



HAL
open science

Beneficial effect of Ni substitution on the thermoelectric properties in partially filled $\text{Ca}_y\text{Co}_{4-x}\text{Ni}_x\text{Sb}_{12}$ skutterudites

M. Puyet, A. Dauscher, Bertrand Lenoir, M. Dehmas, C. Stiewe, E. Müller, J. Hejtmanek

► **To cite this version:**

M. Puyet, A. Dauscher, Bertrand Lenoir, M. Dehmas, C. Stiewe, et al.. Beneficial effect of Ni substitution on the thermoelectric properties in partially filled $\text{Ca}_y\text{Co}_{4-x}\text{Ni}_x\text{Sb}_{12}$ skutterudites. *Journal of Applied Physics*, 2005, 97 (8), pp.083712. 10.1063/1.1868083 . hal-03996342

HAL Id: hal-03996342

<https://hal.science/hal-03996342>

Submitted on 19 Feb 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Beneficial effect of Ni substitution on the thermoelectric properties in partially filled $\text{Ca}_y\text{Co}_{4-x}\text{Ni}_x\text{Sb}_{12}$ skutterudites

Cite as: J. Appl. Phys. **97**, 083712 (2005); <https://doi.org/10.1063/1.1868083>

Submitted: 27 September 2004 • Accepted: 12 January 2005 • Published Online: 11 April 2005

M. Puyet, A. Dauscher, B. Lenoir, et al.



View Online



Export Citation

ARTICLES YOU MAY BE INTERESTED IN

[Anomalous barium filling fraction and n-type thermoelectric performance of \$\text{Ba}_y\text{Co}_4\text{Sb}_{12}\$](#)

Journal of Applied Physics **90**, 1864 (2001); <https://doi.org/10.1063/1.1388162>

[Low thermal conductivity and high thermoelectric figure of merit in n-type \$\text{Ba}_x\text{Yb}_y\text{Co}_4\text{Sb}_{12}\$ double-filled skutterudites](#)

Applied Physics Letters **92**, 182101 (2008); <https://doi.org/10.1063/1.2920210>

[High performance \$\text{In}_x\text{Ce}_y\text{Co}_4\text{Sb}_{12}\$ thermoelectric materials with in situ forming nanostructured InSb phase](#)

Applied Physics Letters **94**, 102114 (2009); <https://doi.org/10.1063/1.3099804>

Journal of Applied Physics **Special Topics** Open for Submissions [Learn More](#)

Beneficial effect of Ni substitution on the thermoelectric properties in partially filled $\text{Ca}_y\text{Co}_{4-x}\text{Ni}_x\text{Sb}_{12}$ skutterudites

M. Puyet, A. Dauscher, and B. Lenoir^{a)}

Laboratoire de Physique des Matériaux, UMR 7556, Ecole Nationale Supérieure des Mines de Nancy, Parc de Saurupt, F-54042 Nancy, France

M. Dehmas

Laboratoire de Science et Génie des Matériaux et de Métallurgie, UMR 7584, Ecole Nationale Supérieure des Mines de Nancy, Parc de Saurupt, F-54042 Nancy, France

C. Stiewe and E. Müller

German Aerospace Center (DLR), Institute of Materials Research, Linder Hoehe, 51147 Cologne, Germany

J. Hejtmanek

Institute of Physics Academy of Sciences of the Czech Republic, Cukrovarnicka 10, CZ-162 53 Praha 6, Czech Republic

(Received 27 September 2004; accepted 12 January 2005; published online 11 April 2005)

We have investigated the influence of nickel doping in a series of n -type CoSb_3 skutterudite materials partially filled with Ca. The electrical resistivity, thermopower, and thermal conductivity have been measured in the 300–800 K temperature range on $\text{Ca}_y\text{Co}_{1-x}\text{Ni}_x\text{Sb}_{12}$ compounds prepared by a powder metallurgy route. The chemical composition and structure have been analyzed by electron probe microanalyses and x-ray diffraction, respectively. It was found that the presence of nickel substantially decreases the electrical resistivity without any detrimental effect on the thermopower, resulting in an improvement of the power factor. The dimensionless thermoelectric figure ZT increases with increasing temperature and reaches a maximum value of 1 at 800 K. © 2005 American Institute of Physics. [DOI: 10.1063/1.1868083]

