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Effects of valence fluctuation and pseudogap formation on phonon thermal conductivity of Ce-based compounds with ϵ-TiNiSi-type structure

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We have measured the thermal conductivity of isostructural compounds CePtSn, CeNiSn, CeRhSb, and CeRhAs with the orthorhombic ϵ-TiNiSi-type structure. It is found that the phonon thermal conductivity is reduced in a systematic way with increasing Kondo temperature T_K. The scattering of phonons by valence fluctuations should play a dominant role in such a reduction. The gap formation in the electronic density of states enhances the phonon thermal conductivity significantly in CeRhAs with a gap width of 280 K, while it is weak in CeNiSn or CeRhSb with a pseudogap of 20–30 K. A phenomenological model is proposed for the unusual temperature dependence of phonon thermal conductivity by taking account of the strong dependence of the electron-phonon scattering rate on both T_K and the energy gap.

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I. INTRODUCTION

Recently, many efforts were devoted to explore materials with high thermoelectric efficiency exceeding that of the state-of-the-art systems based on Bi-Te alloys. One of the central issue in this research field is how to reduce the thermal conductivity κ, maintaining good electrical conductivity. Slack has proposed the concept “phonon glass and electron crystal (PGEC)” to reconcile these incompatible conditions.[1] This concept insists that an extremely short phonon mean free path (mfp) caused by a phonon glassy state leads to a significant reduction of the phonon thermal conductivity κ_{ph}, while the longer charge carrier mfp is secured in a crystalline part of the material. According to this concept, one has to add an extra phonon scattering source, and several good possibilities such as “rattling”[2,3] and “disorder”[4] are suggested. In some clathrates[2] (e.g., $Eu_8Ga_{16}Ge_{30}$) and in filled skutterudites[3] (e.g., $CeFe_4Sb_{12}$), a rattling motion of a rather heavy atom caged in a rigid polyhedron causes an extra phonon scattering while charge carrier well conduct via the polyhedron’s frame. The atomic disorder in $NaCo_2O_4$ can be considered as point defects for phonons. In this compound, a layer composed of Na atoms and vacancies is sandwiched by electrical conducting CoO_2 layers.[4]

It has been claimed that phonon scattering by a valence fluctuating (VF) state is also a promising process to reduce κ_{ph}.[5–7] For example, in the skutterudite $Ru_{0.5}Pd_{0.5}Sb_3$, the VF between Ru^{2+} and Ru^{4+} states is believed to scatter heat carrying phonons.[6,7] But the role of the phonon-VF (ph-VF) scattering in κ_{ph} is less understood compared to that of the rattling and the atomic disorder, probably due to the absence of sophisticated experiments for VF compounds. Therefore it stimulated us to carry out systematic experiments of κ of isostructural VF compounds. Ce-based VF compounds with Ce^{3+} and Ce^{4+} states showing good electrical conductivity are characterized by the Kondo temperature T_K, which ranges from 50 to 1000 K. Aiming to obtain better insight into the influence of the ph-VF scattering with a change of T_K, we focus on the isostructural systems CePtSn, CeNiSn, CeRhSb, and CeRhAs, all of which crystallize into the orthorhombic ϵ-TiNiSi-type structure. We further discuss on the possibility of the PGEC state.

CePtSn is a metallic system where Ce ions are in the trivalent state with $T_K \simeq 10$ K, and undergoes two magnetic phase transitions at 7.5 K and 5.0 K.[8] CeNiSn and CeRhSb are VF semimetals with $T_K = 50$ and 90 K, respectively.[9–15] On cooling below a characteristic temperature T^*, of 15 K for CeNiSn (20 K for CeRhSb), a pseudogap of 20 K (30 K) is formed leaving a residual density of states at the Fermi level, $D_{res}(E_F)$.[16–18] CeRhAs with $T_K = 1350$ K is a VF semiconductor where a pseudogap of 280 K opens below $T^* = 370$ K.[19,20] The gap formation in CeRhAs is intimately related to successive phase transitions accompanying lattice modulations at $T_1 = 370$ K, $T_2 = 235$ K, and $T_3 = 165$ K.[20] The rapid development of the pseudogap occurs below T_3.[20] From these facts, one can expect that the effect of ph-VF scattering on κ_{ph}’s of the four compounds primarily depends on the value of T_K, without perturbing significantly other phonon-scattering processes.

