, giving more bands per k-point. The bands are degenerate along different directions in k-space, but if there is disorder (structural or substitutional) there will be slightly different band dispersions along different directions. The average energy of a band along say k_x and k_y may be similar to the energy for the ordered case, but the non-degeneracy along different directions can be interpreted as a band broadening of the original band. Thus, the band broadening or smearing of the bands near the gap, which becomes important for the properties of the FeSi-like materials, is because of a number of non-degenerate states that deviate from the original energy as the degree of disorder increases. These effects, as well as a possible drift of the average energy due to disorder, are contained in the supercell approach. Disorder of real alloys does not show the long-range periodicity of the supercell, but this a minor problem when large supercells can be used.

The spin-polarized version of LDA can be used to determine the magnetic moment, but the question of spiral order of the spin moments in FeGe is not addressed in this work. The calculated moments will be compared with saturation moments at high field (0.3 T) at which the moments are aligned. Since a magnetic field of this amplitude is very small on the energy scales in a band calculation (1 mRy corresponds to 230 T) it is unlikely that this field can modify exchange splitting or the electronic structure.

The self-consistent Linear Muffin-Tin Orbital method is applied to 64-atom supercells (8 basic unit cells of the B20-structure) as is described for the calculation for structurally disordered FeSi [13]. The linearization energies are taken near the center of each ℓ-band. The LDA potential contains no special on-site correction due to correlation. All sites are non-equivalent in the disordered cells. The self-consistent iterations use initially 8 k-points in $\frac{1}{8}$ of the Brillouin Zone, while they are terminated by iterations using 27 k-points. The band gaps in the two sets of k-points agree to within 0.5 mRy, but the magnetic moments in the metallic cases can

differ by 20–30 percent for some configurations. This difference comes from difference in the DOS near the gap between the two sets of k-points. A comparison of the DOS from a case using of 27 and 64 k-points show no large difference and it is expected that the convergence of the moments from 27 k-points is satisfactory. The calculations include a thermal smearing of 1 mRy in the electronic occupation (Fermi–Dirac). This stabilizes the self-consistency, but there is also a physical reason behind the smearing; The zero-point motion of the atomic positions, leading to some structural disorder, can be estimated to be of the order 0.5 percent of interatomic distances for appropriate values of force constants and atomic masses [15,24]. From various arguments it can be concluded that an essential effect of band smearing on the electronic structure near the Fermi energy, E_F, can to some extent be modeled through the Fermi–Dirac occupation. Although the role of structural disorder (zero-point motion, thermal disorder as function of temperature and possible disorder because of Si/Ge substitutions) merits a more careful analysis, we may include some of the effects from zero-point motion through the Fermi–Dirac function. All calculations are made with the same internal structural parameters of the B20 structure and with no structural disorder. Thus, only the effect of substitutional disorder appears in these calculations, although it is probable that different relaxation around Si and Ge will increase the effects of disorder in real $FeSi_{(1-x)}Ge_x$.

The calculations do not determine the equilibrium volumes through minimization of the total energies for each composition, but the calculated pressures (P) are used as a guidance for finding the volumes relative to that of pure FeSi. Absolute values of direct calculations of the pressure are less reliable than when P is calculated through the volume derivative of total energies, but they converge more rapidly and can be useful for studies of relative variations. The bands of pure FeSi at $T = 0$ (no disorder) have a gap of 6 mRy at the Fermi energy, E_F, in agreement with other calculations using different methods [9–14]. This is for a lattice constant, $a_0 = 4.39$ Å, between the experimental one (4.52 Å) and the theoretical one (at the minimum of the total energy). This reflects the usual problem of using the LDA for 3d transition metals, in which the lattice constants come out 2–3 percent too small compared to experiment [23]. This uncertainty could be relatively severe for FeSi because of the narrow gap. However, the theoretical E_g agrees well with experiment and it decreases only slowly when the lattice constant increases, in agreement with the pressure dependence of the magnetic susceptibility [12,14].

