AIP | Journal of Applied Physics

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Citation: J. Appl. Phys. **113**, 17E155 (2013); doi: 10.1063/1.4799620
View online: http://dx.doi.org/10.1063/1.4799620
View Table of Contents: http://jap.aip.org/resource/1/JAPIAU/v113/i17
Published by the American Institute of Physics.

Van Hove scenario and superconductivity in full Heusler alloy Pd_2ZrGa

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(Presented 15 January 2013; received 25 October 2012; accepted 22 January 2013; published online 22 April 2013)

Ab-initio band structure calculation using the state-of-the-art density functional theory was carried out for the sample Pd_2ZrGa. The equilibrium lattice parameter was found by fitting the energy vs volume data to Murnaghan equation of state and the value was observed to be 6.467 Å. Non analytical behavior of the energy functional was observed in band structure as well as in density of states diagram near the Fermi level. Polycrystalline sample synthesized using arc-furnace showed compositional variation in X-ray diffraction and energy dispersive analysis of X-ray spectrum studies. Magnetic measurements showed Meissner diamagnetic shielding in the as-cast sample below 2 K. From the Zero Field Cooled (ZFC) and Field Cooled (FC) measurements, we observed that the system is a type II BCS superconductor. The volume susceptibility at 2 K was observed to be 3.1 emu/Oe cm^3. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4799620]

INTRODUCTION

In the field of condensed matter physics and material sciences, there are only few materials that are as versatile as Heusler alloys.[1–3] Superconductivity in Heusler alloys was first observed in Pd based Heusler alloys by Ishikawa *et al*. in 1982.[4] But the discovery of half-metallic ferromagnetism and quest for finding magnetic superconductors brought renewed interest in these materials. In conventional *s*-wave superconductors, small amount of ferromagnetic impurities or proximity effect will destroy the spin singlet state. Hence, in BCS type superconductors, magnetism and superconductivity are considered to be mutually exclusive. Keizer *et al*. have observed in the $NbTiN/CrO_2$ (superconductor/half-metal) hetero-structure that the spin triplet super current sustained over length scales much above the correlation length of the spin singlet correlations.[5] These findings motivated many researchers to search for new superconducting material which has good lattice matching with the existing half-metals. Among many possible Heusler alloys, a sub set of systems (27 valence electrons) possess van Hove singularity and superconductivity, viz., Pd_2YZ, Ni_2ZrGa, MPd_2Sn, Ni_2NbSn, and Pd_2ZrAl.[6–9] We report the analysis of electronic and phonon band structure along with some experimental observations on the iso-structural Pd_2ZrGa.

COMPUTATIONAL AND EXPERIMENTAL DETAILS

The band structure calculations were done using the state-of-the-art density functional technique with the Plane Wave Self-Consistent Field (PWSCF) package.[10,11] The exchange-correlation functionals were treated within the generalized gradient approximation. The self-consistency was achieved with $25 \times 25 \times 25$ Monk-horst pack grid of k-points.

The phonon calculations were performed using density functional perturbation theory in the linear response approach. The energy threshold for the convergence was set to be 1×10^{-14} Ry. For experimental purpose, we prepared the sample Pd_2ZrGa by arc melting the high pure elements in argon atmosphere. The ingot was remelted several times and homogenized in vacuum (10^{-6} mbar) at 800 °C for a week.

The phase analysis and structural characterization were carried out with PANAnalytic (XPert Pro) X-ray diffractometer and scanning electron microscopy. Magnetic measurements were done using QD SQUID magnetometer in the temperature range of 1.8 K to 10 K.

RESULTS AND DISCUSSIONS

The structural optimization was done by relaxing the lattice parameter value from 12.0 to 13.0 (atomic units). The lattice parameter versus energy data was fitted using Murnaghan equation of state (EOS) to find out the equilibrium lattice parameters and the equilibrium pressure (Fig. 1). The equilibrium lattice parameter value was observed to be 6.467 Å. The system was found to be in non-magnetic ground state as the magnetic calculations yielded zero total magnetic moment in the unit cell. The band structure calculations were carried out along the path with the higher symmetry in the irreducible Brillion zone. The low lying *sp* states of Ga are not included in the band structure as these states are located −10 eV below the Fermi level (Figure 2(a)). The states near the Fermi level are mainly due to the bonding and anti-bonding hybrids of Pd and Zr *d*-states and these states are located between −4 eV to 4 eV energies. The partial density of states gives a clear picture of the contribution of the each atom towards the total density of states (Figure 2(b)). The DOS vs energy graph (Figure 2(b)) showed a logarithmic divergence of the DOS near the Fermi level which reflected in the energy spectrum at L point

