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The study of phonon thermal conductivity of CoSi-CoGe solid solutions using *ab initio* lattice dynamics

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Lattice thermal conductivity of solid solutions based on cobalt monosilicide and monogermanide was studied. Electrical and thermal conductivities of CoSi and solid solutions of $\mathrm{CoGe}_x\mathrm{Si}_{1-x}$ ($x = 0.03$ and 0.07) were experimentally measured in the temperature range of 80−350 K. Phonon spectra and thermal conductivity in $\mathrm{CoGe}_x\mathrm{Si}_{1-x}$ solid solutions were calculated using *ab initio* lattice dynamics. The results of calculations are in good agreement with the results of measurements obtained in the present work and with the literature data. It was shown that already at a content of 10−15 at.% of Ge, the lattice thermal conductivity decreases by about a factor of 2 compared with pure cobalt monosilicide, and at a germanium content of about 70 at.%, the decrease can reach 3.5 times.

Keywords: lattice thermal conductivity, thermoelectrics, first principle lattice dynamics.

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1. Introduction

Materials based on cobalt monosilicide are considered as promising thermoelectric materials due to their high power factor, mechanical strength, and stability at high temperatures. They are composed of cheap, accessible, and non-toxic components. Improvement of their thermoelectric figure of merit requires studying of the possibility to reduce lattice thermal conductivity.

Cobalt monosilicide crystallizes in a B20 cubic noncentrosymmetric structure (space group $P2_13$, No. 198) [1]. It has a high power factor, however, lattice thermal conductivity in pure CoSi is high as well, i.e., approximately $\kappa_{\mathrm{ph}} = 10.7-12.3\,\mathrm{W/m\,K}$ at a room temperature [2,3]. The lattice thermal conductivity can be reduced using the method of solid solutions. Previously solid solutions based on cobalt monosilicide were studied in details with cobalt substituted by iron or nickel [2,4,5]. However, in addition to the change in thermal conductivity, changes in the concentration of current carriers, thermopower, and electrical conductivity take place in them. In addition, the differences in masses of Co and Fe(Ni) atoms are small, that implies a little reduction of the lattice thermal conductivity. In addition to monosilicides with the B20 structure, there are isostructural monogermanides, for example, CoGe. Due to the significant (about 2.5 times) difference between Si and Ge masses, a significant lowering of κ_{ph} can be expected. Isoelectronic substitution of silicon by germanium should not change the concentration of current carriers, therefore, in principle, a possibility arises to change electron and lattice properties creating solid solutions with the substitution in both sublattices.

Pure cobalt monogermanide was studied in a number of works [9–13]. In [9] the polymorphism of monogermanides under high pressure and temperature was studied. The CoGe modification with the B20 structure can be synthesized under high pressure. At normal pressure this modification exists, however, probably, is metastable. In [10] it was noted that as a result of annealing at 600°C it is transformed into a monoclinic modification. In [10] also magnetic properties, electrical conductivity, and thermopower of CoGe were studied, and the thermopower was found to be $-32\,\mu\mathrm{V/K}$ at a room temperature. With a decrease in temperature down to 120 K, a transition from paramagnetic to antiferromagnetic state was observed. At the same time the dependencies of magnetization on a magnetic field in CoGe at 5 K and 300 K measured in [11], demonstrated low diamagnetic susceptibility. In [11,12] also the electronic band structure, mechanical and thermal properties of CoGe in the B20 structure were investigated and the conclusion was made on the sufficient stability of the material. In [13] CoGe and solid solutions with the substitution of Co by Fe or Ni were studied. The highest thermoelectric figure of merit, i.e., 0.11, was obtained for pure CoGe at a room temperature, while the thermopower appeared to be close to that of CoSi and was equal to $-80\,\mu\mathrm{V/K}$. With the total thermal conductivity of 9 W/m K, the lattice part appeared to be 5.3 W/m K.

Solid solutions of CoSi-CoGe were studied in [6,8]. In [6] solid solutions were studied with germanium content of up to 15 at.% in the range of temperatures below and near the room temperature. In this case a noticeable lowering of thermal conductivity was found with a little change in thermopower, which gave the thermoelectric figure of merit

$zT = 0.11$ at 350 K [6]. In [8] CoGe$_x$Si$_{1-x}$ compounds with up to 50 at.% of Ge were studied. A significant increase in power factor (up to 6 mW/m K^2) was obtained, maximum thermopower (about $-100\,\mu$V/K) was observed with the addition of 5 at.% Ge, as well as the possibility of noticeable reduction of thermal conductivity in these solid solutions was noted, although no experimental data was presented. We did not found in literature any values of thermal conductivity for solid solutions of CoGe$_x$Si$_{1-x}$ with a high content of germanium.

