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Influence of Vanadium on Thermoelectric Properties of $Fe_2Ti_{1-x}V_xSn$ Heusler Alloys

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ABSTRACT

$Fe_2Ti_{1-x}V_xSn$ (x = 0, 0.06, 0.15, and 0.2) Heusler alloys were studied experimentally and theoretically. It is established that the studied compositions exhibit the transport properties typical of semiconductors, while the partial substitution of titanium atoms by vanadium atoms leads to a change in the conductivity from *p*-type to *n*-type. Theoretical calculation of Seebeck coefficient revealed that taking into account B2-type partial disorder of the Heusler $L2_1$ superstructure makes it possible to acquire values of the Seebeck coefficient closer to the experimental results.

1. Introduction

Full-Heusler alloys are ternary intermetallic or metallic compounds with the general formula X_2YZ, where X and Y are transition 3*d* or 4*d* elements or rare earth metals, while Z is a nonmagnetic metal or a nonmetallic element. The crystal-lattice structural type is $L2_1$, and the position in the cube center is occupied by an X atom, while Z and Y atoms are alternately arranged in lattice sites [1]. The unit cell contains 24 valence electrons, varying the number of which, it is possible to control the thermoelectric parameters [2].

Due to the fact that Heusler alloys are thermally stable, possess a high electrical conductivity, and rather large Seebeck coefficient, and the elements included in compositions are widely available, they can be considered as promising among low-temperature and mid-temperature thermoelectric materials [3].

According to theoretical calculations, the power factor reaches the maximal value in comparison with the undoped sample with an increase in the number of valence electrons for Fe_2TiSn from 24 to 24.06 [4]. Theoretical calculations [4] predict that the partial substitution of titanium atoms by vanadium or other elements with a similar electron configuration lead to incresing in the Seebeck coefficient and power factor due to the introduction of an additional electron into the system per unit cell. In order to verify the theoretical predictions, we investigated the thermoelectric properties of $Fe_2Ti_{1-x}V_xSn$ compounds (x = 0, 0.06, 0.15, and 0.2).

2. Method

Samples of the chemical composition $Fe_2Ti_{1-x}V_xSn$ (x = 0, 0.06, 0.15, and 0.2) were fabricated and characterized by a variety of experimental techniques as described elsewhere [5]. *Ab initio* calculations were performed in terms of density functional theory with the help of the Vienna *ab initio* Simulation Package (VASP) using the projector augmented plane wave method. The substitution levels x = 0.0625, 0.125, and 0.25 in the $Fe_2Ti_{1-x}V_xSn$ alloy were theoretically attained by the unit cell translation and substitution of a definite number of Ti atoms by V atoms.

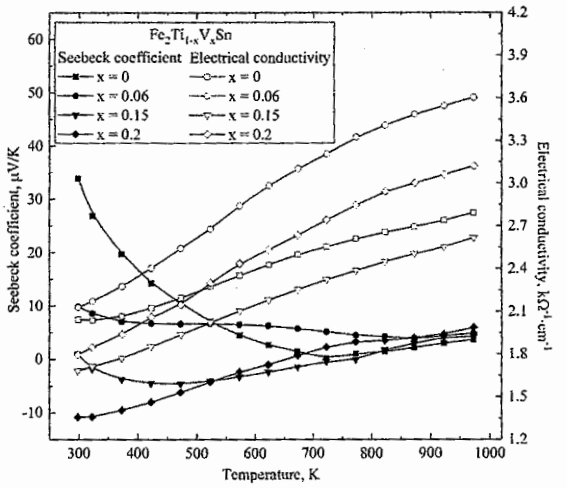

Fig. 1 Temperature dependences of the Seebeck coefficient and electrical conductivity of the studied $Fe_2Ti_{1-x}V_xSn$ (x = 0, 0.06, 0.15, and 0.2) samples.

3. Results and Discussion

Temperature dependences of the Seebeck coefficient and electrical conductivity in $Fe_2Ti_{1-x}V_xSn$ are shown in Fig. 1. It is evident that the alloys under study belong to semiconductors because their electrical conductivity also rises with increasing temperature. The maximal Seebeck coefficient is observed at 300 K for the undoped Fe_2TiSn sample being 35 μV/K, which is smaller than the claimed theoretical value by an order of

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magnitude [4]. The dominant type of conductivity changes from *p*-type to *n*-type with the partial substitution of titanium by vanadium with a subsequent increase in the concentration of the latter.

In the case of the completely ordered $L2_1$ structure and uniform distribution of vanadium atoms, the change in the sign of the Seebeck coefficient from "+" for undoped Fe_2TiSn to "–" for all doping levels of the studied $Fe_2Ti_{1-x}V_xSn$ is observed. It shows a tenfold increase in S in modulo when compared with undoped Fe_2TiSn, which agrees with the conclusion of the previous theoretical investigation of this alloy [4]. However, when compared with the results of the experimental investigation of similar Heusler alloys [5]

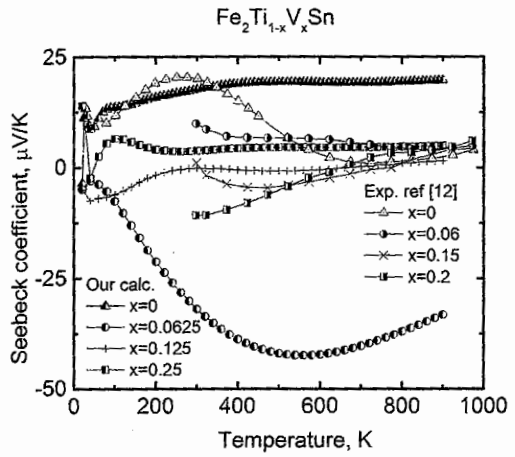

Fig. 2 Temperature dependence of the Seebeck coefficients for the $Fe_2Ti_{1-x}V_xSn$ Heusler alloys (x = 0, 0.0625, 0.125, and 0.25) with random atomic distribution. Comparative experimental curves with substitution levels of titanium x = 0, 0.06, 0.15, and 0.2 are taken from Ref. [5].

with the close substitution levels of Ti by V, it is evident that the applied calculation method greatly overestimates the influence of the substitution of titanium by vanadium on the thermoelectric properties of the $Fe_2Ti_{1-x}V_xSn$ alloy.

The results of calculations for the case of a partially disordered structure of the B2 type and nonuniform distribution of V atoms are more realistic. We can conclude from Fig. 2 that the Seebeck coefficient reaches –42 μV/K in the best case, which is fivefold smaller in modulo than S calculated for the $L2_1$ structure with a uniform distribution of vanadium. The best substitution level for increasing the thermoelectric voltage with the nonuniform atomic distribution in the supercell is x = 0.0625, which corresponds to predictions of the previous theoretical investigation [4].

4. Concluding Remarks

It is shown that theoretical assumptions on an increase in the thermoelectric efficiency of the Fe_2TiSn alloy with the partial substitution of titanium atoms by vanadium did not find experimental confirmation. The Seebeck coefficient maximum found experimentally is 35 μV/K only, which is smaller than the theoretically calculated value by an order of magnitude. The substantial difference of the theoretical calculations and experimental results can be explained by the fact that the theory does not take into account the nonideality of the experimental samples. The calculation taking into account stacking faults, vacancies, and the nonuniform distribution of vanadium atoms in the supercell allows us to find values of the thermoelectric voltage closer to the experimental data.

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