Other Half-Metallics I Michael Coey, Chairman

Possible half-metallic ferromagnetism in zinc blende CrSb and CrAs (invited)

M. Shirai[a)]
Research Consortium for Synthetic Nano-Function Materials Project, Research Institute of Electrical Communication (RIEC), Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

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Theoretical study based on a first-principles band structure calculation is carried out for new room-temperature ferromagnets, zinc blende CrSb and CrAs. It is found from the total-energy calculation that the ferromagnetic state is energetically favorable for both materials. By using the value of the difference in total energy between ferromagnetic and the antiferromagnetic states, the Curie temperatures of these ferromagnets are estimated as 1600–1800 K within mean-field approximation of the Heisenberg model. The magnetic moment is evaluated to be 3 Bohr magnetons per formula unit for both materials, which agrees well with the saturation moments estimated experimentally. Furthermore, these ferromagnets are half metallic, and the spin polarization at the Fermi level is almost unaffected even if spin–orbit interaction is taken into account. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1558604]

I. INTRODUCTION

Half-metallic ferromagnets have attracted increasing interest, since they are expected to be utilized as materials for spintronic device applications, such as a source of spin-polarized carriers injected into semiconductors and an electrode of magnetic tunnel junctions. Ferromagnets that have a highly spin-polarized band structure are required to improve the efficiency of spin injection into semiconductors or the tunneling magnetoresistance ratio. The degree of the spin polarization is defined by

$$P=\frac{D_{\uparrow}-D_{\downarrow}}{D_{\uparrow}+D_{\downarrow}}, \tag{1}$$

where D_{σ} denotes the spin-σ component in the density of states (DOS) at the Fermi level. In half-metallic ferromagnets, the electronic band structure of one spin state is metallic while the other semiconducting, leading to an ideal value of spin polarization, i.e., $P=1$. Half metallicity has been found theoretically so far in some Heusler alloys,[1] rutile-type CrO_2,[2] Fe_3O_4 (magnetite), perovskite manganites, and others.

Previously, we explored ferromagnets compatible with III–V semiconductors and designed new half-metallic ferromagnets, zinc blende MnAs and CrAs theoretically by using first-principles electronic band structure calculations.[3,4] Recently, zinc blende CrAs and CrSb thin films were grown on III–V semiconductors by molecular-beam epitaxy, and were confirmed to exhibit ferromagnetic behavior at room temperature.[5,6] These experimental investigations were motivated by our preceding theoretical prediction.

In this article, our theoretical study on the electronic band structure of zinc blende CrSb and CrAs is reported. The magnetic coupling between neighboring Cr spins and the degree of the spin polarization are evaluated for these materials, and are discussed in comparison with observations. Furthermore, the effect of spin–orbit interaction on spin polarization at the Fermi level is also investigated.

II. PROCEDURE

First-principles electronic band structure calculation in the present work is based on density-functional theory within the local spin-density approximation (LSDA) for the exchange-correlation energy and potential. The calculation was carried out by the full-potential linearized augmented-plane-wave (FLAPW) method and the linear-muffin-tin-orbital (LMTO) method within atomic sphere approximation (ASA).

In the FLAPW method, the potential and the charge (or spin) density in the crystal are treated with no shape approximation. The basis functions are expanded in terms of the spherical harmonics up to $\ell=7$ inside each muffin-tin sphere and expressed as plane waves in the interstitial region. Here, we take about 300 basis functions per formula unit into account. Relativistic effects other than spin–orbit interaction are included, i.e., so-called scalar-relativistic treatment, in the calculation of radial wave functions in each muffin-tin sphere.