I. INTRODUCTION

During the last decade, many efforts have been made in the search for innovative highly efficient thermoelectric materials. Several promising families have attracted much attention including semi-Heusler phases,¹ skutterudites,² lamellar oxides,³ clathrates,⁴ and more recently the $\text{AgPb}_m\text{SbTe}_{2+m}$ system.⁵ Let us remember that the thermoelectric performance of a material is characterized by its dimensionless figure of merit, $ZT = \alpha^2 T / \rho \lambda$, where T , α , ρ , and λ are the absolute temperature, the thermopower, the electrical resistivity, and the total thermal conductivity (equal to the sum of the lattice, λ_L , and the electronic, λ_E , contributions), respectively. Maximizing the thermopower coherently while minimizing the electrical resistivity and the thermal conductivity leads to high ZT values and thus to high performance thermoelectric materials.

Skutterudite materials based on CoSb_3 display exceedingly rich manners of tuning the thermal or the electrical properties in an independent way. The electric and thermal transport of skutterudites can be significantly modified either through partial or total filling of the open “cages” by different atoms and/or via substitutions of constituent atoms of the framework structure. Regarding this connection, a lot of combinations have been investigated in the past few years.^{2,6–19} Both n - and p -type skutterudite materials exhibiting ZT values exceeding those of the current standard ther-

molectrics at moderated temperatures have been put forward.^{6,17} Quite recently, Ca ions were identified as other appropriate filler elements.²⁰ At high temperatures, these partially filled $\text{Ca}_y\text{Co}_4\text{Sb}_{12}$ compounds exhibit high thermopower values and a favorable thermal conductivity but, unfortunately, to the detriment of an excessive electrical resistivity. Consequently, the thermoelectric performance remains moderated up to high temperatures ($ZT \sim 0.45$ at 800 K).²¹ In an effort to further reduce the electrical resistivity of $\text{Ca}_y\text{Co}_4\text{Sb}_{12}$ compounds, we have investigated the influence of nickel doping on the cobalt sites. Previous results showed that the addition of a small amount of nickel in both unfilled and Ba-filled CoSb_3 can be an effective means of optimizing their thermoelectric properties.^{17,22} In this article, we provide additional proof that a minute amount of Ni is beneficial to improving thermoelectric performance in skutterudite compounds. In the $\text{Ca}_y\text{Co}_{4-x}\text{Ni}_x\text{Sb}_{12}$ compounds investigated, a ZT value more than twice as high as in Ni-free compounds is reached at 800 K.

II. EXPERIMENT

The $\text{Ca}_y\text{Co}_{4-x}\text{Ni}_x\text{Sb}_{12}$ samples with nominal $y=0.4$ and $0 \leq x \leq 0.06$ concentrations have been prepared by a solid-state reaction method. Appropriate quantities of high-purity Ca pellets (99.5%), Sb shots (99.999%), Co (99.998%), and Ni (99.995%) powders were loaded into a quartz ampoule. The ampoule was sealed under a reducing He–H₂ atmosphere and heated in a vertical furnace up to 1023 K for 84 h with the heating rate fixed at 1 K/min. The grown ingot was

^{a)}Author to whom correspondence should be addressed; electronic mail: lenoir@mines.inpl-nancy.fr

TABLE I. Nominal and actual chemical compositions determined by EPMA, relative densities, lattice parameters deduced from x-ray diffraction data, Hall mobilities (μ_H), and Hall carrier concentrations (n) at 300 K of the $\text{Ca}_x\text{Co}_{4-y}\text{Ni}_y\text{Sb}_{12}$ samples.