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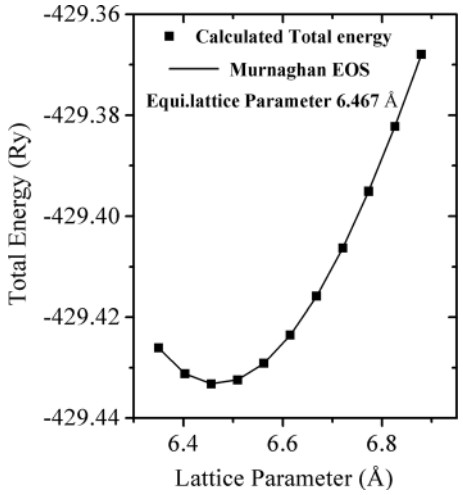

FIG. 1. Calculated total energy as a function of lattice parameter and the solid line represents the Murnaghan EOS fitting.

known as van Hove singularity. In the energy spectrum, it is observed that the non analytical behavior is located exactly at the Fermi level. The DOS at the peak of the singularity was observed to be 3.06 states/eV and the value is less compared to MPd_2Sn (M = Sc, Y, and Lu) samples and that could be one of the reasons for low T_c values ~2–3 K in the case of Pd_2ZrZ compounds, whereas maximum T_c of 4.9 K was observed in the case of Pd_2YSn.[7,12] The low transition temperature in these systems can be explained using the BCS relation $T_c = 1.13\Theta_D \exp(-1/VN(E_F))$, where Θ_D is the Debye temperature, $N(E_F)$ is the density of states at the Fermi level, and the electron-electron attractive interaction is given as V. The above expression is an increasing function with $N(E_F)$ and V. It is necessary that the material should possess large DOS at the Fermi level and strong electron-electron interaction to have high transition temperature. Full

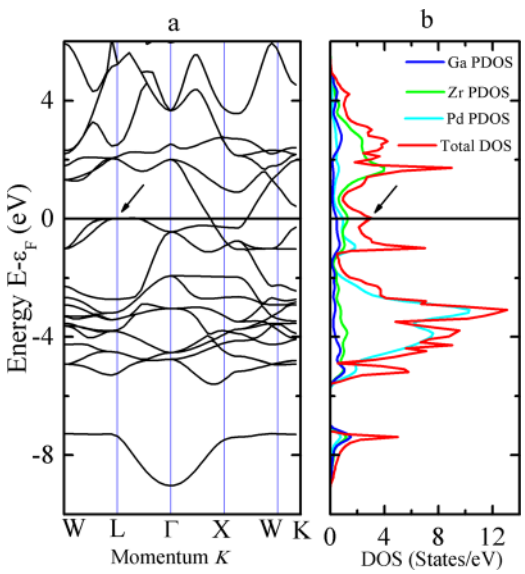

FIG. 2. (a) The electronic band structure spectrum along higher symmetrical points. (b) The calculated total density of states with atom projected partial density of states as function of energy for the compound Pd_2ZrGa. The arrows at the Fermi level indicate the van-Hove singularity in the energy spectrum and logarithmic divergence of DOS of states in the N(E) vs E diagram.

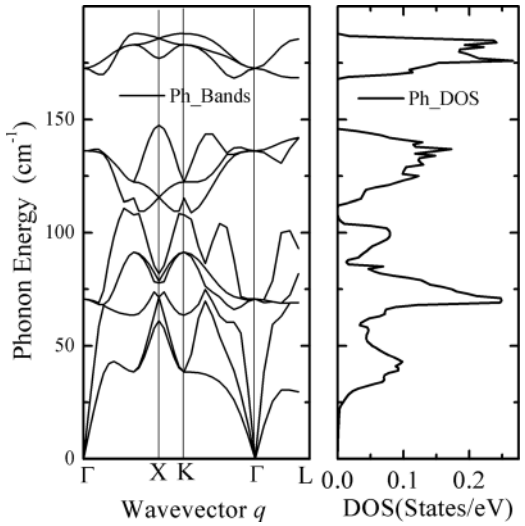

FIG. 3. (a) Vibrational spectrum and phonon dispersion relation for the compound Pd_2ZrGa. (b) The calculated phonon density of states as a function of energy.