In the LMTO-ASA method, the potential and the charge (or spin) density inside each atomic sphere are assumed to have spherical symmetry. The basis functions are expanded

a)Electronic mail: shirai@riec.tohoku.ac.jp

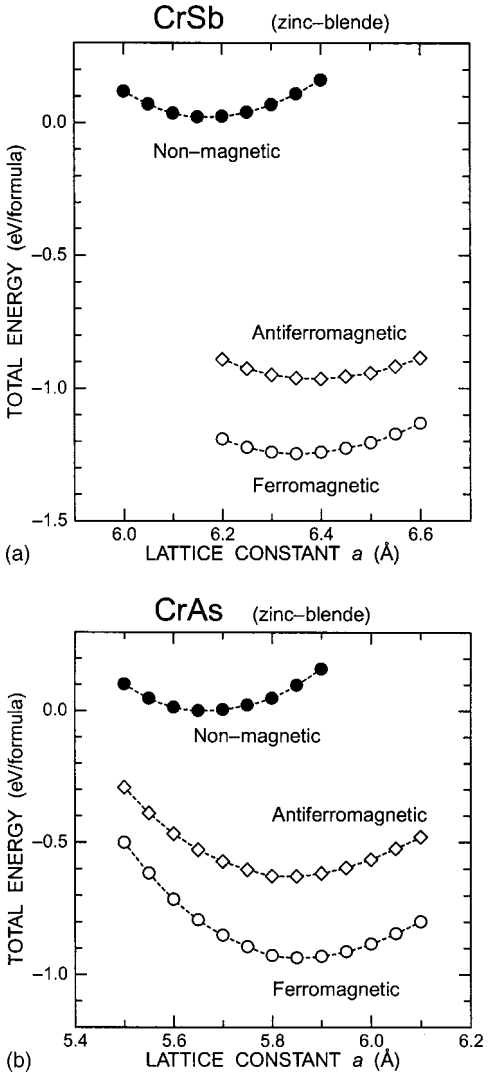

FIG. 1. Total energy as a function of the lattice constant calculated by the FLAPW method for the nonmagnetic, ferromagnetic, and antiferromagnetic states of zinc blende (a) CrSb and (b) CrAs.

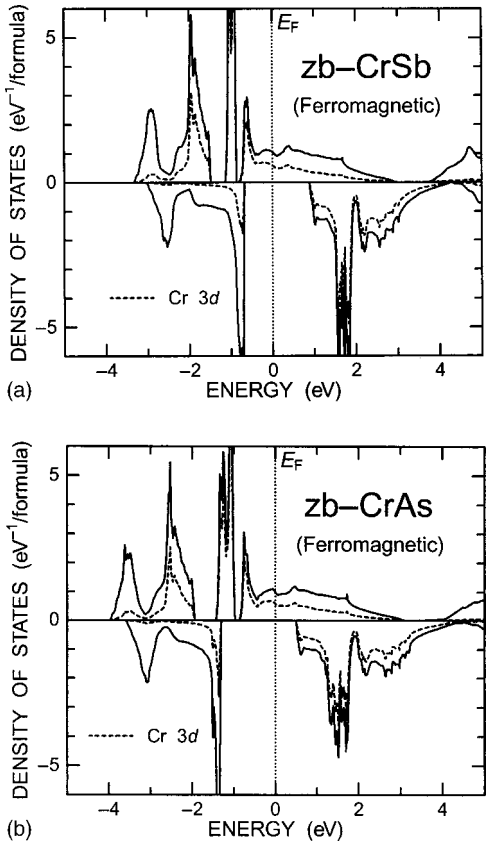

FIG. 2. Density of states for the ferromagnetic state of zinc blende (zb) (a) CrSb and (b) CrAs calculated by the scalar-relativistic FLAPW method. Broken curves denote the partial DOS for the Cr $3d$ orbitals.

in terms of spherical harmonics up to $\ell=2$ inside each atomic sphere. The atomic sphere radii are chosen to be equal to each other for all constituent atoms and empty-sphere sites, so as to reproduce the overall features of the band structure obtained by the FLAPW method. Spin–orbit interaction is included by the second variational treatment to the scalar-relativistic calculation.

III. RESULTS

Total energy was calculated as a function of the lattice constant for the nonmagnetic, ferromagnetic, and antiferromagnetic states of zinc blende CrSb and CrAs. The results for zinc blende CrSb and CrAs are shown in Figs. 1(a) and 1(b), respectively. It is found that the ferromagnetic state is energetically favorable for both materials. The delocalized character of Cr $3d$ electrons may be responsible for stabilizing the ferromagnetic state in these materials. The difference in total energy between the ferromagnetic and the antiferromagnetic states, ΔE, which is a measure of magnetic coupling between neighboring Cr spins, is evaluated as 0.28 and 0.30 eV for zinc blende CrSb and CrAs, respectively. These values are significantly larger than those for zinc blende MnAs (0.10 eV) and VAs (0.20 eV).[4]