Therefore, it was interesting to theoretically and experimentally study in more details the thermal conductivity of CoGe$_x$Si$_{1-x}$ solid solutions. In this work with the use of *ab initio* approach we have calculated phonon spectra of solid solutions of cobalt monosilicide and monogermanide in the B20 structure, as well as lattice thermal conductivity for the entire range of compositions. We have measured experimentally the electrical and thermal conductivity of CoSi and CoGe$_x$Si$_{1-x}$ samples with 3 and 7 at.% of Ge in a temperature range of 80–350 K. Results of these calculations were compared with the experimental data obtained in this study and found in literature.

2. Experimental study of electrical and thermal conductivity

Samples of pure CoSi and solid solutions of CoGe$_x$Si$_{1-x}$ ($x = 0.03$, 0.07) were produced by direct melting together in an induction furnace followed by the Bridgman crystallization. X-ray powder diffraction analysis of the structure has shown that these samples were in single phase with the B20 cubic structure. The samples were polycristalline, with the grain size from several tens of micrometers and larger. Thermal conductivity was measured by the stationary method. Electrical conductivity was measured by the four-probe method [7]. The results of measurement for the pure sample match well with the previously obtained results [2,14]. The results of electrical conductivity measurements for pure CoSi and above-listed solid solutions are shown in Fig. 1. In all samples the electrical conductivity decreases with a decrease in temperature, which is related to the scattering of current carriers on phonons. Electrical conductivity in solid solutions decreases in comparison with CoSi and its temperature dependence becomes flatter due to the additional scattering on point defects.

Fig. 2 shows the total and lattice thermal conductivity as a function of temperature. Lattice thermal conductivity was extracted from the total thermal conductivity taking into account the contribution of electrons $\kappa_e = LT\sigma$ calculated by the Wiedeman–Franz law with the Lorentz number for degenerate statistics $L = \pi^2/3(k_B/e)^2$, where k_B — Boltzmann constant, e — electron charge. It can be seen from the figure, that the additional scattering on point defects in the solid solution decreases thermal conductivity, especially at low temperatures. At the same time, the temperature dependence of thermal conductivity becomes smoother. The lattice thermal conductivity of pure CoSi at a room temperature was 12.5 W/m K. In the examined solid solutions with 3 and 7 at.% of Ge it appeared to be approximately the same and equal to 7.3 and 7.5 W/m K. Thus, the lowering of lattice thermal conductivity was about 40%. These results match the literature data.

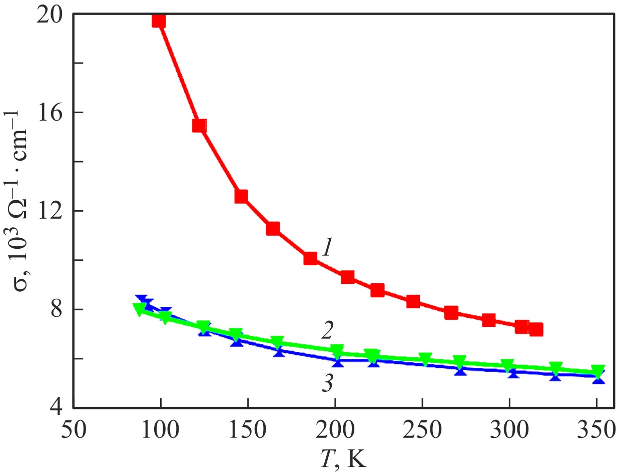

Figure 1. Temperature dependencies of electrical conductivity for samples of pure CoSi (*1*) and solid solutions with substitution of Si by 3 at.% (*2*) and 7 at.% (*3*) of Ge.

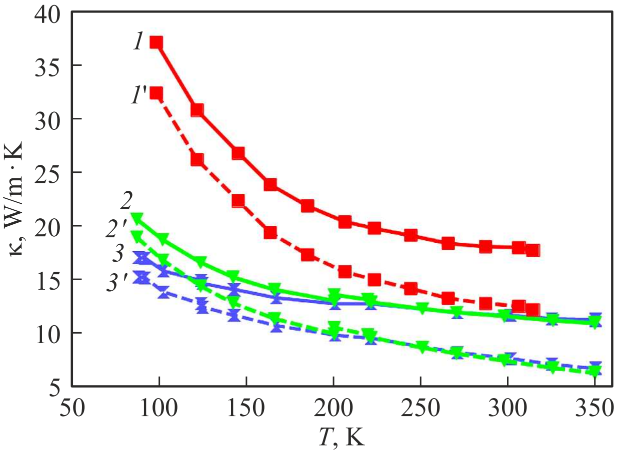

Figure 2. Temperature dependencies of total (solid lines *1*–*3*) and lattice (dashed lines *1'*–*3'*) thermal conductivity for samples of pure CoSi (*1, 1'*) and solid solutions with substitution of Si by 3 at.% (*2, 2'*) and 7 at.% (*3, 3'*) of Ge.

