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Heat capacity of Heusler alloys Ni_2MnSb, Ni_2MnSn, NiMnSb, CuMnSb

S.M. Podgornykh[a,b,*], S.V.Streltsov[a,b], V.A.Kazantsev[a], E.I.Shreder[a]

[a]*Institute of Metal Physics, 18, Sofia Kovalevskaya St., 620219 Ekaterinburg, Russia*
[b]*Ural State Technical University-UPI, 19 Mira St., 620002 Ekaterinburg Russia*

Abstract

We report about the results of the investigation of the specific heat of the ferromagnetic Heusler Ni_2MnSn, Ni_2MnSb, ferromagnetic semi-Heusler NiMnSb and antiferromagnetic semi-Heusler CuMnSb alloys. The low-temperature behaviour of the specific heat may be described as $C = \gamma T + \beta T^3$ for ferromagnetic compounds and as $C = \gamma T + \delta T^2 + \beta T^3$ for antiferromagnetic CuMnSb. The values of the density of states from the heat capacity measurements are higher than those from electronic band structure calculations. Debye temperatures are in a good agreement with those obtained from thermal expansion measurements. The Grüneisen parameter is calculated for Ni_2MnSn and CuMnSb from magnetic contribution to the specific heat in vicinity of T_C or T_N.

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Keywords: Heusler alloys; CuMnSb; NiMnSb; Ni_2MnSb; Ni_2MnSn; Heat capacity; Density of states; Thermal expansion;

1. Introduction

The ferromagnetic (FM) Heusler alloys Ni_2MnSb (the Curie temperature T_C = 350 K) and Ni_2MnSn (T_C = 340 K) are intermetallic compounds with the $L2_1$ cubic structure. The semi-Heusler FM compounds NiMnSb (T_C = 730 K) and antiferromagnetic (AFM) CuMnSb (the Néel temperature T_N = 47 K) crystallize into the $C1_b$ cubic structure. The electronic band structure calculations [1] showed that NiMnSb has a deep pseudogap in the density of states (DOS) with one of the spin projections centered at the Fermi level and were classified as a half-metallic ferromagnet (HMF).

We previously studied the thermal expansion coefficient (TEC) of these alloys [2]. It was found that TEC has universal temperature dependence of the positive magnetic contribution at T_C or at T_N. In order to continue our investigation FM and AFM Heusler alloys and to obtain the DOS value at Fermi level we performed the heat capacity measurements in the temperature range from 1.8 K up to 400 K and band structure calculations.

2. Specific heat: results and analysis

The heat capacity measurements were performed using a PPMS-9 (Quantum Design) at the Cryomagnetic Center of the Institute of Metal Physics. It has been found that the low-temperature

* Corresponding author. Tel.: +7-343-378-3619; fax: +7-343-374-5244. *E-mail address*: sp@imp.uran.ru.

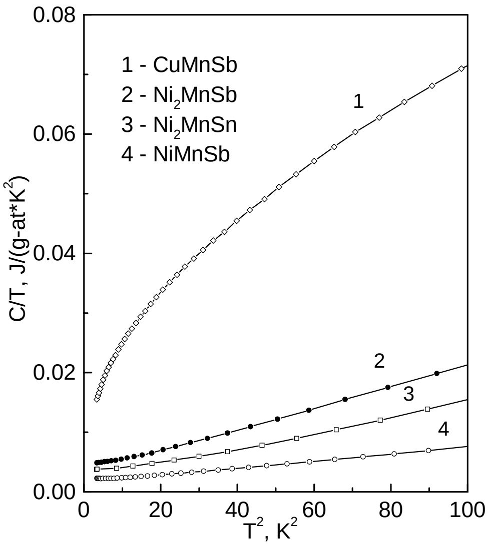

Fig.1. Low temperature specific heat of Heusler alloys: 1 - CuMnSb, 2 - Ni_2MnSb, 3 - Ni_2MnSn, 4 - NiMnSn in plots of C/T versus T^2.

behavior of the heat capacity of FM compounds may be described as $C = \gamma T + \beta T^3$ and for AFM CuMnSb as $C = \gamma T + \delta T^2 + \beta T^3$ (see Fig.1). The values of γ, β, δ, DOS at Fermi level $g(E_F) = 3\gamma / (\pi^2 N_A k_B^2)$ and Debye temperature $\Theta_D = \sqrt[3]{12\pi^4 N_A k_B/(5\beta)}$ are presented in Table 1. The values of Θ_D are in a good agreement with our thermal expansion data [2].