Nominal composition	Actual composition	Relative density (%)	Lattice parameter (Å)	μ_H ($\text{cm}^2/\text{V s}$)	n (cm^{-3})
$\text{Ca}_{0.4}\text{Co}_4\text{Sb}_{12}$	$\text{Ca}_{0.2}\text{Co}_4\text{Sb}_{12.46}$	92	9.0498	7.2	2.8×10^{20}
$\text{Ca}_{0.4}\text{Co}_{3.98}\text{Ni}_{0.02}\text{Sb}_{12}$	$\text{Ca}_{0.15}\text{Co}_{3.98}\text{Ni}_{0.02}\text{Sb}_{11.80}$	92	9.0484	20.1	3.1×10^{20}
$\text{Ca}_{0.4}\text{Co}_{3.95}\text{Ni}_{0.05}\text{Sb}_{12}$	$\text{Ca}_{0.18}\text{Co}_{3.97}\text{Ni}_{0.03}\text{Sb}_{12.40}$	94	9.0488	24.5	4.4×10^{20}
$\text{Ca}_{0.4}\text{Co}_{3.92}\text{Ni}_{0.08}\text{Sb}_{12}$	$\text{Ca}_{0.18}\text{Co}_{3.94}\text{Ni}_{0.06}\text{Sb}_{12.40}$	96	9.0489	18.7	5.3×10^{20}

then ground in an agate mortar into powders ($\sim 100 \mu\text{m}$) that were again annealed and powdered under the same conditions. The resulting powders were pressed into pellets that were annealed at 893 K for 84 h. These pellets were crushed and powdered into 25 μm grains. Final compaction was performed in graphite dies by hot pressing in an argon atmosphere at 873 K for 2 h under 51 MPa.

X-ray powder diffraction and electron microprobe analysis (EPMA) data show that a homogeneous skutterudite phase is obtained in all samples with a Ca-rich minor second phase that was also present in the Ni-free samples.²⁰ Table I lists the nominal and actual chemical compositions of the skutterudite compounds, the lattice parameters, and the relative densities.

For the transport properties measurements, all samples were cut and analyzed in a direction perpendicular to the pressing direction except for thermal conductivity measurements. Thermal diffusivity was measured by a laser flash technique in an argon atmosphere over the 300–800 K temperature range. Four-probe electrical resistivity based on the van der Pauw method and standard Seebeck measurements were realized in the same temperature range.

III. RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of the electrical resistivity. As previously described,²¹ the nickel-free skutterudite sample containing calcium exhibits a negative temperature coefficient of the resistivity above room temperature. In contrast, the Ni doping induces a “metallic” behavior together with substantial decrease of the value of the resistivity. Such a behavior is characteristic of degenerated conduction in heavily doped semiconductors in the extrinsic region. The resistivity depression is particularly apparent at

room temperature where the resistivity is reduced by a factor of 4–5. The reduced resistivity results not only from an increase of the carrier concentration but, simultaneously, from an increase of the Hall mobility (see Table I). Similar observations were also noted when Ni was substituted in the structure framework of CoSb_3 and $\text{Ba}_y\text{Co}_4\text{Sb}_{12}$.^{17,22}

Figure 2 displays the temperature dependence of the thermopower. All samples possess negative thermopower with a nearly linear increase in magnitude with temperature and behavior that is consistent with degenerated electron transport. We can note that although the carrier concentration increases (Table I), the thermopower remains composition independent (within $\sim 10\%$ error) below 800 K. Moreover, the substitution of Co by Ni atoms has no detrimental effect on the absolute values of the thermopower, suggesting, in a first approximation, that the effective electron masses remain high in Ni-doped compounds. With regard to the increase of mobility in the Ni-doped samples, another possible factor favoring high thermopower values could be a change in scattering mechanisms as already demonstrated.¹⁷ The power factors α^2/ρ , plotted for all the samples in Fig. 3, thus significantly exceed that of the Ni-free $\text{Ca}_{0.2}\text{Co}_4\text{Sb}_{12.46}$ over the whole temperature range. For similar actual Ca content, the higher power factor is reached for the lowest Ni-containing sample ($x=0.03$) in the whole temperature range investigated.

The total thermal conductivity of the compounds is reported in Fig. 4. The studied skutterudites possess thermal conductivities ranging between 4.5 and 5.7 W/mK at room temperature which decrease down to 3.2–4.3 W/mK at 800 K. It was observed in Ba-filled skutterudites that the presence of Ni results in a suppression of the total thermal conductivity.¹⁷ In this study with Ca, the situation is less

