Journal of the Korean Vacuum Science & Technology; JKVST
Vol.6, No.4, 2002, pp.153 ~ 157

Electronic Structures of Giant Magnetocaloric $Gd_5Si_2Ge_2$ Alloy

Joo Yull Rhee†

Dept. of Physics, Hoseo University, Asan, Choongnam 336-795

(Received December 2, 2002)

Abstract

The electronic structures of $Gd_5Si_2Ge_2$ compound, which has a giant magnetocaloric effect, in the monoclinic and orthorhombic phases were calculated using the tight-binding linear-muffin-tin-orbital method within the atomic-sphere approximation. The calculated total energies of the monoclinic and orthorhombic structures in the paramagnetic phase confirm that the orthorhombic structure is more stable than monoclinic structure. The density of states (DOS) at the Fermi level of the orthorhombic phase is higher than that of the monoclinic phase in the paramagnetic phase, fulfilling the Stoner criterion. The calculated charge density verified the breaking of Ge(Si)-Ge(Si) bonding in the basal plane upon the orthorhombic→monoclinic phase transition. The DOS curve fairly well reproduces the photoemission spectrum.

1. Introduction

It is impossible to imagine a life without refrigerators in this modern technological era. If the refrigeration temperature is not much lower than room temperature the conventional refrigerators use the freon gas as the refrigeration medium. Although the freon gas is a very versatile and convenient medium for the refrigeration, it causes serious environmental problems. Therefore, it is inevitable to search for new materials which can substitute the freon gas for the refrigeration medium. Recently, researchers at Ames Laboratory have discovered a new material which can substitute the freon gas for the refrigeration medium [1].

Pecharsky and Gschneidner have found out that the $Gd_5Si_2Ge_2$ compound has a very large magnetocaloric effect, which can be utilized for a new magnetic refrigeration medium [1]. The effect is so large that they called the effect the giant magnetocaloric effect (GMCE). The magnetocaloric effect has been discovered about 80 years ago [2] and is common to all magnetic materials. The effect is the result of interaction between the magnetic sublattice and the applied magnetic field. In an adiabatic process the temperature of a magnetic system is lowered if an external magnetic field is applied ($\triangle T_{ad}$), and *vice versa*. The entropy of the system can also be altered by applying a magnetic field while the temperature is kept constant. Conventional magnetic materials do not have such an effect large enough to be used for the everyday-life refrigeration and thus the magnetic cooling is used only at very low temperature.

Upon cooling, $Gd_5Si_2Ge_2$ compound undergoes two magnetic phase transitions; a) from the high-temperature paramagnetic (PM) phase to the low-temperature ferromagnetic (FM1) phase near room temperature (~299 K), and b) from FM1 phase to another ferromagnetic phase (FM2) at ~276 K. A structural phase transition from monoclinic to orthorhombic also occurs at ~299 K and the phase transition at ~276 K is first order, exhibiting GMCE. This compound has so large magnetocaloric effect that it is a promising candidate for the substitution of the freon gas [3]. Furthermore, both transition temperatures can be adjusted by an addition of some impurities [4].

† E-mail : rheejy@office.hosco.ac.kr

The knowledge of electronic structures is crucial to understand the underlying physics of these phenomena. There were several electronic structure calculations [5,6], however, the major part of the knowledge of electronic structure is still missing. In this paper I will present the results of the electronic structure calculations using a tight-binding linear-muffin-tin-orbital (TB-LMTO) method within the atomic-sphere approximation (ASA). The calculated electronic structure can successfully explain some properties of the alloy.

2. Calculational Details

The electronic band structures of the orthorhombic and monoclinic phases of $Gd_5Si_2Ge_2$ compound were calculated using a scalar-relativistic version of TB-LMTO-ASA within the local-(spin)-density approximation [L(S)DA]. Gd 4*f* electrons are treated as an open-core (PM phase) or valence (FM phase) electrons. Although Gd 4*f* electrons are strongly correlated, we did not apply the 'LDA+U' method to simulate the large on-site Coulomb interaction for the ferromagnetic phase.

Space group is either $P112_1/a$ for orthorhombic phase or P_{nma} for monoclinic phase, and there are 4 formula units per unit cell and thus 36 atoms(20 Gd atoms, 8 Si atoms and 8 Ge atoms) are present in a unit cell. The x-ray diffraction analyses [7] show that the Si and Ge atoms do not occupy their own unique crystallographic positions. Rather, they are distributed randomly. However, in my band structure calculations I placed Ge atoms in T' positions (with x=0.8470, y=0.4598 and z=0.5293) and Si atoms in the T positions (x=0.0235, y=0.75 z=0.1021 for Si_1, and x=0.2683, y=0.75 z=0.8711 for Si_2) [7] for the orthorhombic structure and they are correspondingly adjusted in the monoclinic structure.

