PHYSICAL REVIEW B **67**, 220403(R) (2003)

Curie temperatures of zinc-blende half-metallic ferromagnets

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(Received 6 April 2003; published 17 June 2003)

Using density-functional theory in the local-density approximation and spin-fluctuation theory, the Curie temperatures of the zinc-blende half-metallic ferromagnets VAs, CrAs, MnAs and the Heusler compound NiMnSb have been estimated, the lower bounds obtained being *ab initio*. The orders of magnitude are the same as the Curie temperature of the half-metallic ferromagnet NiMnSb with $T_c = 701$ K. Of the three compounds VAs, CrAs, and MnAs, the highest T_c is calculated for CrAs, for which the Fermi energy is in the middle of the minority-spin electron gap; its Curie temperature might be as high as 1000 K. The Curie temperature drops sharply when the Fermi energy moves into the minority-electron conduction band as in the case of MnAs.

DOI: 10.1103/PhysRevB.67.220403 PACS number(s): 75.50.Pp, 75.30.Et, 71.15.Mb

Half-metallic ferromagnets are metals having 100% spin-polarized electrons at the Fermi surface. They are thus of particular interest in the newly developing field of spin-based electronics, or spintronics. After de Groot *et al.*[1] first predicted half-metallic ferromagnets (HMF) in Heusler compounds in 1983, several HMF have been theoretically predicted and experimentally fabricated in the laboratory. A list of these materials include NiMnSb,[1] CrO_2,[2,3] and the colossal-magnetoresistance manganates.[4,5]

Recently, zinc-blende CrAs (zb-CrAs) was grown on GaAs by molecular-beam epitaxy and shown to be ferromagnetic at room temperature.[6] Its Curie temperature was stated to be above 400 K. Electronic structure calculations by these authors revealed zb-CrAs to be a half-metallic ferromagnet. In fact, a large number of recent electronic structure calculations concentrated on zinc-blende compounds of transition elements, in some notable cases, comparing the electronic properties in the unstable zinc-blende phase with that of the stable NiAs crystal structure.[7–9] A systematic study of zinc-blende compounds involving transition-metal elements with N, P, As, Sb, S, Se, and Te is that by Galanakis and Mavropoulos[10] who also examined the half-metallic behavior of the transition-element terminated surfaces. These large theoretical and experimental efforts warrant an attempt to estimate the Curie temperatures T_c of some of the compounds that might be of technological importance and relate trends in T_c to salient features of the electronic structure.

A quantitative *ab initio* theory of thermodynamic properties of metallic magnets has been a great challenge for decades. While simple models can often reveal physical mechanisms that determine thermal properties of magnets, they do not, in general, succeed in supplying hard numbers for realistic materials. The density-functional theory,[11] however, although designed for ground-state properties, seems well suited for such problems. For even without making an explicit use of time-dependent density-functional theory,[12] one can model low-lying excited states by constrained calculations,[13] provided the adiabatic approximation is applicable,[14] which will be assumed here. Elementary metals were treated this way using different methods,[15–17] but very little was done on compounds. A notable exception is a recent study of the Curie temperature of the magnetic semiconductor (Ga,Mn)As.[18]

Taking a point of view that emphasizes the fact that the electrons responsible for the magnetic properties are identical with those causing metallic conductivity,[14,15,19] we build on previous work of Moriya,[20] Lonzarich and Taillefer[21] as well as Uhl and Kübler.[16] The salient features of the theory are easily stated by beginning with the fluctuation-dissipation theorem[20,22] which is exact in the linear-response theory. For the νth component of the spin fluctuation with wave vector $\mathbf{k}$, denoted by $\langle |m_{\mathbf{k}\nu}|^2 \rangle$, one writes

$$\langle |m_{\mathbf{k}\nu}|^2 \rangle = \frac{2}{\pi} \int_0^\infty d\omega \ \mathrm{Im}\{\chi_\nu(\mathbf{k},\omega)\} N(\omega), \tag{1}$$

where $\chi_\nu(\mathbf{k},\omega)$ is the frequency-dependent, nonuniform magnetic susceptibility and $N(\omega)$ denotes the Planck distribution function (zero-point fluctuations are omitted here). Moriya's formula connects the summed fluctuations $n_\nu^2 \doteq \Sigma_{\mathbf{k}} \langle |m_{\mathbf{k}\nu}|^2 \rangle$, with the temperature-dependent magnetization $M(T)$:

$$\frac{M(T)^2}{M_0^2} = 1 - \frac{2n_t^2 + 3n_l^2}{M_0^2}, \tag{2}$$

where M_0 is the magnetic moment at $T=0$, and t and l denote transverse and longitudinal fluctuation components, respectively. Equation (2) may be derived from the free energy which is written as

$$F(M,T) = \frac{\alpha}{2} M^2 + \frac{\beta}{4} M^4 + F_1(M,T). \tag{3}$$

The first two terms are a Landau-type expansion, the coefficients α and $\beta = -\alpha/M_0^2$ are independent of the temperature and may be thought of as describing the energy gained in the magnetic state (this point will be taken up below again). The remaining term of the free energy[23] involves the imaginary part of the susceptibility, which together with an approximation for the latter enables one to derive Eq. (2). For this, the susceptibility is assumed such that the real part agrees with the result of a Gaussian approximation.[16] It contains no adjustable parameters and can be reliably calculated in the local-density functional approximation. For the imaginary