It is reported that κ_{ph} of CeNiSn and CeRhSb is enhanced when the pseudogap is formed below T^*.[21–23] This enhancement was attributed to the increase of the phonon mfp by the diminishing of the charge carrier density, in analogy to high-T_C superconductors below the superconducting transition temperatures T_C. However, a systematic study of κ_{ph} by changing T^* has not been reported so far. Thus, the second aim in this study is to investigate the relationship between the enhancement of κ_{ph} and the magnitude of T^*. In this paper, we present experimental results of κ for CePtSn, CeNiSn, CeRhSb, and CeRhAs, and discuss the effect of both the VF and the pseudogap formation on κ_{ph}.

II. EXPERIMENTAL METHODS

Single crystalline samples of CePtSn and CeNiSn were grown by the Czochralski pulling method in a radiofrequency furnace. On the other hand, the Bridgman technique using a sealed tungsten crucible was employed to prepare single crystals of CeRhSb and CeRhAs with high vapor pressures. Details of the crystal growth were reported in separate

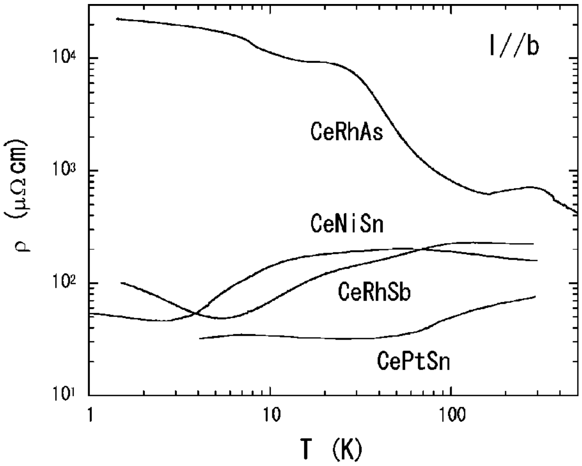

FIG. 1. The temperature dependence of ρ for CePtSn, CeNiSn, CeRhSb, and CeRhAs.

papers.[8,10,20,24] The measurement of κ in the range 4.2–300 K was performed by the conventional steady-heat-flow method with a radiation-shielded vacuum probe. The accuracy within $\pm 5\%$ of the absolute value was checked by the separate measurement of a standard steel sample purchased from NBS. In this study the thermal gradient ΔQ was applied along the orthorhombic b axis for all compounds. The typical sizes of the samples were $0.6\times 0.6\times 3$ mm^3. The electrical resistivity ρ along the b axis was measured in the range 1.5–500 K by a conventional four-probe method to estimate the electronic contribution to κ.