3. Results and Discussion

$Gd_5Si_2Ge_2$ alloy undergoes magnetic and structural phase transition at the same time, and GMCE is closely related to these transitions. If a $Gd_5Si_2Ge_2$ alloy is cooled down from high temperature, it undergoes the first magnetic (PM→FM1) and structural phase transition (monoclinic →orthorhombic) near 299K. At T=276K another magnetic phase transition (FM1→FM2) takes place. This phase transition is first order and entropy changes dramatically. This effect is called GMCE. Therefore, the electronic structures have been calculated for three different cases; PM and FM orthorhombic phase, and PM monoclinic phase.

Since the structural stability is determined by the total energy(E_{TOT}) of the system, E_{TOT}'s of orthorhombic and monoclinic phases in PM state are compared with each other. The monoclinic phase has a higher E_{TOT} than the orthorhombic phase. It means that the orthorhombic phase is energetically more stable than the monoclinic phase. It is interesting to note that, even though the orthorhombic phase is crystallographically more symmetric than the monoclinic phase, the orthorhombic phase is thermodynamically more stable. Usually, when an intermetallic compound undergoes a structural phase transition, it transforms from high-symmetry to low-symmetry structure upon cooling. NiTi alloy, the best-known shape-memory alloy, for instance, undergoes a martensitic transformation from high-temperature $B2$ structure (cubic) to low-temperature $B19'$ structure (monoclinic) upon cooling. For the case of $Gd_5Si_2Ge_2$, it happens in reverse direction, from high-temperature monoclinic to low-temperature orthorhombic upon cooling.

DOS at the Fermi level [$N(E_F)$] is an important factor to determine whether a certain material is magnetic. For the orthorhombic structure $N(E_F)$=33.75 states/eV/cell and for the monoclinic structure $N(E_F)$=21.23 states/eV/cell. The Stoner criterion for the material requires that $N(E_F)$ should be large in order to be ferromagnetic, *i.e.* $IN(E_F)>1$, where I is Stoner exchange integral given by

$$I \equiv \iint \phi_\alpha^*(r_1)\phi_\beta^*(r_2)\frac{e^2}{r_1-r_2}\phi_\alpha(r_2)\phi_\beta(r_1)dr_1dr_2$$

The Stoner exchange integral can be considered as a Coulomb overlap integral. In $Gd_5Si_2Ge_2$ alloy there

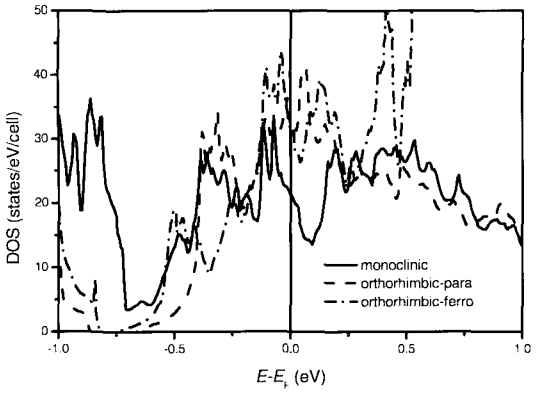

Fig. 1. DOS curves for the monoclinic and orthorhombic structures.

is only 1% difference in the unit- cell volume between two structures and the change in the positions of the individual atoms are not enough to give a significantly different Stoner exchange integral I. Although the length of Ge(Si)-Ge(Si) bond changes about 33 % upon monoclinic→orthorhombic structural transition, this change is not large enough to give a substantial influence to the Stoner exchange integral. The angular-momentum decomposed DOS at the Fermi level reveals that the wave function of the state at the Fermi level is mostly composed of Gd 5*d* character. Despite the *sp*-character of the wave function is sensitive to the structural change, its contribution to the Stoner exchange integral I is less important than Gd 5*d* characters. The Gd 5*d* wave function, however, is very insensitive to the structural change, since it is well localized, and thus the Stoner exchange integral I does not change appreciably upon the structural phase transition. Therefore, the most important factor that determines the ferromagnetism is $N(E_F)$. Since the orthorhombic phase has more $N(E_F)$ than the monoclinic phase, this explains why the orthorhombic phase is ferromagnetic.