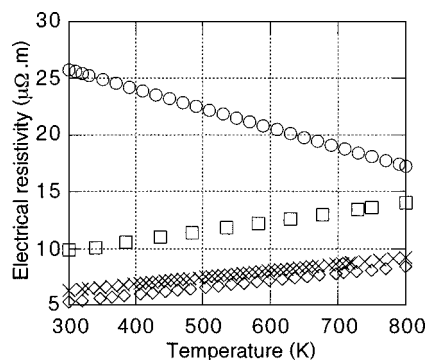


FIG. 1. Temperature dependence of the electrical resistivity of: \circ — $\text{Ca}_{0.2}\text{Co}_4\text{Sb}_{12.46}$, \square — $\text{Ca}_{0.15}\text{Co}_{3.98}\text{Ni}_{0.02}\text{Sb}_{11.80}$, \diamond — $\text{Ca}_{0.18}\text{Co}_{3.97}\text{Ni}_{0.03}\text{Sb}_{12.40}$, and \times — $\text{Ca}_{0.18}\text{Co}_{3.94}\text{Ni}_{0.06}\text{Sb}_{12.40}$.

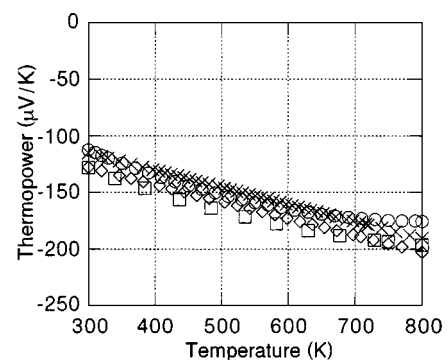


FIG. 2. Temperature dependence of the thermopower of: \circ — $\text{Ca}_{0.2}\text{Co}_4\text{Sb}_{12.46}$, \square — $\text{Ca}_{0.15}\text{Co}_{3.98}\text{Ni}_{0.02}\text{Sb}_{11.80}$, \diamond — $\text{Ca}_{0.18}\text{Co}_{3.97}\text{Ni}_{0.03}\text{Sb}_{12.40}$, and \times — $\text{Ca}_{0.18}\text{Co}_{3.94}\text{Ni}_{0.06}\text{Sb}_{12.40}$.

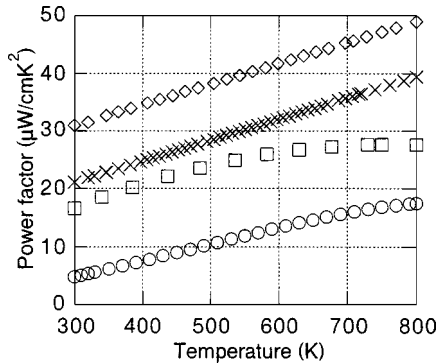


FIG. 3. Temperature dependence of the power factor of: \circ — $\text{Ca}_{0.2}\text{Co}_4\text{Sb}_{12.46}$, \square — $\text{Ca}_{0.15}\text{Co}_{3.98}\text{Ni}_{0.02}\text{Sb}_{11.80}$, \diamond — $\text{Ca}_{0.18}\text{Co}_{3.97}\text{Ni}_{0.03}\text{Sb}_{12.40}$, and \times — $\text{Ca}_{0.18}\text{Co}_{3.94}\text{Ni}_{0.06}\text{Sb}_{12.40}$.

clear and it is difficult to conclude definitively about the role of Ni because we were not able to ensure the reproducibility of the filling fraction of Ca in all samples investigated. Now, the presence of Ca has a dominant influence on the phonon transport.²³ Based on the Wiedemann–Franz law, we have estimated the electronic contribution, λ_E , to the total thermal conductivity (Fig. 4). The data at 300 K signify that, independent of the chemical composition, the lattice contribution, λ_L , to the thermal conductivity amounts to 4.3 ± 0.2 W/mK, whereas the electronic part increases from 0.3 ($x=0$) to 1.5 ($x=0.03$) W/mK. On the other hand, the high-temperature data at 800 K suggest higher scatter of the phononic part of the thermal conductivity; the highest $\lambda_L=2.5$ W/mK is observed for $x=0.02$, the lowest $\lambda_L=1.7$ W/mK for the most electrically conducting $x=0.03$ sample. The lowered phonon part of the thermal conductivity leads to the modified proportions between the electronic and lattice parts. The significance of the electronic contribution increases and, moreover, in the most metallic sample $\text{Ca}_{0.18}\text{Co}_{3.97}\text{Ni}_{0.03}\text{Sb}_{12.40}$ the electronic part dominates the thermal conductivity amounting to $\lambda_E=2.2$ W/mK which represents 55% of the total thermal conductivity.