3. Calculation of phonon spectra and lattice thermal conductivity

To calculate phonon spectrum and thermal conductivity taking into account three-phonon processes of scattering, it is necessary to determine the second and the third order force constants composed of the Taylor's expansion coefficients for the total energy of the crystal with respect to components of atomic displacements. Forces of interatomic interaction are related to derivatives of the total energy with respect to atomic displacements, therefore they are also expressed through the force constants and components of atomic displacements. Force constants can be determined using supercell method. In this method displacements from the equilibrium state are set for one atom or a pair of atoms and using *ab initio* approaches the arising interatomic interaction forces are calculated. By performing such calculations for a number of atomic configurations, a system of equations can be obtained that relates forces to displacements. This system can be used to determine unknown force constants. This method is implemented in Phono3Py software [15,16].

Interatomic forces were calculated using a $3 \times 3 \times 3$ cubic supercell to determine force constants of the 2-nd order and a $2 \times 2 \times 2$ cubic supercell to determine force constants of the 3-rd order. Interatomic forces were calculated by VASP software [17,18] in scalar-relativistic approximation using gradient-corrected density functional GGA-PBE (with a boundary energy of 500 eV, grid in k-space equivalent to $6 \times 6 \times 6$ for the lattice cell). For CoSi optimum lattice parameters ($a_0 = 4.429$ Å, $x_{\mathrm{Co}} = 0.145$, $x_{\mathrm{Si}} = 0.843$), phonon spectrum, and lattice thermal conductivity were previously calculated by us in [14] and match well with experiments [1,2]. For CoGe the relaxation of atom positions and lattice constant resulted in the following values: $a_0 = 4.642$ Å, $x_{\mathrm{Co}} = 0.136$, $x_{\mathrm{Ge}} = 0.839$. Experimental data for the lattice constant in literature are $a_0 = 4.637$ Å [9] and 4.631 Å [10], and literature values for atomic positions are $x_{\mathrm{Co}} = 0.135$, $x_{\mathrm{Ge}} = 0.840$ [9]. Thus, the calculated values match the experimental data to a precision of about 0.1%.

Phonon spectra and partial density of phonon states are shown in Figs. 3 and 4. Masses of cobalt and silicon atoms in CoSi are significantly different, therefore in the low-frequency range of the phonon spectrum the density of states is mainly contributed by vibrations of Co atoms, while in the high-frequency range it is mainly contributed by Si. The masses of atoms in CoGe are closer to each other, and average atomic mass increases as compared with CoSi, therefore the range of phonon frequency decreases from 14 THz in CoSi down to 9 THz in CoGe, and partial contributions to the density of states from vibrations of Co and Ge atoms have close values and distributed in a similar manner over the entire frequency range.

Thermal conductivity in CoGe, taking into account three-phonon processes of scattering in relaxation time approximation was calculated over the $25 \times 25 \times 25$ grid, that ensured agreement by κ_{ph} to a precision of 0.1 W/m K. At a room temperature the following value was obtained: $\kappa_{\mathrm{ph}} = 4.8$ W/m K. This value matches well the experiment (about 10% below the experimental value of 5.3 W/m K from [13]). The calculated value for CoSi was 10.8 W/m K, and experimental values have a certain scatter: from 10.7 [2] to 12.3 [6,3] and 12.5 W/m K in this work, i.e., the error is about 10%.

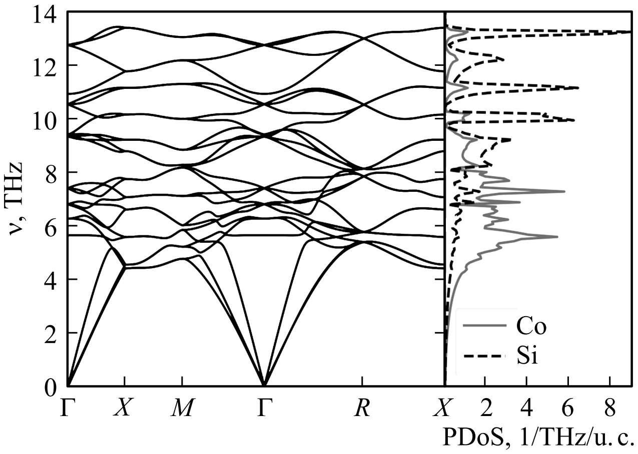

Figure 3. Phonon spectrum in CoSi and contribution to the density of phonon states from vibrations of Co and Si.