In order to understand the magnetism of $Gd_5Si_2Ge_2$ alloy, it is very crucial to elucidate whether the RKKY interaction is essential interaction for the ferromagnetic behavior of the alloy. Since the Gd atoms are surrounded by the Ge or Si atoms [7], it is unlikely to be ferromagnetically aligned through direct interaction between the Gd atoms. The Ge or Si atoms mediate the ferromagnetic alignment of the Gd atoms through RKKY interaction in which the Gd 5*d* electrons and Ge/Si *sp*-electrons (conduction electrons) are hybridized and give an appreciable overlap in the RKKY exchange interaction given by

$$J(\mathbf{R}_{i,j}) = \frac{4}{N^2}\sum_{\mathbf{k},\mathbf{k}'}\sum_{n,n'}\frac{\left|I_{n,n'}(\mathbf{k},\mathbf{k}')\right|^2 e^{i(\mathbf{k}-\mathbf{k}')\mathbf{R}_{i,j}} f_{n,\mathbf{k}}\left(1-f_{n',\mathbf{k}'}\right)}{E_n(\mathbf{k})-E_{n'}(\mathbf{k}')},$$

where

$$I_{n,n'}(E,E')$$
$$= \sum_{\mu}\iint \Psi^*_{l,E}(\mathbf{r}_1)\Phi^*_{4f,\mu}(\mathbf{r}_2)\frac{2}{r_{12}}\Phi_{4f,\mu}(\mathbf{r}_1)\Psi_{l,E'}(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2$$
$$= I_{n,n'}(\mathbf{k},\mathbf{k}').$$

The wave function of *f*-electron, $\Phi_{4f,\mu}(\mathbf{r}_1)$ is well localized and thus doees not give any appreciable contribution to the integral. It is the *d*-electron wave function, $\Psi_{l,E'}(\mathbf{r})$, which give the most significant contribution. Therefore, it is very important to know how much of the Gd 5*d*-character is present near the Fermi level. As shown in Table 1 and 2, the Gd 5*d*-character is not very significant in the monoclinic structure, while it is almost comparable to that of the pure Gd metal in the orthorhombic structure. The RKKY interaction is the mediating interaction for the magnetism in pure Gd metal. Therefore, it is quite possible that the mediating interaction for the ferromagnetic alignment of the Gd 4*f* moment in the orthorhombic phase in which the Gd

Table 1. Gd 5d-DOS at the Fermi level in different crystallographic sites in the monoclinic phase.

	Gd1A	Gd1B	Gd2A	Gd2B	Gd3
$N(E_F)$	0.882	0.586	0.604	0.529	0.951

Table 2. The same as Table I except for the orthorhombic phase. The last column is for the pure Gd metal case.

	Gd1	Gd2	Gd3	Gd
$N(E_F)$	1.318	0.891	0.883	1.63

5d character is prominent and thus it plays an important role for the alignment.

In Ref. [7] it was pointed out that the Ge(Si)-Ge(Si) bonding is broken upon the monoclinic→orthorhombic structural transition. It is clearly seen in the chrage-density plot (see Fig. 2) in which the charge density in between the Ge(Si) and Ge(Si) atoms is aprreciably large, while it is very small in one of the Ge(Si)-Ge(Si) bondings. This indicates that the cahnge in the electronic structure is the driving force for the observed martensitic transformation from monoclinic to orthorhombic phases upon cooling.

Figure 3 shows the total DOS curve of $Gd_5Si_2Ge_2$ in the orthorhombic FM phase. The theoretical DOS curve has a small (wide) gap at 0.8 eV (4 eV) below the Fermi level. They are clearly seen in the experimental photoemission spectrum (see lower panel of Fig. 3). In the experimental spectrum there are no perfect gaps, however, the theoretical gaps can easily be smeared out

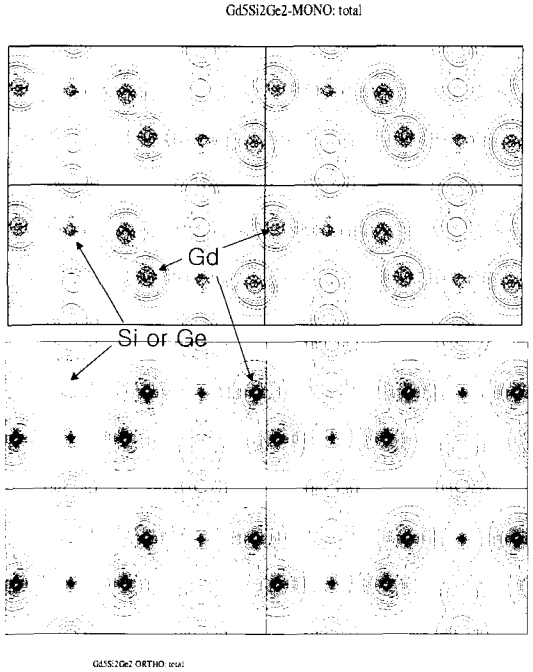

Fig. 2. Charge density plot of $Gd5Si_2Ge_2$ in orthorhombic(lower panel) and monoclinic(upper panel) phases.