The exchange coupling constant between the nearest neighbor Cr spins, J, can be estimated from the value of ΔE, assuming that the system is described well by the Heisenberg model with the effective exchange interaction between the nearest neighboring Cr spins $S=3/2$. The value of J/k_B, where k_B denotes the Boltzmann constant, is estimated to be 54 and 58 K for zinc blende CrSb and CrAs, respectively. That for zinc blende MnTe has been reported as -16 K, indicating that the coupling between Mn spins is antiferromagnetic in this material.[7] It should be noted that the magnitude of magnetic coupling for zinc blende CrSb and CrAs is considerably larger than that for zinc blende MnTe. The strong ferromagnetic coupling in zinc blende CrSb and CrAs could originate from the remarkable hybridization between Cr $3d$ orbitals and Sb (or As) p orbitals as shown in Figs. 2(a) and 2(b).

By using the mean-field approximation of the Heisenberg model, the Curie temperatures of zinc blende CrSb and CrAs are obtained to be about 1600–1800 K. Although the Curie temperature is generally overestimated in the mean-field approximation, the estimate is consistent with experimental results that show the Curie temperatures of both zinc blende CrSb and CrAs are over 400 K. Furthermore, the magnetic moment is predicted to be 3 Bohr magnetons per formula unit for both materials according to the band struc-

ture calculation. The result also agrees well with the saturation moments estimated experimentally.[5,6]

The density of states calculated for the ferromagnetic state of zinc blende CrSb and CrAs is shown in Fig. 2(a) and 2(b), respectively. These results were obtained by the so-called scalar-relativistic calculation, in which the spin–orbit interaction is neglected. It is found that both zinc blende CrSb and CrAs have half-metallic band structures. In minority-spin states with energy gaps near the Fermi level, the wave functions near the top of valence bands are constructed mainly of As $4p$ (or Sb $5p$) orbitals which hybridize with the Cr $3d$ orbitals, while those near the bottom of conduction bands from Cr $3d$ nonbonding orbitals. In the majority-spin state, on the other hand, the conduction bands which cross the Fermi level are composed of well-hybridized Cr $3d$ and As $4p$ (or Sb $5p$) orbitals and have an antibonding character. The conducting electrons in the hybridized bands may play an important role in stabilizing the ferromagnetic state of these materials from the viewpoint of the so-called double-exchange mechanism.[8,9]

Once spin–orbit interaction is included in the band structure calculation, then mixing of the spin-up and spin-down bands takes place. As a result, the degree of the spin polarization at the Fermi level is reduced from unity for half metallics. However, highly the spin-polarized electronic band structure in zinc blende CrSb and CrAs is almost unaffected, even if spin–orbit interaction is taken into account. The degree of the spin polarization at the Fermi level is estimated as 0.983 and 0.998 for zinc blende CrSb and CrAs, respectively. According to theoretical work on electrical spin injection, these values are enough for ferromagnetic metals to inject detectable spin-polarized current into semiconductors even in the purely diffusive regime.[10] In zinc blende CrSb and CrAs, the energy gap in the minority-spin state is about 2 eV, which is larger than the magnitude of the spin–orbit coupling constant ($\leqslant$0.1 eV). This is the reason why the effect of spin-orbit interaction on spin polarization at the Fermi level is quite small.

IV. CONCLUSION

First-principles band structure calculation was carried out for new room-temperature ferromagnets, zinc blende CrSb and CrAs. It was found from the total-energy calculation that the ferromagnetic state is energetically favorable for both materials. By using the value of the difference in total energy between the ferromagnetic and the antiferromagnetic states, the Curie temperatures of these ferromagnets are estimated as 1600–1800 K within the mean-field approximation of the Heisenberg model. Furthermore, it was found theoretically that these ferromagnets are half metallic, and that the spin polarization at the Fermi level is almost unaffected even if spin–orbit interaction is taken into account. In conclusion, zinc blende CrSb and CrAs could be promising materials for spintronics, since they are compatible with III–V semiconductors and have highly spin-polarized conducting electrons.

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