Based on measured transport properties, we have calculated the dimensionless figure of merit, ZT , that is shown in Fig. 5. For all samples, ZT increases monotonically with increasing temperature. As a consequence of the large increase of the power factor due to Ni doping, the ZT values show a

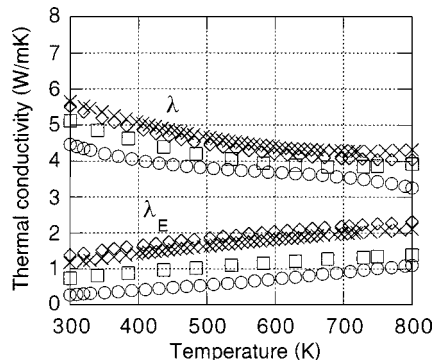


FIG. 4. Temperature dependence of the total thermal conductivity of: \circ — $\text{Ca}_{0.2}\text{Co}_4\text{Sb}_{12.46}$, \square — $\text{Ca}_{0.15}\text{Co}_{3.98}\text{Ni}_{0.02}\text{Sb}_{11.80}$, \diamond — $\text{Ca}_{0.18}\text{Co}_{3.97}\text{Ni}_{0.03}\text{Sb}_{12.40}$, and \times — $\text{Ca}_{0.18}\text{Co}_{3.94}\text{Ni}_{0.06}\text{Sb}_{12.40}$. The electronic part, λ_E , as deduced from the Wiedemann–Franz law is also shown.

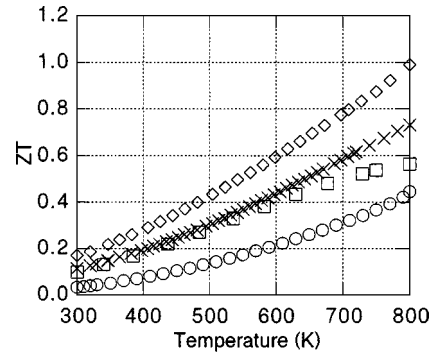


FIG. 5. Temperature dependence of the dimensionless figure of merit (ZT) of \circ — $\text{Ca}_{0.2}\text{Co}_4\text{Sb}_{12.46}$, \square — $\text{Ca}_{0.15}\text{Co}_{3.98}\text{Ni}_{0.02}\text{Sb}_{11.80}$, \diamond — $\text{Ca}_{0.18}\text{Co}_{3.97}\text{Ni}_{0.03}\text{Sb}_{12.40}$, and \times — $\text{Ca}_{0.18}\text{Co}_{3.94}\text{Ni}_{0.06}\text{Sb}_{12.40}$.

spectacular improvement by more than 100% at 800 K for $\text{Ca}_{0.18}\text{Co}_{3.97}\text{Ni}_{0.03}\text{Sb}_{12}$ in comparison to $\text{Ca}_{0.2}\text{Co}_4\text{Sb}_{12.46}$, making this compound an outstanding n -type skutterudite material.

IV. CONCLUSION

In an effort to optimize the thermoelectric performance of n -type $\text{Ca}_y\text{Co}_4\text{Sb}_{12}$ skutterudite compounds, we have studied the effect of Ni doping. Polycrystalline $\text{Ca}_y\text{Co}_{4-x}\text{Ni}_x\text{Sb}_{12}$ samples have been prepared and their transport properties have been evaluated at temperatures between 300 and 800 K. The obtained results have demonstrated the beneficial effects of the presence of a small amount of Ni, and support the idea that the doping with Ni in skutterudite materials is an effective way to enhance the dimensionless figure of merit. A ZT value of unity is reached at 800 K in the $\text{Ca}_y\text{Co}_{4-x}\text{Ni}_x\text{Sb}_{12}$ series which represents an increase of more than 100% compared to the Ni-free series.

ACKNOWLEDGMENTS

The authors would like to thank SERRAS Thermoelectrics and ADEME for their interest in this work and for their financial support.