Heusler alloys crystallize in cubic $L2_1$ structure and the structure has 4 atoms in the unit cell. Hence, there are 12 phonon branches are possible for the Heusler structure with 3 acoustics and 9 optical modes of vibrations. All acoustics phonon modes are exhibiting positive frequencies which indicate that the mechanical instabilities were not present and suggesting that the structural optimization of the lattice is indeed stable. By comparing with iso-structural compounds, such as Ni_2ZrGa and Pd_2ZrAl, we identified that in the low energies the main contribution to the vibrational states is from Pd and large contribution arises from Zr atom in the higher energies above 150 cm^{-1}.[6,8,9] It is observed that in the superconducting Heusler alloy family, the X site atom vibrational modes are responsible for the large electron-phonon coupling which eventually favors superconductivity in these systems (Fig. 3).

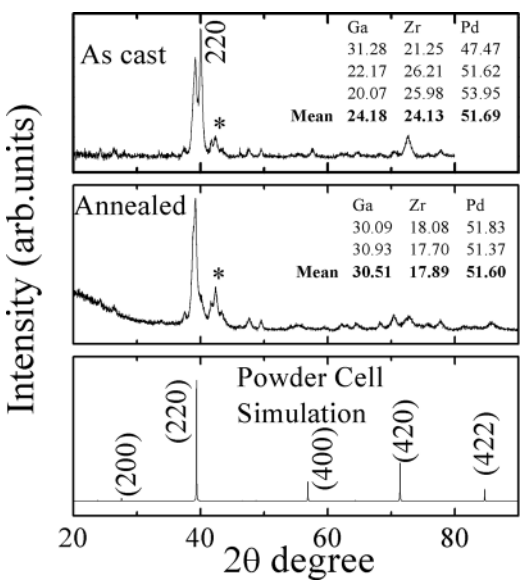

FIG. 4. Powder XRD patterns for the as-cast, annealed sample and the inset table shows the corresponding energy dispersive analysis of X-ray spectrum (EDAX) data.

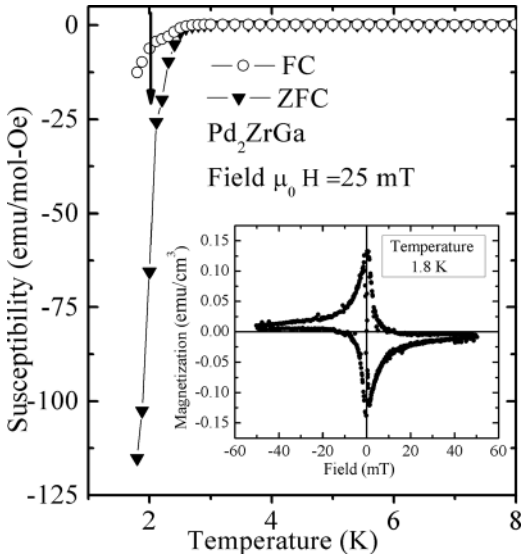

FIG. 5. ZFC and FC measurements show the superconducting transition at 2 K. The inset shows isothermal magnetization data recorded at 1.8 K.

Polycrystalline samples were made by arc melting the pure elements under argon atmosphere. XRD studies on the as-cast sample showed that the order independent high intensity reflection (220) is split into two which signifies there could be compositional disorder present in the system; hence, within the same Heusler phase, the lattice parameter variation could lead to the splitting of the peak (Figure 4). The experimental lattice parameter was estimated using CMPRlogic program and the value was found to be 6.375 Å. The heat treated sample showed enhancement of a secondary phase which is indicated as asterisk symbol in the XRD pattern. To identify the phases, scanning electron microscopic studies were carried out on a finely polished sample. Stoichiometry variations were observed in the as cast sample. The average stoichiometry compositions were found to be $Pd_{2.06}Zr_{0.97}Ga_{0.97}$ in the case of as cast sample and the annealed sample showed uniform stoichiometry of $Pd_{2.06}Zr_{0.7}Ga_{1.24}$. The small secondary phase indicated in the Figure 4 by an asterisk symbol was not observed in both annealed and as cast sample.