III. RESULTS AND DISCUSSION

Figures 1 and 2 show $\rho(T)$ and $\kappa(T)$ of all compounds studied in this work, respectively. As mentioned in the Introduction, metallic $\rho(T)$ for CePtSn, semimetallic ones for CeNiSn and CeRhSb, and semiconducting one for CeRhAs are clearly observed. The present $\kappa(T)$ values of CePtSn are larger than those of the previous report[22] measured between 1.5 K and 100 K. This difference amounting to 15% at 40 K cannot be adjusted by multiplying either data with an appropriate factor and is probably caused by the better sample quality in this study than that used in the previous one. In the case of CeNiSn or CeRhSb, the difference in κ between the present value and the previous one[22] is at most 5%, which, however, can be adjusted by multiplying either data by an appropriate factor. Therefore, these differences are ascribed to geometrical uncertainties. The thus combined data are given in Fig. 2 for CeNiSn and CeRhSb. For CePtSn, a shoulderlike structure around 40 K is the main feature in $\kappa(T)$. This structure is significantly reduced in $\kappa(T)$'s of CeNiSn and CeRhSb with an increase of T_K. On going from CePtSn, CeNiSn, CeRhSb, to CeRhAs along the enhancement of T_K, κ above 150 K is also considerably reduced by an order of magnitude. These facts signal a strong effect of the VF on $\kappa(T)$. At low temperatures, a highly contrasted effect of the pseudogap formation is revealed by comparing $\kappa(T)$ of CeRhAs with those of CeNiSn and CeRhSb. While a pronounced enhancement of κ below $T_3=165$ K is observed in CeRhAs with T^* of 370 K, CeNiSn and CeRhSb both of which possess T^* of 15–20 K exhibit rather faint ones below 10 K for CeNiSn and 20 K for CeRhSb, respectively. For CeRhAs, the jump in $\kappa(T)$ at $T_3=165$ K corresponds to the occurrence of a structural phase transition with the lattice modulation.

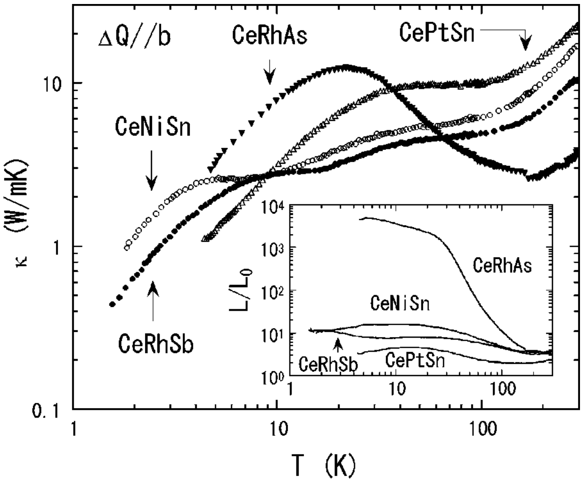

FIG. 2. The temperature dependence of κ for CePtSn, CeNiSn, CeRhSb, and CeRhAs. The thermal gradient was applied along the orthorhombic b axis. The inset shows the reduced Lorenz number of each compound.

The reduced Lorenz number L/L_0 is given in the inset of Fig. 2. The Lorenz number, L is defined by $\kappa\rho/T$, and L_0 is the Sommerfeld value of 24.5 nW$\,\Omega$K^{-2}. The L/L_0 of CeRhAs increases rapidly on cooling and reaches a value as high as 5×10^3 at 4.2 K, reflecting the semiconducting behavior of ρ. On the contrary, L/L_0's of other compounds are situated between 2 and 20 in the measured temperature range, which is ascribable to the metallic behavior of ρ. It should be noted that the values of L/L_0's for CeNiSn, CeRhSb, and CeRhAs are larger than those of typical heavy-fermion compounds such as $CeCu_6$ and $CeRu_2Si_2$.[25,26] In $CeRu_2Si_2$, the inelastic scattering of charge carriers by $4f$ spin fluctuations leads to the reduction of L/L_0 below 1.[26] The large L/L_0 indicates that the dominant heat carriers are phonons, and spin scattering of charge carriers would not play a significant role in L/L_0. Therefore, in these VF systems one can extract a precise phonon contribution, and it guarantees a reliable discussion on the effects of the VF and the pseudogap formation on κ_{ph}. This criterion may be applied also for CePtSn at least up to 100 K, above which L/L_0 has a rather small value.