The first calculation for FeGe is made with $a_0 = 4.52$ Å, i.e. about 3 percent larger than for FeSi. This choice is based on the differences in covalent radii and lattice constants of pure Ge and Si, and as for FeSi we consider the LDA-bands for a lattice constant which is a few percent smaller than the experimental value (4.7 Å). The calculated gap in FeGe, 1.5 mRy, is close to the LDA result of Ref. [20]. For intermediate compositions a_0 is assumed to vary linearly with x, which turns out to be consistent with the calculated variations of the pressure. The discontinuities of the potential at the limits of the different Wigner–Seitz spheres are small when the Wigner–Seitz radii are 1.44 Å for Fe, and 1.37 Å for Ge and 1.27 Å for Si in FeGe and FeSi respectively. Almost the same values are maintained in the calculations for the $FeSi_{(1-x)}Ge_x$-systems. The s- and p-bands of Si and Ge are similar, both concerning the position relative to the Fe bands and the band widths. The unoccupied 3d band in Si is almost 0.5 Ry closer to E_F than the 4d band in Ge. This makes a difference for the hybridization with the Fe-d bands near E_F and for the degree of disorder of the band structure in the alloys.

Calculations are made for pure $Fe_{32}Si_{32}$ and $Fe_{32}Ge_{32}$ and for configurations with 4, 7, 10, 11, 12, 14, 16, 17, 19, 22, 25, 28, 30 and 31 number of Ge sites per supercell. The distribution of Ge vs. Si sites is random in the different cells for different x, but two calculations are made in which the Ge sites (4 and 12, respectively) are clustered together within the cell. Two calculations are made for pure FeGe, labeled II and III, in which a_0 is increased by 1 and 2 percent, respectively. As will be discussed later, the results for the moment agree

best with experiment in calculation FeGe-III, although the lattice constant is smaller than the experimental one.

3. Results

3.1. Bandgap and magnetic moments

The width of the gap, E_g^{para}, and the DOS at E_F, N_{para}, from the paramagnetic calculations, and the exchange splittings, ξ, from the spin-polarized calculations are shown in Table 1. The interest of displaying paramagnetic results is to show that ferromagnetism coincides with cases where the gap is closed or smaller than 1.5 mRy. As seen in the table, the gap becomes closed for x between 0.25 and 0.91 approximately. This is an effect of disorder. For x outside this range, closer to the pure compositions, there are not sufficient smearing of the bands coming from disorder and the alloyed system still has a gap in the DOS. The gap remains in the two spin-polarized DOS functions even when a magnetic moment has removed E_F from the gaps. As discussed later, additional disorder coming from an uneven distribution of local moments can make the gaps less visible in the weakly magnetic systems. The effect of disorder would not appear in a simplified calculation like the virtual crystal approximation, and this effect of disorder on the bandstructure of the $FeSi_{1-x}Ge_x$ system is the most important result from the present calculations.

The gap, E_g, is about 2.5 mRy in both calculations with 4 Ge atoms, either randomly distributed or clustered within one basic cell of FeGe together with 7 basic cells of FeSi. The effect on the gap from Ge substitutions is relatively weak compared to other dopants replacing Fe or Si [18]. As might be expected, the effects of disorder on the DOS are to reduce E_g and to make the DOS peaks near the gap wider. The gap is reduced when the concentration of Ge is increased, and the alloy becomes metallic at about 8–9 Ge sites per cell. The Fermi energy is near the bottom of a 'valley', or pseudogap, in the DOS for all paramagnetic calculations, showing that the gap is never completely washed out. A real gap is restored for the two highest Ge concentrations when only one or two Si remain in the cell.