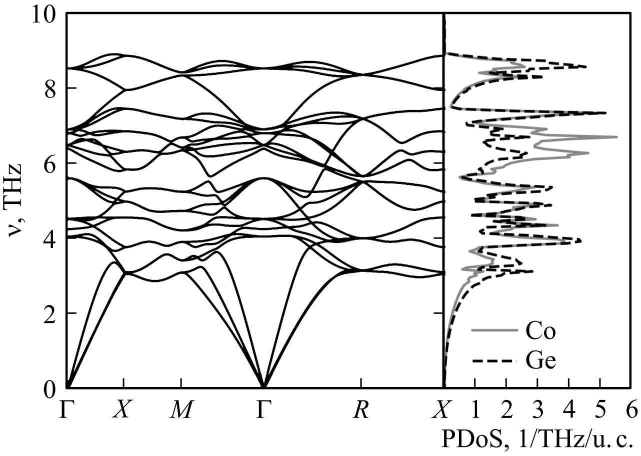

Figure 4. Phonon spectrum in CoGe and contribution to the density of phonon states from vibrations of Co and Ge.

The lattice thermal conductivity in solid solutions was calculated using *ab initio* approach that combines the method of virtual crystal and lattice dynamics (virtual crystal ab initio lattice dynamics, VC-ALD). In this method force constants are calculated for the extreme compositions of the solid solution. Then the force constants and atomic masses for each composition are obtained by means of linear interpolation. When calculating the lattice thermal conductivity, the phonon-phonon scattering is taken into consideration in the approximation of a virtual crystal, however, as shown in [19–22], it appears necessary to additionally take into account the scattering of phonons on point defects due to the difference in masses of ions. A similar approach was initially applied within the Debye model to solid solutions of Si-Ge, GaAs-InAs, and InP-AsP by Abeles [23]. It was applied to thermoelectric materials, for example, for solid solutions of Mg_2Si-Mg_2Sn, Mg_2Ge-Mg_2Sn, and Mg_2Si-Mg_2Ge in [24]. A more advanced variant with the use of information about spectrum and phonon-phonon scattering from *ab initio* calculations was successfully applied to a number of materials, for example, to solid solutions of $PbTe_{1-x}Se_x$ [19], $Mg_2Si_xSn_{1-x}$ [20], Si-Ge [25], semi-Heusler alloys [21]. In [22] a comparison was made between the results of calculation in the VC-ALD approximation and more precise approach based on methods of molecular dynamics for two model systems on the basis of argon and silicon with artificially introduced disordering due to the change in masses of a part of the atoms. The analysis of relaxation times and thermal conductivity has shown that calculations by the VC-ALD method match the results of molecular dynamics in the absence of abnormally large contribution to the thermal conductivity from high-frequency phonons, which occurred in the argon-based model system [22]. With such contribution a significant underestimation of the thermal conductivity value takes place due to the decrease in relaxation time for the scattering of high-frequency phonons on point defects [22].

Partial contributions to thermal conductivity from phonons with different frequencies for CoSi and CoGe are shown in Fig. 5. It can be seen that in CoSi the largest contribution is from acoustic modes in the range up to 5.5 THz and the middle-frequency range from 5.5 to 8 THz. In this range the oscillatory contribution from Co atoms prevails. The spectrum range from 8 to 14 THz, corresponding to oscillations of Si, gives almost no contribution to thermal conductivity. Frequencies in CoGe are shifted downwards: acoustic range — up to 4.5 THz, and middle frequencies — from 4.5 to 7 THz. The range from 7 to 11 THz gives almost no contribution to thermal conductivity as well. Due to the lower difference of masses in CoGe, the acoustic modes are contributed by both the oscillations of Co and oscillations of Ge with the latter slightly prevailing. The oscillatory contribution from Co atoms prevails near 6 THz. Since the dependencies (Fig. 5) have no distinguished contribution from high-frequency modes to thermal conductivity, then, in accordance with conclusions of [22], it can be expected that the use of the VC-ALD method for these solid solutions should give reasonable results.