The temperature dependence of κ_{ph} for all compounds are shown in Fig. 3. The data of κ_{ph} were obtained by subtracting the electronic contribution κ_{el} from the measured data. Thereby, the validity of the Wiedemann-Franz law $\kappa_{el}=L_0T/\rho$ is assumed, and κ_{el} is calculated by using the data of $\rho(T)$ shown in Fig. 1. For CePtSn, the shoulderlike structure in $\kappa(T\simeq 40\ K)$ (see Fig. 2) is converted to a broad maximum in $\kappa_{ph}(T\simeq 30\ K)$ in Fig. 3. This maximum may represent the crossover from dominating phonon-phonon (ph-ph) scattering above about 30 K to electron-phonon (el-ph) interaction below 30 K. The broad maximum in $\kappa_{ph}(T)$

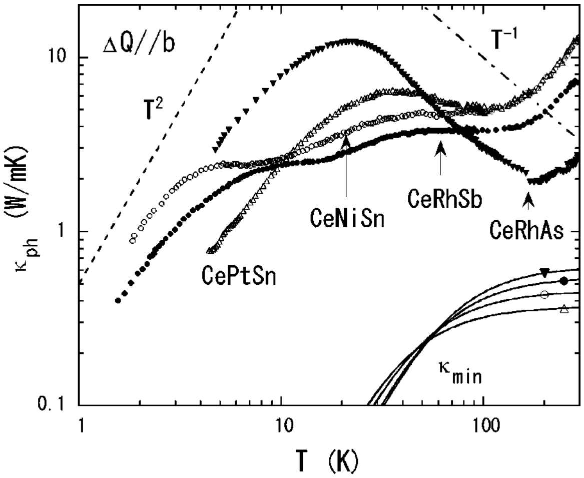

FIG. 3. The temperature dependence of κ_{ph} for CePtSn, CeNiSn, CeRhSb, and CeRhAs. The solid curves are κ_{min}'s of respective compounds. The dashed and dash-dotted lines represent the T^2 and the T^{-1} dependences, respectively.

of CeNiSn and CeRhSb with higher values of T_K is depressed compared to that for CePtSn. At temperatures above 165 K, κ_{ph} is systematically reduced on going from CeNiSn, CeRhSb, to CeRhAs in line with the enhancement of T_K. It should be noted that the lattice modulation may contribute to the reduction of κ_{ph} of CeRhAs as well.

We discuss now the origin of the reduction of κ_{ph} with increasing T_K. At high temperatures, κ_{ph} is dominated by ph-ph scattering, and thus depends essentially on the Debye temperature Θ_D. In isostructural compounds with the same ph-ph scattering rate, κ_{ph} becomes larger with increasing Θ_D.[27] Since Θ_D's of none of the present compounds are reported, we use the Θ_D's of the La counterparts; LaNiSn ($=228$ K) and LaRhSb ($=275$ K).[11] If Θ_D's of CeNiSn and CeRhSb are assumed to be those of the La counterparts, κ_{ph} of CeRhSb is expected to be larger than that of CeNiSn at high temperatures, which, however, contradicts the experimental result. The second important process of phonon scattering at high temperatures is that by isotope atoms; the mechanism of which is similar to that of point defect scattering.[28,29] The scattering rate associated with the isotope effect can be expressed by $\tau_{iso}^{-1}=D_{iso}\omega^4=(V/4\pi v_{ph}^3)\Gamma_{AV}\omega^4$, where V is the unit cell volume, v_{ph} the average phonon velocity, Γ_{AV} the averaged scattering parameter given in Eq. (1), and ω the phonon frequency.[28,29] The v_{ph} is obtained from $v_{ph}=k_B\Theta_D/\hbar\sqrt[3]{6\pi^2 n}$, where k_B is the Boltzmann constant, $\hbar$ the Planck constant divided by 2π, and n the number of atoms per unit volume. The n is obtained by using lattice constants listed in Table I. The Γ_{AV} for CeNiSn is determined as follows:

$$\Gamma_{AV}(\mathrm{CeNiSn})=\frac{1}{3}\left(\frac{m_{\mathrm{Ce}}}{m_{AV}}\right)^2\Gamma(\mathrm{Ce})+\frac{1}{3}\left(\frac{m_{\mathrm{Ni}}}{m_{AV}}\right)^2\Gamma(\mathrm{Ni})+\frac{1}{3}\left(\frac{m_{\mathrm{Sn}}}{m_{AV}}\right)^2\Gamma(\mathrm{Sn}), \qquad (1)$$