Table 1
Calculated band gap and DOS at E_F, $N_{para}(E_F)$, in units of states/cell/Ry from paramagnetic calculations, and exchange splitting, ξ, from the spin-polarized calculations

Cell	E_g (mRy)	N_{para}	ξ (mRy)
$Fe_{32}Si_{32}$	6	0	—
$Fe_{32}Si_{28}Ge_4$	2.5	0	—
$Fe_{32}Si_{28}Ge_4$-c	2.5	0	—
$Fe_{32}Si_{25}Ge_7$	2	0	—
$Fe_{32}Si_{22}Ge_{10}$	—	16	1
$Fe_{32}Si_{21}Ge_{11}$	—	3	2
$Fe_{32}Si_{20}Ge_{12}$	—	110	9
$Fe_{32}Si_{20}Ge_{12}$-c	—	190	6
$Fe_{32}Si_{18}Ge_{14}$	—	90	5
$Fe_{32}Si_{16}Ge_{16}$	—	80	7
$Fe_{32}Si_{15}Ge_{17}$	—	100	5
$Fe_{32}Si_{13}Ge_{19}$	—	110	9
$Fe_{32}Si_{10}Ge_{22}$	—	75	9
$Fe_{32}Si_7Ge_{25}$	—	27	12
$Fe_{32}Si_4Ge_{28}$	—	13	13
$Fe_{32}Si_2Ge_{30}$	0.5	0	12
$Fe_{32}Si_1Ge_{31}$	0.8	0	3
$Fe_{32}Ge_{32}$-I	1.3	0	5
$Fe_{32}Ge_{32}$-II	1.1	0	18
$Fe_{32}Ge_{32}$-III	0.8	0	78

The labels "-c" mean clustered configuration (see text), and I,II and III for pure FeGe are for lattice constants 4.52, 4.56 and 4.61 Å.

The Fe d-bands contribute most to the large DOS near the gap, with some local variations from site to site due to the differences of near neighbor atoms. Magnetic, Stoner-type ordering can start at sites with the largest $N(E_F)$. The magnetic instability occurs when $N(E_F)I \geqslant 1$, where I is the exchange integral, but the size of the moments is determined by other parameters. (As seen in Table 1, the calculation with 12 clustered Ge atoms has a higher paramagnetic $N(E_F)$ than the case with random site occupation, but for ξ and the moment it is the other way around.) Typically there is more than a factor of two between the lowest and highest local moments on different Fe when disorder plays a role, i.e. for x not too close to 1. The difference in local moments leads to an additional disorder in the spin-polarized part of the potential, so that the majority and minority

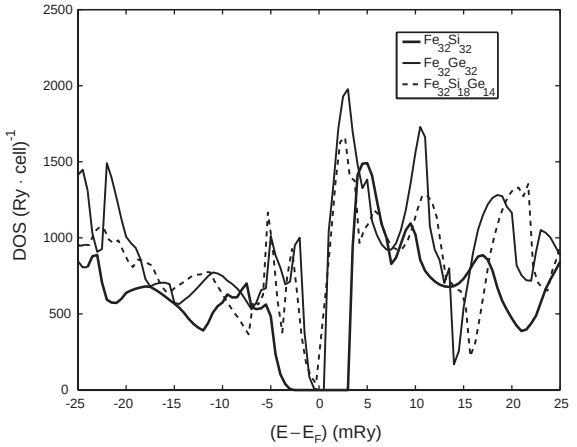

Fig. 1. Paramagnetic DOS of FeSi, FeGe and $FeSi_{0.56}Ge_{0.44}$ as calculated for the supercells containing totally 64 atoms. The energy is relative to E_F.

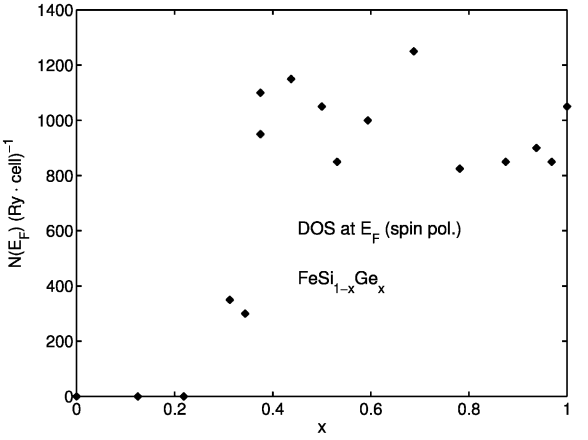

Fig. 2. Spin-polarized DOS at the Fermi energy, $N(E_F)$, as function of the Ge concentration x in unitcells containing 64 atoms.