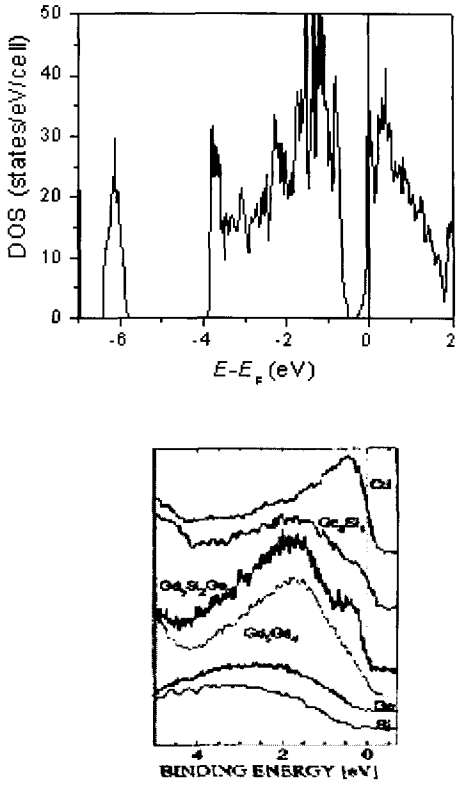

Fig. 3. Total DOS curve of $Gd5Si_2Ge_2$ in the orthorhombic FM phase. The lower panel shows the experimental phtoemission spectra of various Gd compounds.

owing to the thermal broadening and the spectral resolution of the experimental setup.

4. Conclusions and Further Suggestions

The electronic structures of $Gd_5Si_2Ge_2$ alloy were calculated using TB-LMTO-ASA method, and can successfully explain main characteristics of the $Gd_5Si_2Ge_2$ alloy. The total energy of orthorhombic structure is lower than that of monoclinic structure, therefore the orthorhombic structure is more stable at low temperature than monoclinic case. The calculated DOS near the Fermi level of monoclinic structure is lower than that of orthorhombic structure, implying that the orthorhombic phase is ferromagnetic, and the ferromagnetic ordering is mediated

by the RKKY interactions. It was experimentally observed that the Ge(Si)-Ge(Si) bonding is broken upon monoclinic →orthorhombic structural transition, and it was also theoretically shown in charge density plots. The calculated DOS curve fairly well reproduces the phtoemission spectrum.

Although I have successfully explained the main characteristics of the compound, the method of calculation was not very accurate. Therefore, it should be elaborated to elucidate more reasonable explanation for many other properties. First, since the Ge and Si atoms are randomly distributed in the same crystallographic sites, it is neccessary to use the supercell method to simulate the random distribution of Ge and Si atoms. Second, for more accurate calculation for the FM phase, the LDA+U method should be applied to simulate the strong on-site *f-f* Coulomb repulsion for Gd atoms. This method will push the *f*-bands away from the Fermi level. Third, since most of the martensitic transformations are accompanied by the phonon softening of certain branch along the particular direction and the softening is due to a strong Fermi-surface nesting effects, it is necessary to find the accurate Fermi surface to check the possibility of the Fermi-surface nesting. Fianlly, I want to suggest a experimental investigation for the phonon softening using the inelastic neutron scattering using the sample that the Gd atoms are switched with Tb atoms, because the Gd atoms are very neutron absorptive.

Acknowledgments

This work was supported by grant No. 2001-1-11400-006-1 from the Basic Research Program of the Korea Science & Engineering Foundation and through the Quantum Photonic Science Research Center.

References

[1] V. K. Pecharsky and K. A. Gschneidner, Jr., Phys. Rev. Lett. **78**, 4494 (1997).

[2] E. Wargurg, Ann. Phys. **13**, 141 (1881).

[3] V. K. Pecharsky and K. A. Gschneidner, Jr., Cryogenics **78**, 4494 (1997).

[4] V. K. Pecharsky and K. A. Gschneidner, Jr., App. Phys. Lett. **70**, 3299 (1997).

[5] G. D. Samolyuk and V. P. Antropov, J. App. Phys. **91**, 8540 (2002).

[6] B. N. Harmon and V. N. Antonov, J. App. Phys. **91**, 9815 (2002).

[7] W. Choe, V. K. Pecharsky, A. O. Pecharsky, K. A. Gschneidner, Jr., V. G. Young, Jr., and G. J. Miller, Phys. Rev. Lett. **84**, 4617 (2000).