TABLE I. Physical properties of CePtSn, CeNiSn, CeRhSb and CeRhAs.

	a (Å)	b (Å)	c (Å)	T_K (K)	T^* (K)	$n\times10^{28}$ (m^3)	θ_D (K)	v_{ph} (m/s)
CePtSn	7.463[a]	4.628[a]	8.016[a]	10		4.33	188	1798
CeNiSn	7.540[b]	4.602[b]	7.614[b]	51[c]	15	4.54	228	2147
CeRhSb	7.415[d]	4.619[d]	7.857[d]	89[c]	20	4.46	275	2606
CeRhAs	7.535[d]	4.308[d]	7.365[d]	1350	370	5.02	306	2787

[a] See Ref. 8.
[b] See Ref. 10.
[c] See Ref. 11.
[d] See Ref. 41.

$$m_{AV}=\frac{m_{\mathrm{Ce}}+m_{\mathrm{Ni}}+m_{\mathrm{Sn}}}{3}, \qquad (2)$$

$$\Gamma(X)=\sum_i c_i\frac{(m_{Xi}-m_X)^2}{m_X^2}, \qquad (3)$$

and

$$m_X=\sum_i c_i m_{Xi}, \qquad (4)$$

where m_X means the mass of an atom denoted by X, m_{Xi} that of an isotope X atom of type i, and c_i is the concentration of the atom denoted by Xi. The Γ_{AV} of CeRhSb is calculated by the same method. Using the isotope atoms tabulated by Strominger *et al.*,[30] and Θ_D's and n's listed in Table I, one obtains $D_{iso}=42.5\times10^{-44}$ (s^3) for CeNiSn and 3.87×10^{-44} (s^3) for CeRhSb. Therefore, the reduction of κ_{ph} due to the isotope effect in CeNiSn is an order of magnitude larger than that in CeRhSb. This would lead finally to a larger value of κ_{ph} for CeRhSb in comparison to CeNiSn. Hence, neither ph-ph scattering nor the isotope effect can explain the experimental relation $\kappa_{ph}(\mathrm{CeNiSn})>\kappa_{ph}(\mathrm{CeRhSb})$ as shown in Fig. 3 for high temperatures. Thus, the most probable mechanism in reducing κ_{ph} of CeRhSb below that of CeNiSn should be the stronger ph-VF scattering in CeRhSb. The above brief discussion combined with the overall systematic trend with T_K leads to the idea that the strength of the ph-VF scattering depends on T_K. Based on this idea, we will propose a phenomenological model as described below.

In order to examine the possibility of the PGEC state, we have calculated the minimum κ_{ph}, κ_{min} for each compound. κ_{min} is a lower limit of κ_{ph}, which was proposed to describe the phonon glassy states in amorphous systems especially at high temperatures.[27,31] This was applied to judge the degree of the phonon glassy states in rattling systems ($\mathrm{Eu_8Ga_{16}Ge_{30}}$ and $\mathrm{CeFe_4Sb_{12}}$)[2,3] and disordered systems ($\mathrm{NaCo_2O_4}$).[4] In these systems, κ_{ph} approaches κ_{min} at high temperatures. Provided no distinction is made between the longitudinal and transverse acoustic phonon modes, the phenomenological expression for κ_{min} is given by[31,32]

$$\kappa_{min}=\left(\frac{3n}{4\pi}\right)^{1/3}\frac{k_B^2T^2}{\hbar\Theta_D}\int_0^{\Theta_D/T}\frac{x^3e^x}{(e^x-1)^2}dx, \tag{5}$$