DOS functions are not exactly like a rigid splitting of the paramagnetic DOS (Fig. 1). This makes the remaining pseudogaps in the DOS of the two spins more 'washed out' than in the paramagnetic DOS. The mechanism leading to magnetism is accelerated as soon as the exchange splitting allows for E_F to enter into the high peaks of the DOS of majority and minority spin above and below the gap, respectively. This process slows down the self-consistent convergence in some cases. As will be shown later, it also provides an explanation for the large variation of the moment in FeGe as function of volume.

The spin-polarized $N(E_F)$ and magnetic moments m are summarized in Figs. 2 and 3. The differences in local environment among the different configurations make the total moments as function of x to 'fluctuate' in Fig. 3. Such fluctuations concern also the local moments and they appear to be more important when the moments are not yet very large. This is probably because the conditions for having the Stoner criterion fulfilled or not may differ from site to site when there is no general trend towards strong magnetism. When the moments are large there is a shift of E_F into the high DOS peaks. This makes all (Fe-)sites clearly magnetic, and the effect of an uneven distribution of local moments becomes smaller. As was discussed above, the effect of

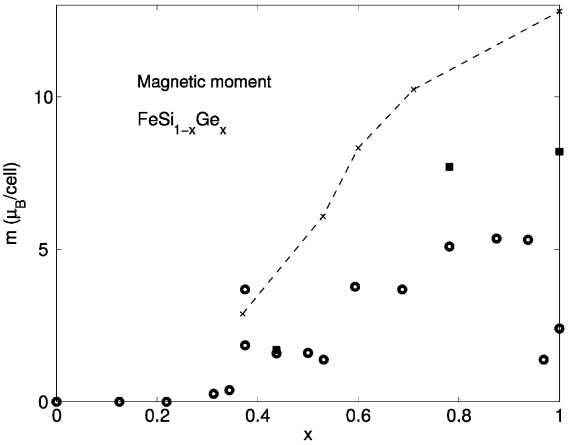

Fig. 3. Magnetic moments as function of the Ge concentration x in cells containing 64 atoms. The points connected by the broken line are values taken from the inset of Fig. 2 in the paper by Yeo et al. [19] and they represent the measured moments at low temperature in a field of 0.1 T. Note that the saturation moment for $x = 1$ is larger [19,21,22]. The calculated moments for $a_0(x)$ interpolated linearly between 4.39 Å ($x = 0$) and 4.52 Å ($x = 1$) are shown by the circles. Three calculations at $x \approx 0.44$, 0.78 and 1.0, in which a_0 are increased by 1 percent, shown by the filled squares, show that the moment increases only for the Ge rich cases (to 7.7 and 8.2 μ_B/cell, respectively). An additional calculation for $x = 1$, in which a_0 is increased once more by 1 percent to 4.61 Å, gives a much larger moment, 33.8 μ_B/cell.

disorder is smaller for x near the pure compositions (0 or 1), and this effect extends to the variation of moments as well. Calculations for 4 and 7 Ge per cell give vanishing moments, while those for 30 and 31 Ge have finite moments despite a small gap. The latter can be understood from the thermal smearing that overcomes gaps smaller than about 1.5 mRy. These results show that weak magnetism can be the result of substitutional disorder of the $FeSi_{(1-x)}Ge_x$-system for x larger than ~ 0.3. This range for ferromagnetism between $x \approx 0.3$ and 1, agrees well with experiment [19], c.f. Fig. 3. The moments are smaller, and as will be discussed later, this discrepancy is mostly due to the large sensitivity of the moments to variations of the volume.