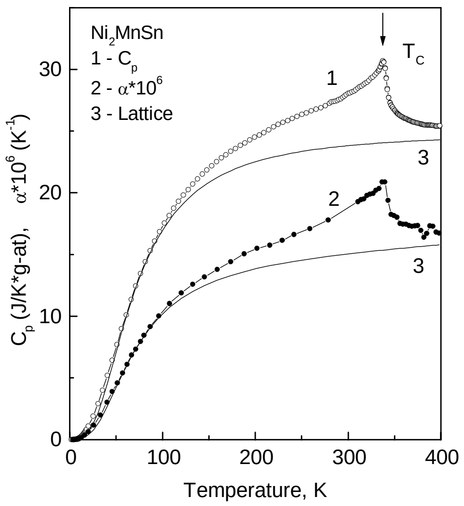

Fig.2. Specific heat C_p and the thermal expansion coefficient α of Ni_2MnSn versus T.

NiMnSb has lower value of $g(E_F)$ and it means that the $C1_b$ structure is more favorable for the HMF state formation than $L2_1$ one. CuMnSb has high value of γ and an additional contribution δT^2, which can result from many electron effects. Earlier it was shown that the heat capacity of CuMnSb is not affected by the magnetic field up to 14 T [3]. Therefore, we suppose that the low-temperature heat capacity of CuMnSb does not include spin-wave contributions.

The free electron gas approximation heat

Table 1. Values of the coefficients of low temperature specific heat and some characteristics Heusler alloys

	Ni_2MnSb	Ni_2MnSn	NiMnSb	CuMnSb
γ, mJ/(g-at·K^2) / γ, mJ/(f.u.·K^2)	3.42 / 13.68	2.62 / 10.48	1.68 / 5.04	5.19 / 15.57
$g(E_F)$, (eV·f.u)$^{-1}$	5.81	4.44	2.14	6.61
Theory: $g(E_F)$, (eV·f.u.)$^{-1}$	2.11	2.77	0.77	1.77
m (LMTO)*	2.1	1.2	2.8	3.4
$\beta 10^5$,mJ/(g-at·K^4)	17.76	11.79	5.81	6.32
Θ_D, (K)	222	255	322	313
$\delta 10^3$,mJ/(g-at·K^3)	-	-	-	6.00
T_C or T_N, K	350	340	730	47
T_{SPT}, K	455	745	-	740
$\kappa \Gamma_M$, 10^{-3} $kBar^{-1}$	-	2.2	-	6.8

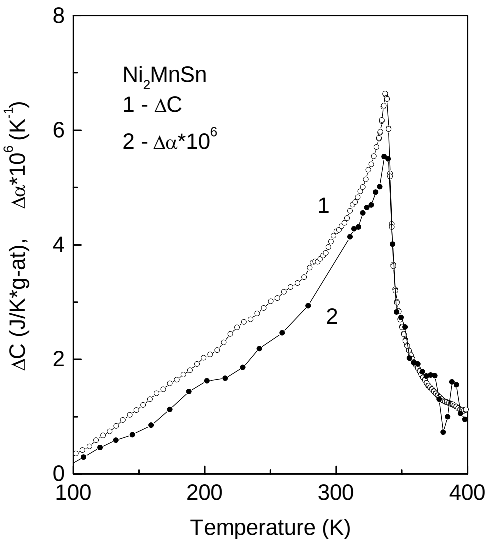

Fig.3. Magnetic contributions of Ni_2MnSn: 1-ΔC and 2-$\Delta\alpha$ versus T.

capacity is known to be related to the density of states at the Fermi level. In order to clear up the origin of the difference in heat capacity of the presented Heusler alloys we performed band structure calculation within the Local Spin Density Approximation (LSDA). The calculation was realized in the framework of the linear muffin-tin orbitals (LMTO) method [4] based on the Stuttgart TB-LMTO-47 computer code. According to the experimental results Ni_2MnSb, Ni_2MnSn and NiMnSb were supposed to be ferromagnetic and CuMnSb - antiferromagnetic in the present calculations. Integration in the course of self-consistency iterations was carried over mesh of 12x12x12 k-point in the irreducible part of the Brillouin zone.