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part, the leading term in the low-wavelength and the low-frequency expansion is assumed,[20,21] so that the inverse dynamic susceptibility reads

$$\chi_\nu^{-1}(\mathbf{k},\omega)=\chi_\nu^{-1}(\mathbf{k})-\frac{i\omega}{\Gamma k}, \tag{4}$$

where the real part for $\nu=l$ is the inverse, static longitudinal susceptibility given by

$$\chi_l^{-1}(\mathbf{k})=\alpha+\beta(3M^2+2n_t^2+3n_l^2)+2j(\mathbf{k}) \tag{5}$$

and for $\nu=t$ the inverse, static transverse susceptibility given by[16]

$$\chi_t^{-1}(\mathbf{k})=\alpha+\beta(M^2+4n_t^2+n_l^2)+2j(\mathbf{k}). \tag{6}$$

In the simpler Ginzburg-Landau approach of Lonzarich and Taillefer,[21] the function $j(\mathbf{k})$ is approximated by a constant times k^2. In the present work it is calculated *ab initio*; it is this important improvement of the Ginzburg-Landau approach together with the replacement of the integral over k space (containing a cut-off parameter) with a sum over the Brillouin zone (no cut-off parameter needed) which enables an estimate of a lower bound to the Curie temperature. The imaginary part describes relaxation phenomena in a simple lorentzian and contains a parameter Γ that could be approximately obtained from an evaluation of the dynamic Kohn-Sham susceptibility,[24] but this is a difficult undertaking which was not attempted here. Instead the value of Γ is taken from experiment as will become apparent below.

The ''exchange'' function $j(\mathbf{k})$ (times M_0^2) measures the energy cost of noncollinear configurations of the magnetization and describes thus one of the essential aspects of spin fluctuations. As in previous work,[16,18] it is obtained from the total energy for *spiral* magnetic configurations; the latter are defined by a magnetization vector $\mathbf{M}$ given by $\mathbf{M}=M_0[\cos(\mathbf{k}\cdot\mathbf{R})\sin\theta,\sin(\mathbf{k}\cdot\mathbf{R})\sin\theta,\cos\theta]$ that depends on the lattice site $\mathbf{R}$ and a polar angle θ (cartesian coordinates being separated by commas). Because of the generalized translational symmetry of spin spirals first explored by Herring[25] and Sandratskii,[26] the total energy can be obtained very efficiently for such a magnetic configuration. Further simplifications are possible by virtue of the force theorem which allows the total-energy differences for constrained-moment configurations to be obtained from the energy differences of the non-self-consistent band states. The validity of this theorem for magnetic systems was recently discussed critically by Bruno.[27] Thus, denoting the total-energy increase in the spiral state counted from the ferromagnetic ground state by $\Delta E(\mathbf{k})$, the exchange function is obtained from[16,19]

$$\Delta E(\mathbf{k})=M_0^2 j(\mathbf{k})\sin^2\theta. \tag{7}$$

For the calculation of the spin-wave stiffness constant, one needs[28] the limit $\theta\to 0$, but for the calculation of the Curie temperature, $\theta=\pi/2$ is a good choice.[16]

With the approximations stated, the frequency integral in Eq. (1) can be carried out exactly and subsequently fitted to a simple fraction.[21] The summed longitudinal and transverse spin fluctuations needed to evaluate the magnetization, Eq. (2), and to carry through the self-consistent calculations for the susceptibility, are finally obtained from

$$n_\nu^2=\sum_{\mathbf{k}}\langle|m_{\mathbf{k}\nu}|^2\rangle$$

$$=k_BT\sum_{\mathbf{k}}\chi_\nu(\mathbf{k})-\xi\Gamma\sum_{\mathbf{k}}k\left[1+\frac{\xi\Gamma k}{k_BT}\chi_\nu^{-1}(\mathbf{k})\right]^{-1}. \tag{8}$$

The constant $\xi=0.897$ and $\nu=l,t$. We are now ready to turn to numerical results.