3.2. Specific heat

The DOS near the gap is very peaked, and statistical fluctuations of $N(E_F)$ can be seen for the different configurations. The total, spin-polarized $N(E_F)$ values shown in Fig. 2 are scattered around 800 states/Ry/cell for large Ge concentrations, while the maximal values (1000–1200 states/Ry/cell) are found for $x \approx 0.5$. The electron–phonon coupling λ is calculated to be about 0.2 for disordered FeSi having a DOS of 700 states/Ry/cell [13]. As λ is proportional to $N(E_F)$ one can estimate the electronic specific heat coefficient $\gamma = \frac{1}{3}\pi^2 k_B^2 N(E_F)(1+\lambda)$ to be $\approx$ 5–9 mJ/mol K^2 when $N(E_F)$ varies between 800 and 1200 states/Ry/cell. The measured γ, shown in Fig. 4 in the paper by Yeo et al., increases from zero at $x \sim 0.25$, has a peak beyond 20 mJ/mol K^2 for $x \approx 0.37 \pm 0.1$, then decreases to about 11 mJ/mol K^2 at $x \sim 0.6$ and thereafter stays flat at this level for larger x. Thus, the calculated values of the DOS and the electron–phonon couplings seem too small in comparison to the measured γ of Yeo et al. [19]. Such discrepancies are often attributed to spin fluctuations that contribute to γ through λ_{sf} in near magnetic systems. A calculation of λ_{sf} for a single 8-atom cell of disordered FeSi (which becomes metallic with a moderate DOS below the limit for Stoner magnetism) indicates that λ_{sf} can be large, between 0.5 and 1. This DOS is comparable or lower than the DOS in the FM

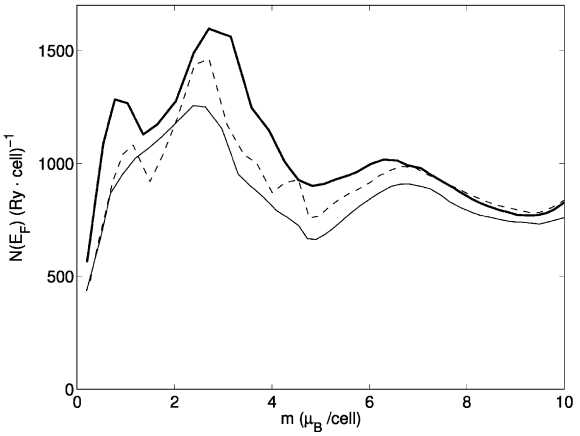

Fig. 4. Total $N(E_F)$ as function of magnetic moments calculated from a rigid spin splitting of the paramagetic DOS functions in Fig. 1. The heavy line is obtained when using the DOS for $x = 0$, the broken line for $x = 0.44$ and the thin line for $x = 1$. The variations of the observed specific heat of Yeo et al. (shown in the inset of Fig. 4 of Ref. [19]) show one peak near $x = 0.37$, corresponding to a small m.

phases of $FeSi_xGe_{(1-x)}$. It should be noted that λ_{sf} is often lower on the magnetic side of a FM transition [25]. With considerations of these facts it can be expected that spin fluctuations contribute more to γ just at the very beginning of FM and less when magnetism becomes stable at larger x. The peak in the measured γ of ~ 20 mJ/mol K^2 appears near $x = 0.37$ [19], i.e. rather close to the critical x for the metallic transition. From the DOS of Fig. 1 it is possible to understand this behavior. All DOS functions (for all x) show the largest peaks quite near to the gap or pseudogap, while the DOS is a bit lower further away from the gap. Larger disorder will smear the DOS, but the peak positions remain even in the spin polarized majority and minority DOS functions. An inspection of the DOS functions shows that a moderately large moment of 3 μ_B per 64 atom cell (corresponding to a ξ of about 9 mRy) will have E_F on the first peak above the gap within the majority DOS, and on the second peak below the gap within the minority DOS, cf. Fig. 1. Thus the total $N(E_F)$ is large for a moment of this size, from Fig. 1 one can estimate that the combined $N(E_F)$ (majority plus minority) is about 1200 states/cell/

Ry. If the moment is larger, then E_F is found further to the right on the majority DOS and further to the left on the minority DOS. $N(E_F)$ is lower for both spins, and the combined $N(E_F)$ taken from Fig. 1 is 700–800 states/cell/Ry for a large moment (7–8 μ_B/cell) and a large ξ of 12–15 mRy. This discussion is exemplified in Fig. 4 by rigid-band spin splittings on the paramagnetic DOS for three different compositions. The total charge is conserved, whereas a moment 'm' is obtained from the differences in the number of occupied spins. If m shows a linear increase as function of x it is expected that $\gamma(x)$ has the same shape as in Fig. 4.