The magnetic measurements were done in the temperature range of 1.8 K to 10 K. ZFC measurements on the as-cast sample showed a sharp superconducting transition at 2 K above which, in the normal state, the susceptibility showed temperature independent Pauli-paramagnetic behavior (Figure 5). Further, ZFC-FC measurements showed an appreciable difference in the transition indicating that the system is a type II superconductor. Magnetic measurements on the annealed sample did not show the Meissner diamagnetic effect in the temperature of the investigations. The volume susceptibility of the as-cast sample was calculated using the formula $\chi_v = \left(\frac{M}{H}\right) \cdot \left(\frac{W}{\rho}\right)$ emu/Oe cm^3, where W is the mass of the sample (g) and ρ is density of the sample. The theoretical density was deduced from the equilibrium lattice parameter and the value was observed to be 9.17 g/cm^3. From the above formula, the bulk superconductivity fraction was observed to be only 4% of the value $\left(-\frac{1}{4\pi}\right)$. The reason could be both due to the stoichiometry variation of the sample, which we observed through microscopy studies, and due to the arbitrary shape of the sample, which was used for the magnetic measurement, could lead to different demagnetization factor. Further heat treatment and metallographic studies must be done to quantify the superconducting fraction in the as-cast sample. The isothermal magnetization studies on the as-cast sample (inset of Figure 5) showed a butterfly loop which is indicating that the sample is a type II superconductor.

CONCLUSIONS

Band structure calculations using PWSCF have been carried out on the sample Pd_2ZrGa. The calculations showed a van Hove singularity in the electronic energy spectrum at equilibrium lattice parameter value of 6.467 Å and the experimental lattice parameter was observed to be 6.357 Å. The DOS value at the Fermi level was observed to be 3.06 states/eV and the low T_c value can be explained in terms of weak coupling and low DOS near the Fermi level. XRD and SEM studies showed that the sample crystallized in cubic Heusler phase with some compositional disorder and annealing the sample did not favour for the Pd_2ZrGa phase. The magnetic measurements revealed that the as-cast sample is a type II superconductor.

[1]C. Felser, G. H. Fecher, and B. Balke, Angew. Chem., Int. Ed. **46**, 668 (2007).
[2]I. Galanakis and P. H. Dederichs, *Half-Metallic Alloys Fundamentals and Applications* (Springer, Berlin, 2005), Chap. I, pp. 1–39.
[3]T. Graf, C. Felser, and S. S. P. Parkin, Prog. Solid State Chem. **39**, 1 (2011).
[4]M. Ishikawa, J. Jorda, and A. Junod, in *Superconductivity d- and f-Band Metals*, edited by W. Buckel and W. Weber (Kernforschungszentrum, Karlsruhe, 1982), p 141.
[5]R. S. Keizer, S. T. B. Goennenwein, T. M. Klapwijk, G. Miao, G. Xiao, and A. Gupta, Nature **439**, 825 (2006).
[6]J. Winterlik, G. H. Fecher, and C. Felser, Solid State Commun. **145**, 475 (2008).
[7]T. Klimczuk, C. H. Wang, K. Gofryk, F. Ronning, J. Winterlik, G. H. Fecher, J. C. Griveau, E. Colineau, C. Felser, J. D. Thompson, D. J. Safarik, and R. J. Cava, Phys. Rev. B **85**, 174505 (2012).
[8]J. Winterlik, G. Fecher, A. Thomas, and C. Felser, Phys. Rev. B **79**, 064508 (2009).
[9]W. Ming, Y. Liu, W. Zhang, J. Zhao, and Y. Yao, J. Phys.: Condens. Matter **21**, 075501 (2009).
[10]P. Giannozzi *et al.*, J. Phys.: Condens. Matter **21**, 395502 (2009).
[11]We used the pseudopotentials Zr.pbe-nsp-van.UPF, Pd.pbe-nd-rrkjus.UPF, Ga.pbe-n-van.UPF from http://www.quantum-espresso.org.
[12]J. Wernick, G. Hull, T. Geballe, J. Bernardini, and J. Waszczak, Mater. Lett. **2**, 90 (1983).