It seems advantageous to begin with a half-metallic ferromagnet which has been described in great detail by de Groot *et al.*[1] and for which the Curie temperature is known, this is NiMnSb with a measured $T_c=701$ K. Using the local spin-density-functional approximation the electronic structure is calculated with the augmented spherical wave method.[29]

For NiMnSb, the gap in the minority-spin electrons is found to be 0.25 eV. The exchange function $j(\mathbf{k})$ is obtained from the band-energy differences for 60 special k points that sample the irreducible part of the Brillouin zone using the self-consistent ground-state potential, i.e. the force theorem is used. This allows a sufficiently accurate and quick evaluation of the Brillouin-zone sums in Eq. (8).

The ''static'' approximation for the magnetization is the self-consistent solution of Eqs. (2) and (8), together with Eqs. (5) and (6), using for the relaxation constant the value $\Gamma=0$. The Landau coefficient α should be obtained from the total-energy difference between the magnetic and the nonmagnetic states. This, however, gives rise to a first-order phase transition. Furthermore, this choice seems unphysical since in this case the energy reference is the gap-less state. The coefficient is therefore chosen much smaller than the Brillouin-zone average of the $j(\mathbf{k})$ (which is about 12 mRy), observing that the Curie temperature becomes independent of α in this limit and is given by

$$k_BT_c=\frac{2}{5}M_0{}^2\left(\sum_{\mathbf{k}}\frac{1}{j(\mathbf{k})}\right)^{-1}, \tag{9}$$

which is easily proved since at T_c the fluctuations become equal, i.e., $n_l^2=n_t^2\doteq n^2$, and hence from Eq. (2) $n^2/M_0^2=1/5$, which with Eq. (8) gives the desired result. One implies in these steps that the transition is of second order. The choice of α affects, of course, the susceptibility in the paramagnet state given by $\chi_0=[\alpha(1-5n^2/M_0^2)]^{-1}$, which, however, is not discussed any further here. The numerical result for the Curie temperature, denoted by T_c^{stat}, in the static approximation is 601 K.

The ''dynamic'' approximation requires a relaxation constant $\Gamma>0$. For reasons discussed above, we cannot yet determine Γ *ab initio* so we adjust its value such that the self-consistency step involving Eqs. (2) and (8) gives the experimental value of $T_c=701$ K denoted by T_c^{dyn}; this requires Γ to be $\Gamma\simeq 1.9\times 10^{-2}$ μeV Å. It is this value, which is used for the following estimates, hoping that the differences in the electronic structure play only a minor role for Γ.

Turning finally to the zinc-blende half-metallic ferromagnets, we choose a representative set of three As compounds with increasing magnetic moments, see Table I. The lattice constant[10] is that of InAs, but for MnAs also that of GaAs is employed. The trend in the electronic structure characteristic

TABLE I. Results for VAs, CrAs, and MnAs[(a)] at the volume of InAs, and MnAs[(b)] at the volume of GaAs, and NiMnSb.

	VAs	CrAs	MnAs[(a)]	MnAs[(b)]	NiMnSb
M_0 (μ_B)	2	3	4	3.65	4
T_c^{stat} (K)	529	820	570	181	601
T_c^{dyn} (K)	784	1041	671	210	701
Gap (eV)	1.72	2.02	1.2	1.2	0.25
$E_c - E_F$ (eV)	0.67	1.0	0.4	−0.22	0.04

for these compounds is shown in Fig. 1, where the *minority*-spin electrons are seen to form a rigid insulating system consisting of an sp-electron valence band (shaded) and a d-electron conduction band, separated by a large gap. The metallic *majority*-spin electrons at the Fermi energy E_F consist largely of d electrons in VAs, which in CrAs, turn into an spd hybrid and in MnAs, depending on the volume, are either of sp character, or no longer half metallic. The size of the energy-gap and distance of E_F from the conduction band are given in Table I.

The determination of the Curie temperature proceeds as in the case of NiMnSb, obtaining the results collected in Table I. Both the static and the dynamic approximations give rise to a remarkable trend in T_c. The largest value (of the order of magnitude of the Curie temperature of iron) is obtained for CrAs where E_F is midway in the large energy gap; T_c decreases when minority-electron states move closer to E_F thus making states more easily available for the formation of spin fluctuations. When E_F moves into the minority-electron conduction band, i.e., when the system is no longer half-metallic, the Curie temperature drops dramatically below room temperature and reaches values that are of the order of magnitude one finds in the magnetic semiconductor (Ga,Mn)As.[18]