The trend of increasing moments towards large Ge concentration is evident from the points in Fig. 3. The calculated moments are typically 2–3.5 μ_B for x in the range 0.35–0.7, while for larger Ge concentrations the moments can reach 5 μ_B or more. Thus, the former range of concentration corresponds to a large $N(E_F)$ (and γ), while in the latter $N(E_F)$ is reduced. (The relative variations in γ will be enhanced over those in $N(E_F)$ because of the coupling factors λ.) This behavior is partly confirmed in Fig. 2; $N(E_F)$ is largest for x between 0.4 and 0.6, although there is scattering among the points due to the small set of configurations. The relative variations of $m(x)$ and $\gamma(x)$ fit reasonably well to the measurements by Yeo et al., but the moments are too small when $x \to 1$. The moment measured by Yeo et al. at $x = 0.37$, about 0.1 μ_B/f.u. (equal to $\sim 3.2\ \mu_B$ for the 64 atom cell), is in fair agreement with the calculations. But the moment (not yet at saturation) for $x \to 1$, $\sim 0.4\ \mu_B$/f.u. [19] ($\sim 12\ \mu_B$ per 64 atom cell), is larger than in the calculation.

3.3. Properties at Ge-rich compositions

The calculations for $x \to 1$ indicate that a small gap will reappear in FeGe if spin-polarization could be prevented. Calculations for undoped FeGe are easier as they can start from results for the smaller 8-atom cells, and a few volumes have been studied. The calculated pressure for FeGe (FeGe–I at $a_0 = 4.52$ Å) is about 0.1 Mbar larger than for FeSi (at $a_0 = 4.39$ Å), which gives a hint that the calculations for $x \to 1$ are made at too small lattice constants. In a calculation (labeled FeGe-II in Table 1), in which a_0 is increased to 4.56 Å, the difference in pressure is reduced to about 0.05 Mbar, and for FeGe-III when a_0 is 4.61 Å the pressure is almost the same as for FeSi. The gap becomes smaller as a_0 is increased (see Table 1). It is unusual that a gap becomes wider with applied pressure. It is more common that the gaps are between different sub-bands, so that the gaps become narrower when the bands become wider at larger pressure. But the gap in FeSi and FeGe is within the Fe-d band, so the gap widens together with the band when the lattice constant is reduced [12], although the effect is small for FeGe as seen in Table 1. A narrower gap for increased lattice constant implies that a metallic transition is approaching and the moment in the spin-polarized calculations increases from 0.08 μ_B/f.u. in FeGe-I to 0.25 and 1.06 μ_B/f.u. for FeGe-II and III, respectively. The increase in moment as a_0 is increased appears very large when there only is a small reduction of the gap. However, in addition to a narrower gap there are sharper increases of the DOS on both sides of the gap when the volume is increased, so that more states come closer to E_F. This is probably more relevant for the evolution of the magnetic moment as function of volume than the value of the gap itself.

The strong volume dependence of m is extended towards increasing Si-compositions, but not too far. When the lattice constant is increased by 1 percent for $Fe_{32}Si_{18}Ge_{14}$ ($x = 0.44$) and $Fe_{32}Si_7Ge_{25}$ ($x = 0.78$), it is found that the moment increases only in the latter case (by more than 50 percent) compared to the moments for the smaller lattice constants shown at the respective composition, see Fig. 3. Thus, when the gap is just closed and the system is not yet a good metal as in the former case, there is not a strong dependence on volume. The DOS has 'tails' near the gap, partly due to disorder. The initially small overlap between the DOS of the conduction band and the valence band makes the system a rather poor metal, and magnetism is still hesitant. But in the latter case, when $x = 0.78$ (as well as when $x = 1$) the DOS is large or increases rapidly near a narrow pseudogap and the effect of pressure is large.

