PECULIAR OPTICAL PROPERTIES OF Co_2MnGa ALLOYS

Joo Yull Rhee

BK21 Physics Research Division and Institute of Basic Science,
Sungkyunkwan University, Suwon 440-746, Korea

Y.V. Kudryavtsev

Institute of Metal Physics, National Academy of Sciences of Ukraine,
36 Vernadsky Str., 03142, Kiev-142, Ukraine

K.W. Kim

Department of Physics, Sunmoon University, Asan, 336-708, Korea

Y.P. Lee

q-Psi and Department of Physics, Hanyang University, Seoul 133-791, Korea

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ABSTRACT

Co_2MnGa alloy was prepared by the conventional arc-melting method. The optical conductivity (OC) spectrum of the alloy was measured by a rotating-analyzer spectroscopic ellipsometer. The OC spectrum was also calculated based on the electronic structure by using the full-potential linearized-augmented-plane-wave method within the local-spin-density approximation to the density-functional theory. The calculated OC spectrum does not agree well with the experimental one. Since the Co_2MnGa alloy could be a strongly-correlated material, the so-called 'LDA+U' method was applied with $U = 5.4$ eV. The calculated OC spectrum using the 'LDA+U' method agrees very well with the experimental one. The inclusion of the on-site Coulomb potential during the self-consistent calculation significantly modifies the minority-spin Co and Mn $3d$ bands, resulting in a contraction of the energy gaps between states which are strongly involved in interband absorption peaks.

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1. INTRODUCTION

The experimental finding of huge polar magneto-optical (MO) Kerr effect in the ferromagnetic semi-Heusler PtMnSb alloy by van Engen [1] has inspired a great deal of interest to the study of the electronic structure, MO and optical properties of similar compounds. Semi-Heusler phases are cubic ternary compounds crystallize in $C1_b$ structure

and have a formula of XYZ , where X and Y are transition metals and Z is a sp element. They are derived from true Heusler phases of formula X_2YZ and crystalline structure of $L2_1$ by removing one X atom leaving a vacant site. The huge MO effect of these alloys is usually explained by the specific electronic structure of such compounds. These compounds are thought to be metallic for one spin direction while at the same time they show semiconducting properties for the opposite spin direction. This phenomenon was called half-metallic ferromagnetism. That is why the MO and optical properties as well as the electronic structures of semi-Heusler [2, 3] and true Heusler alloys (HAs) [4 - 10] were intensively studied experimentally and theoretically since early 1980s.

Among many kinds of HA systems, Mn-containing HAs are intensively studied not only because of the aforementioned half-metallic property but because of the unique martensitic transformation of Ni₂MnGa HA [11 - 13]. The Ni₂MnGa HA undergoes a structural phase transition from the high-temperature austenitic (cubic) structure to the low-temperature martensitic (tetragonal) one at about 220 K upon cooling, accompanied by the ferromagnetic shape-memory effect. The optical and other physical properties of the Ni₂MnGa HA are studied several times [14 - 16]. A systematic studies of the electronic structures of HAs other than Ni₂MnGa HA is very important to understand the peculiar physical properties of the Ni₂MnGa HA. More specifically, since Co₂MnGa HA has two more electrons per formula unit, the electronic structures are expected to be quite similar to the case of Ni₂MnGa HA, except for the position of the Fermi level E_F . Therefore, the study of the physical properties of the Co₂MnGa HA is very helpful for understanding the peculiar physical properties of the Ni HA. In this paper, the calculational results of the electronic structures and optical conductivity (OC) spectrum of Co₂MnGa HA and their comparison with the experimental one are presented. Since the calculated OC spectrum does not agree well with the experimental one, the so-called 'LDA+U' method [17 - 19] was applied with the Hubbard-like on-site Coulomb potential of $U = 5.4$ eV, and the agreement was markedly improved.

2. EXPERIMENTS PROCEDURES AND THEORETICAL CALCULATIONS

Bulk Co₂MnGa alloy was prepared by melting of Co, Mn and Ga pieces of 99.99% purity together in an arc furnace with a water-cooled Cu hearth. In order to obtain the volume homogeneity the ingot was remelted twice, annealed at 1300 K for 6 h and then slowly cooled. Any weight loss after melting and heat treatment was not observed. For the optical measurements a slab of about $15 \times 8 \times 2$ mm³ in dimensions was cut from the ingot using a spark-erosion technique and then polished mechanically with diamond powders. The final stage of polishing was carried out by using Cr₂O₃ powder. After this the sample surface was cleaned with acetone and ethanol using an ultrasonic cleaner. To remove the surface contamination introduced by the mechanical treatment, the sample was annealed in a high vacuum conditions at 760 K for 3 hrs. The structural characterization of the bulk and film Co₂MnGa alloy samples has been performed by using x-ray diffraction study with Cu K_α radiation. The optical properties of Co₂MnGa samples were measured by using the rotating-analyzer spectroscopic ellipsometer at room temperature in a spectral range of 310 - 2500 nm (4.0 - 0.5 eV) at a fixed incidence angle of 73°. The electronic structures and the OC spectra were calculated by using the WIEN2k code [20] utilizing an all-electron full-potential linearized-augmented-plane-wave method [21]. For the exchange-correlation functional, the generalized- gradient-approximation (GGA) version of Perdew, Burke and Ernzerhof [22] was used. The spin-orbit coupling was included. The muffin-tin radii were determined in such a way that all atomic spheres were almost in contact and were the same for all atoms. We used $RK_{max} = 8:0$. A detailed description of the calculational procedures for the OC spectra can be found elsewhere [23].