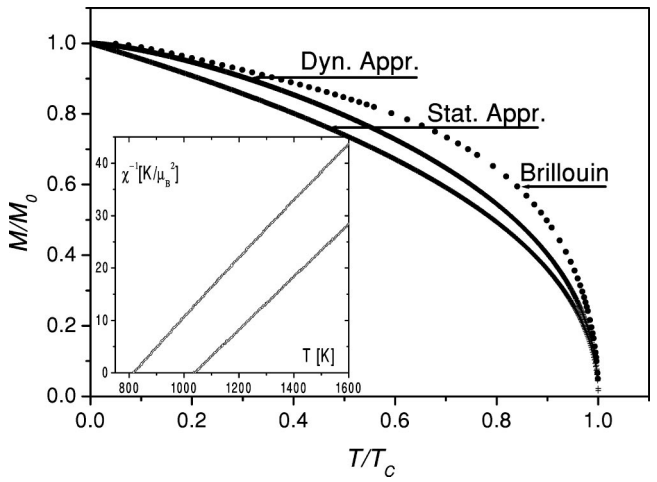

FIG. 2. Reduced magnetization versus reduced temperature. The two approximations indicated are explained in the text. Magnetization calculated with the spin-5 Brillouin function is dotted. The inverse susceptibility shown in the inset is that of CrAs, the two nearly linear curves resulting from the static and dynamic approximations.

In Fig. 2, the reduced magnetic moment as a function of the reduced temperature is shown. The effect of the dynamic approximation are clearly seen in the two curves marked stat. appr. and dyn. appr. For comparison, the mean-field magnetization as obtained by means of the Brillouin function with spin 5 is also included in Fig. 2. The inset demonstrates that the spin fluctuations give rise to a Curie-Weiss law in both

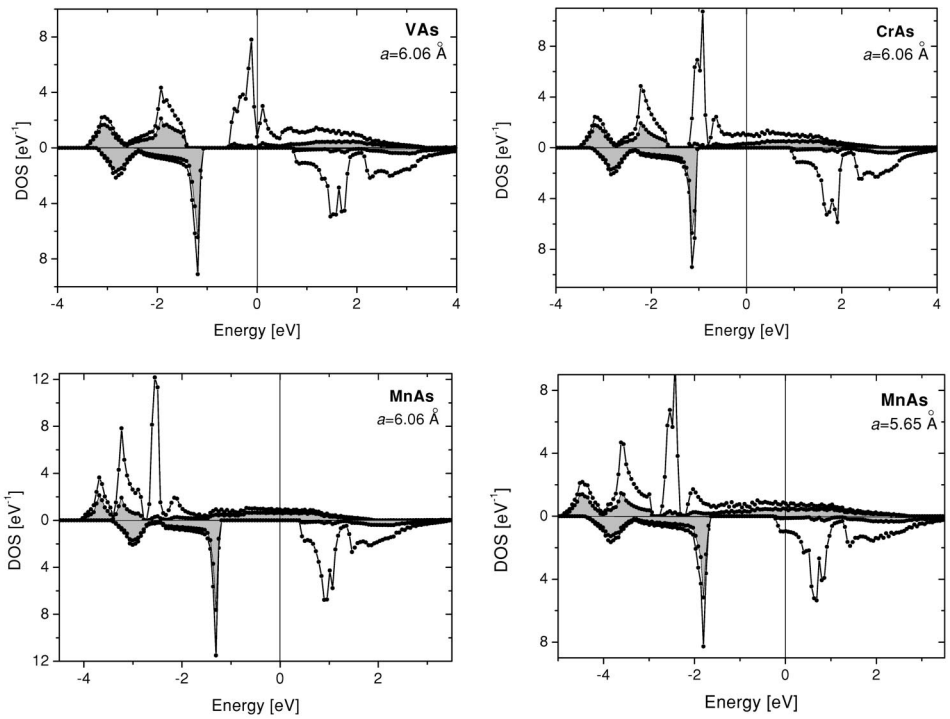

FIG. 1. Density of states (DOS) of VAs, CrAs, and MnAs for two different volumes. Upper parts describe the majority-spin electrons, lower part the minority-spin electrons. Curves bordering shaded areas give the DOS due to sp electrons. Low-lying s states not shown. Fermi energy at 0 eV.

approximations. The slope, however, cannot be considered as a numerical prediction, since it depends on the value of the Landau parameter α, for which we presently have no good *ab initio* estimate.

In conclusion, the Curie temperatures of the zinc-blende half-metallic ferromagnets have been estimated by the density-functional calculations, the lower bounds being *ab initio*. Their orders of magnitude are the same as the Curie temperature of the half-metallic ferromagnet NiMnSb with $T_c = 701$ K. Of the three compounds VAs, CrAs, and MnAs, the highest T_c is calculated for CrAs, for which the Fermi energy is in the middle of the gap; the Curie temperature might be as high as 1000 K in this case, a lower bound being 820 K. The Curie temperature drops sharply when the Fermi energy moves into the minority-electron conduction band as in the case of MnAs.

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