Using the specific heat data in the form $C=C_{el}+C_{lat}+\Delta C$, and thermal expansion data [2] near T_C or T_N, the magnetic Grüneisen parameter Γ_M was obtained (see Fig.2-5). The first two terms represent the electron and phonon parts respectively. Usually ΔC is called as magnetic contribution to specific heat at T_C and T_N. We use the following expression $\Gamma_M = 3V_M\Delta\alpha_M / \kappa\Delta C$, where V_M (0.03 m^3/mole) is the molar volume and κ

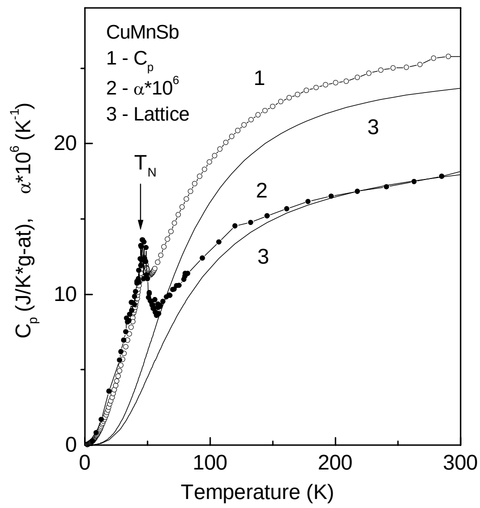

Fig.4. Specific heat C_p and the thermal expansion coefficient α of CuMnSb versus T.

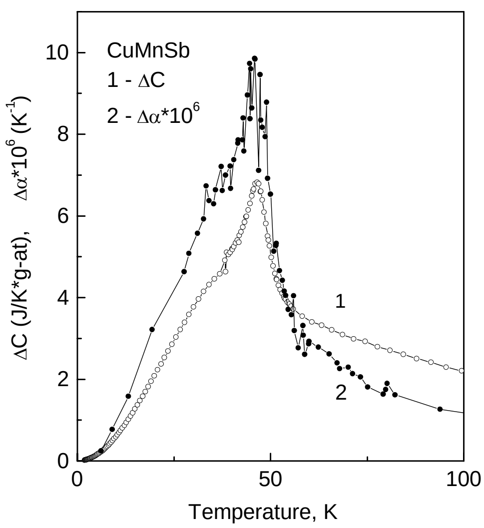

Fig.5. Magnetic contributions of CuMnSb: 1-ΔC and 2-$\Delta\alpha$ versus T.

($8\cdot10^{-7}$ Bar^{-1}) is the compressibility. The values for $\kappa\Gamma_M=\partial lnT_{C,N} / \partial P$ are reported in table 1, where P is applied pressure.

3. Discussion

We found that LSDA underestimates the heat capacity for all Heusler alloys under consideration. The biggest difference between calculated and experimental values of γ is seen to be for CuMnSb. The deviation of theoretical value obtained within LSDA from the experimental one can have two alternative explanations.

On the one hand the discrepancy between experimental value of heat capacity and theoretical one could mean that the free electron gas approximation is not suitable for description of the considered alloys. The corresponding mass renormalization parameters m^* are presented in table 1.

On the other hand the effects of atomic disorder were not properly taken into account in the present calculation. The interchange of transition metal ions should naturally present in Heusler alloys because of the similarity of the ionic radii of these atoms. The atomic disorder can play in the half-metal Heusler alloys the same role as an impurity in insulating compounds. The appearance of highly localized impurity states in pseudo gap is expected in this case. Note that some order-disorder-type phase transitions in these Heusler alloys at the temperature T_{SPT} (see table 1) were observed on TEC [2].

We observe a good correlation between magnetic parts of the specific heat with TEC for FM and AFM alloys at $T<T_{C,N}$ (see Fig.3, Fig.5). It means that they are described by the same temperature dependence. Nevertheless there is a discrepancy between the experimental specific heat and the phonon specific heat curves at $T>T_N$ (see Fig.4, Fig.5). It may be related with a change of magnetic state of the manganese atoms and has the same origin as low-temperature δT^2 part of $C_p(T)$. Recently new results of electron structure calculations has been reported [5], where $g(E_F)$=1.38 state/eV per formula unit for AFM phase and $g(E_F)$=11.38 state/eV per formula unit for paramagnetic phase has been obtain. Other origin of the existence of the low-temperature δT^2 part of $C_p(T)$ can be caused by the increase of the DOS at the Fermi level which traverses the edge of the Cu 3d band when the temperature increases.

The measurements of $\partial lnT_N/\partial P$ [6-7] show the same value $\kappa\Gamma_M$ for Ni_2MnSn. From our specific heat data we can predict the large and the positive value $\partial lnT_N/\partial P$=6.8 kBar^{-1} for CuMnSb.

Acknowledgments

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