3. RESULTS AND DISCUSSION

The XRD patterns of the bulk Co_2MnGa alloy (not shown) reveals that the prepared alloy is a single phase without any detectable secondary phases. Figure 1 presents the OC spectra of bulk Co_2MnGa alloy and that of Ni_2MnGa alloy for the comparison. Since the surface of a metallic alloy is occasionally severely damaged during mechanical polishing, the OC spectra of the as-polished and the annealed bulk Co_2MnGa alloy are measured. A short (less than 1 h) and relatively low-temperature (lower than 150°C) annealing can drastically affect the optical properties of alloys, especially when the skin depth of the sample is longer than the thickness of damaged layer during mechanical polishing [24]. Although the effect of annealing is not very significant for the case of the Co_2MnGa alloy, the width of 1-eV peak sharpens after annealing, which is typical when the crystallinity of alloy sample becomes better.

Fig. 1: OC spectra of as-polished and annealed bulk Co_2MnGa alloys. The OC spectrum of Ni_2MnGa alloy is also included for the comparison

There exist a strong interband-absorption peak near 1 eV and weak structures around 2.5 eV. This kind of two-peak structure in the infrared-visible-ultraviolet region of spectrum is common to the OC spectra of the Mn-containing HAs. As can be seen in Fig. 1, the Ni_2MnGa alloy also has two peaks at ~ 1.8 eV and ~ 3.3 eV in its OC spectrum. The Co_2MnGa alloy also has two-peak structure but at lower energies even though the Ni_2MnGa alloy has a larger lattice constant. It is well known that the decreased lattice constant pushes the bands above (below) E_F toward the higher (lower) energy region [25], resulting in the enhancement of the energy gap between two states participating in a particular interband absorption. It implies that the Ni_2MnGa alloy should have two-peak structure at lower-energy region. Therefore, the discrepancy can not be simply explained by the lattice contraction. Later, it will be shown that some strong correlation causes such disparity.

To understand the origin of the two-peak structure of the OC spectrum of the Co_2MnGa alloy, the OC spectrum was calculated from the electronic structures calculated by using the WIEK2k code. The calculated OC spectrum is presented in Fig. 2. The overall shape of the calculated spectrum resembles the experimental one, however, the peak positions are at the higher-energy region. The 2.4-eV peak of the calculated OC spectrum corresponds to the 1-eV peak of the experimental one. One may be tempted to apply the so-called λ -fitting [26], which resembles the correction to the real part of self-energy, to fit the 2.4-eV peak of the calculated OC spectrum corresponds to the 1-eV peak of the experimental one, however, the energy difference between the experimental and theoretical peaks are too large to apply the λ -fitting and hence the magnitude of λ is unphysically large.

Fig. 2: Experimental and calculated OC spectra of Co_2MnGa alloy

Fig. 3: Minority-spin DOS curves of the Co_2MnGa alloy with $U = 0$ eV (upper panel) and $U = 5.4$ eV (lower panel). The solid and dashed arrows denotes the higher- and lower-energy peaks, respectively, in the two-peak structure

Many transition-metal-containing systems are proven to be strongly correlated systems and the ordinary local-spin-density approximation (LSDA) or even GGA to the density-functional theory can not properly reproduce the physical properties of strongly correlated systems. To remedy this problem, a simple method is proposed. Since in strongly correlated systems the localized d - or f -electrons feel strong on-site Coulomb interactions, which can not be properly treated by the conventional LSDA or GGA, the Hubbard-like U -potential is manually added to the Hamiltonian matrix during self-consistent calculation [17]. This is called 'L(S)DA+ U ' method.

As can be seen in Fig. 2, the 'LDA+ U ' method with $U = 5.4$ eV markedly improves the agreement between the experimental and calculated OC spectra. The 1-eV peak is very nicely reproduced and so is the structures at ~ 3.3 eV as rather strong peaks. As aforementioned, the 1-eV peak and 2.3-eV structure have the same origin as the 1.8-eV and 3.3-eV peaks, respectively, of Ni_2MnGa alloy. Since the Ni_2MnGa alloy has larger lattice constant than the Co_2MnGa alloy, the contraction of the lattice constant has nothing to do with this disparity.

Since the majority-spin states of the Co and Mn $3d$ states are completely occupied, they do not contribute to OC. Furthermore, similar to the case of Ni_2MnIn alloy [27], the most intense optical transitions occur between the minority-spin bands with mostly Co and/or Mn $3d$ characters.

Therefore, the minority-spin DOS curves of the Co_2MnGa alloy with $U = 0$ eV and $U = 5.4$ eV are displayed in Fig. 3. As denoted as the solid and dashed arrows, the energy gaps between the states mostly participated in the interband absorption peaks of the higher and lower energy in the two-peak structure are significantly reduced by applying the 'L(S)DA+U' method with $U = 5.4$ eV.

4. SUMMARY

Polycrystalline Co_2MnGa bulk alloy has been prepared by the conventional arc-melting method. The optical properties were investigated by using a rotating-analyzer spectroscopic ellipsometer, and the experimental OC spectrum exhibits a two-peak structure, which is common to many HA families. Since the calculated OC spectrum could not successfully reproduce the experimental one, the 'L(S)DA+U' method with $U = 5.4$ eV was applied and the agreement was markedly improved. The inclusion of the Hubbard-like on-site Coulomb potential during the self-consistent calculation of the electronic structure significantly modifies the minority-spin Co and Mn $3d$ bands, resulting in the contraction of the energy gaps between states which are strongly involved in those interband absorption peaks. This work was supported by the KOSEF through Quantum Photonic Science Research Center at Hanyang University, Seoul, Korea, and MOST, Korea.

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