- ¹J. S. Poon, in *Semiconductors and Semimetals*, edited by T. M. Tritt (Academic Press, San Diego, CA, 2000), Vol. 70, p. 37.
- ²C. Uher, in *Semiconductors and Semimetals*, edited by T. M. Tritt (Academic Press, San Diego, CA, 2000), Vol. 69, p. 139.
- ³I. Terasaki, Y. Sasago, and K. Uchinokura, *Phys. Rev. B* **56**, 12685 (1997).
- ⁴G. S. Nolas, G. A. Slack, and S. B. Schujman, in *Semiconductors and Semimetals*, edited by T. M. Tritt (Academic Press, San Diego, CA, 2000), Vol. 69, p. 255.
- ⁵K. F. Hsu, S. Loo, F. Guo, W. Chen, J. S. Dyck, C. Uher, T. Hogan, E. K. Polychroniadis, and M. G. Kanatzidis, *Science* **303**, 818 (2004).
- ⁶J.-P. Fleurial, T. Caillat, A. Borshevsky, D. T. Morelli, and P. Meisner, in *Proceedings of the 15th International Conference on Thermoelectrics*, edited by T. Caillat (Institute of Electrical and Electronics Engineers, Piscataway, NJ, 1996), p. 91.
- ⁷B. Chen B., J.-H. Xu, C. Uher, D. T. Morelli, G. P. Meisner, J.-P. Fleurial, T. Caillat, and A. Borshevsky, *Phys. Rev. B* **55**, 1476 (1997).
- ⁸D. T. Morelli, G. P. Meisner, B. Chen, S. Hu, and C. Uher, *Phys. Rev. B* **56**, 7376 (1997).
- ⁹G. S. Nolas, J. L. Cohn, and G. A. Slack, *Phys. Rev. B* **58**, 164 (1998).
- ¹⁰H. Takizawa, K. Miura, M. Ito, T. Suzuki, and T. Endo, *J. Alloys Compd.* **282**, 79 (1999).
- ¹¹N. R. Dilley, E. D. Bauer, M. B. Maple, and B. C. Sales, *J. Appl. Phys.* **88**, 1948 (2000).

- ¹²G. S. Nolas, M. Kaeser, R. T. Littleton, and T. M. Tritt, *Appl. Phys. Lett.* **77**, 1855 (2000).
- ¹³B. C. Sales, B. C. Chakoumakos, and D. Mandrus, *Phys. Rev. B* **61**, 2475 (2000).
- ¹⁴G. S. Nolas, H. Takizawa, T. Endo, H. Sellinschegg, and D. C. Johnson, *Appl. Phys. Lett.* **77**, 52 (2000).
- ¹⁵L. D. Chen, T. Kawahara, X. F. Tang, T. Goto, T. Hirai, J. S. Dyck, W. Chen, and C. Uher, *J. Appl. Phys.* **90**, 1864, (2001).
- ¹⁶G. A. Lamberton, Jr., S. Bhattacharya, R. T. Littleton, IV, M. A. Kaeser, R. H. Tedstrom, T. M. Tritt, J. Yang, and G. S. Nolas, *Appl. Phys. Lett.* **80**, 598 (2002).
- ¹⁷J. S. Dyck, W. Chen, C. Uher, L. Chen, X. Tang, and T. Hirai, *J. Appl. Phys.* **91**, 3698 (2002).
- ¹⁸J. Yang, D. T. Morelli, G. P. Meisner, W. Chen, J. S. Dyck, and C. Uher, *Phys. Rev. B* **67**, 165207 (2003).
- ¹⁹V. L. Kuznetsov, L. A. Kuznetsova, and D. M. Rowe, *J. Phys.: Condens. Matter* **15**, 5035 (2003).
- ²⁰M. Puyet, B. Lenoir, A. Dauscher, P. Weisbecker, and S. J. Clarke, *J. Solid State Chem.* **177**, 2138 (2004).
- ²¹M. Puyet, B. Lenoir, A. Dauscher, M. Dehmas, C. Stiewe, and E. Müller, *J. Appl. Phys.* **95**, 4852 (2004).
- ²²J. S. Dyck, W. Chen, J. Yang, G. P. Meisner, and C. Uher, *Phys. Rev. B* **65**, 115204 (2002).
- ²³M. Puyet, Ph.D. thesis, Institut National Polytechnique de Lorraine, Chapter V, 2004.