Using the obtained force constants for CoSi and CoGe, thermal conductivity was calculated for the entire range of composition by the VC-ALD method. The results are shown in Fig. 6. Data for extreme compositions and for compositions of $CoGe_xSi_{1-x}$ up to 15 at.% from [6] is provided on the graph for comparison. The experimental values obtained in this work match well the literature data. Except for the probable outlier at 5 at.% [6], the difference between calculated and experimental values is from 10 to 18%. The scattering of experimental values can be caused by the probable deviation of samples composition from the setting. This is indirectly confirmed by the difference between the lattice constant dependencies on composition in [6] and the data presented in [8]. If actual content of Ge in [6] appeared to be less than nominal, then the experimental points should be shifted to the left, which will improve the coincidence. From the point of view of the calculation method, the deviations from experiment are related, firstly, to the inaccuracy of description of extreme composition for which the obtained values of κ_{ph} were less by about 10%. This can be related to the inaccuracy of description of the phonon spectrum, as well as to the use of relaxation time approximation to solve the Boltzmann equation. Another cause may be the approximations used in the VC-ALD method itself [20,22]. In particular, perhaps, the equations should be refined that are used to calculate probabilities of scattering on point defects, which were initially obtained for isotopic scattering in the second order of the perturbation theory [26]. In this case the differences in masses of substituted elements are bigger than the typical mass scatter for isotopes. This can result in an overestimated impact of scattering on point defects. It seems that more consistent consideration of the change in spectrum and scattering should be performed by the method of coherent potential.

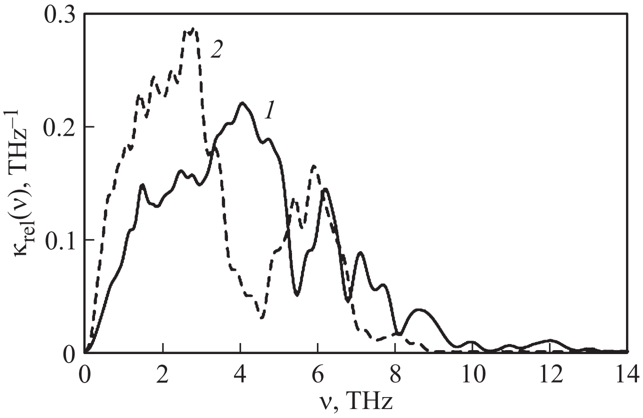

Figure 5. Relative contribution from phonons to the lattice thermal conductivity of CoSi (*1*) and CoGe (*2*).

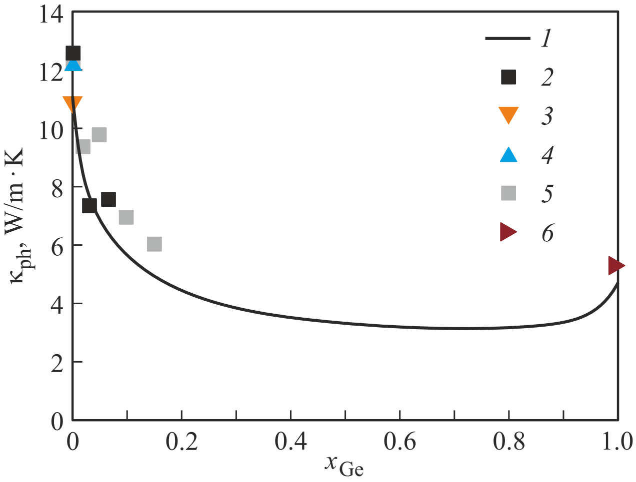

Figure 6. Dependence of lattice thermal conductivity on the composition of $CoGe_xSi_{1-x}$ solid solution at 300 K. Solid line *1* — calculation, symbols — experimental data from this study (*2*) and from literature: 3 [2], 4 [3], 5 [6], 6 [13].

4. Conclusion

Thus, in this work the dependence of lattice thermal conductivity on composition in solid solutions of CoSi-CoGe was investigated theoretically and experimentally. The obtained experimental data match the literature data. An *ab initio* calculation of the lattice thermal conductivity was performed for the above solid solutions that matched well the available experimental data. As a result, both experimental data and estimates indicate the possibility to reduce the lattice thermal conductivity in solid solutions of CoSi-CoGe by approximately 2 times as compared to CoSi at a germanium content of as low as 10−15%. Maximum calculated decrease by 3.5 times is predicted at 70 at.% of Ge. However, at high content of germanium the stability of solid solutions may be lower, and additional scattering of carriers on point defects may decrease the electrical conductivity. Therefore, it seems that more promising for the improvement of zT is to study the range of compositions near CoSi, where a considerable lowering of the thermal conductivity is observed, and the existing experimental data indicates the possibility of the power factor increase [6,8].

Conflict of interest

The authors declare that they have no conflict of interest.

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