As was discussed above, the strong sensitivity of m with volume is possible when the exchange splitting is sufficiently large to make the system clearly metallic within both spins. It might seem strange that a moment develops depite the (small) gap in the DOS for Ge-rich compositions, and it could be suspected to be a metastable state. However, convergence of the total energies for FeGe-II show that the magnetic state is indeed the stable one with a total energy more than 30 mRy lower than the non-magnetic one. The interesting situation of a stable non-magnetic state and a metastable magnetic state with larger total energy is more probable for larger gaps, and the T-dependences of the two states could be very different so that metamagnetism, large magnetoresistance and phase transitions can be imagined.

The moment is very sensitive to volume and disorder, but the combined results of the pressure calculations (compared to that of FeSi) and the size of the calculated moments (compared to the measured one) indicate that the lattice constant should be close to the one used for the calculation FeGe-III, or near 4.6 Å, for an optimal description of the properties of FeGe. The calculated moment is then close to the saturation moment found for fields larger than 0.3 T [19,21,22], of the order 32 μ_B per supercell. It also follows that magnetism on the Ge-rich side of $FeSi_{(1-x)}Ge_x$ depends more on the increased volume than on disorder. The strong volume dependence of m suggests that thermal expansion, apart from effects due to thermal disorder, should lead to an unusual increase of m with temperature. This hypothesis is corroborated by the measured increase of $m(T)$ by about 10 percent between low T and just below the Curie temperature ($T_C \sim 280$ K) at which m drops to zero, seen in the data for $x = 1$ by Yeo et al. By using a typical coefficient for thermal expansion as for Fe, one arrives at an increase of the lattice parameter of the order 0.2 percent between low-T and room temperature. The calculated increase of m as function of a_0 translates into an even larger increase of $m(T)$ within this temperature interval, but this does not take into account the type of moment disorder that finally leads to zero effective moment at T_C.

4. Conclusion

In conclusion, it has been shown that LDA band calculations can give an adequate description of the $FeSi_{(1-x)}Ge_x$ system if disorder and changes in volume as function of x are accounted for. The gap is small enough, so that the combined effects of disorder and increased volume lead to zero gap for $x \approx 0.3$. The system becomes magnetic for larger Ge concentrations, and the behavior of the electronic specific heat is directly related to the DOS structures of the majority and minority bands. The quantitative agreement with experiment for the moments is best when the lattice constants for Ge-rich compositions are 1–2 percent larger than in the results shown in Fig. 3.

Pressure experiments can be suggested from the calculated results of pure FeGe at different volume. The delicate balance between magnetism in metallic FeGe and absence of magnetism in semi-conducting FeGe could be followed continuously as function of increasing pressure. The effect of uniform pressures would be the same as varying x from FeGe towards FeSi, but with the advantage that effects of substitutional disorder can be excluded. Theoretical estimates of the bulk modulus (B) within LDA are often larger than what is found experimentally, as is the case for FeSi [12]. From the results above, leading to $B \approx 1.6$ Mbar, it is expected that a pressure of 0.1 Mbar will be sufficient for a suppression of the moment. This represents an upper limit, since the measured low value of the Debye temperature for FeGe [19] is an indication of a low B. Information about disorder, also structural and thermal ones, is important for calculations of the properties of the isoelectronic alloys $FeSi_{(1-x)}Ge_x$ because of the large DOS peaks close to a very small gap.

Finally, the fact that properties depend on a tiny gap between high DOS peaks motivates a comment about results of band calculations. When the DOS near the Fermi energy is rather flat, as in most metallic materials, there are no big consequences of details (choice of basis, linearization energy, size of atomic spheres, general potential, type of density functional and so on) in the band theory method. But here for FeSi and FeGe, when the DOS varies from zero to very large amplitude

within 1–2 mRy, it might be that differences in the method of calculation lead to quite different properties. It is important to note that the gap of about 6 mRy in FeSi agree with experiments and other calculations. Also the result that $FeSi_{(1-x)}Ge_x$ becomes metallic for x larger than about 0.3 agrees with experiment. But there is little experimental information about the existence of a small gap (1–2 mRy) in the spin polarized bands of pure FeGe. Therefore, experimental results of FeGe as function of pressure would be valuable.

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