where x is a dimensionless parameter, $x=\hbar\omega/k_BT$. The Θ_D values of CePtSn and CeRhAs are tentatively calculated by the relation[33] $\Theta_D\propto 1/\sqrt{M}\sqrt[3]{V}$, where M is the molecular weight, from those of CeNiSn and CeRhSb, respectively, and are tabulated in Table I. The respective κ_{min}'s calculated by Eq. (5) are plotted in Fig. 3. The κ_{min}'s of CePtSn, CeNiSn, and CeRhSb are an order of magnitude smaller than κ_{ph}'s of these compounds at high temperatures. Thus, the PGEC state is not realized in the present Ce compounds.

It is interesting to compare the experimental results of $\kappa_{ph}(T)$ with the representative T-power dependence, i.e., T^2 and T^{-1} as depicted in Fig. 3 at low and high temperatures, respectively. At low temperatures, $\kappa_{ph}(T)$ of CeNiSn and CeRhSb follows nearly a T^2 dependence. An exact T^2 dependence was observed in CeNiSn only below 2 K, where the el-ph scattering becomes dominant in the presence of $D_{res}(E_F)$.[23] At high temperatures, κ_{ph} of CeRhAs follows approximately the T^{-1} dependence between 40 K and 140 K. The T^{-1} dependence means that the ph-ph scattering is dominant. The development of the pseudogap in the electronic density of states would reduce the el-ph scattering so that the phonon mfp associated with the el-ph scattering ($\mathrm{pmfp}_{el\text{-}ph}$) becomes longer than that determined by the ph-ph one ($\mathrm{pmfp}_{ph\text{-}ph}$) in this temperature range.

We propose a phenomenological model to explain the unusual behavior of $\kappa_{ph}(T)$ by taking account of ph-VF scattering. At the first step, the effect of the pseudogap formation is neglected. Let us use conventional formula for κ_{ph} given by the Debye model:[34]

$$\kappa_{ph}=\frac{k_B}{2\pi^2v_{ph}}\left(\frac{k_B}{\hbar}\right)^3T^3\int_0^{\Theta_D/T}\frac{x^4e^x}{(e^x-1)^2}\tau(x,T)dx, \tag{6}$$

where $\tau(x,T)$ is the phonon relaxation time. All employed parameters in the calculation of κ_{ph} are listed in Table I. We consider four processes of phonon scattering as follows:

$$\tau^{-1}=AT^3x^2\exp\left(-\frac{\Theta_D}{2T}\right)+B+CTx+Dx^4T^4. \tag{7}$$

The first term represents the umklapp ph-ph scattering, the second one boundary scattering, the third one the el-ph scattering, and the fourth one the point defect scattering involving the isotope effect as discussed above. In CePtSn, magnons may also carry heat and crystalline-electric-field effects also affect κ_{ph}, but they are tentatively ignored. In VF compounds, it is well known that the el-ph interaction is very strong.[35] The term proportional to Tx in Eq. (7) was invoked to explain why the κ value of a heavy-fermion compound is lower than that of the La counterpart.[36] A strong hybridization between f electrons of Ce ions and conduction electrons occurs in VF compounds. This indicates that the el-ph interaction of the VF state retains the nature of the conduction electrons and allows one to assume that the ph-VF scattering is equivalent to the el-ph scattering as the first approximation. It should be noted that the el-ph scattering rate in VF compounds described in Ref. 5 is identical to the general expression for the el-ph scattering, $(m^*)^2U_{def}^2\omega/2\pi D_m v_{ph}\hbar^3$, where m^* is the effective electron mass, U_{def} the deformation potential, and D_m the material density.[37] The term Tx is generally dominant at low temperatures and causes a T^2 dependence of κ_{ph}. Therefore the enhancement of this term would depress the broad maximum observed in κ_{ph} around 40 K, and moreover, it should be also responsible for the reduction of κ_{ph} above 100 K (see Fig. 3). These considerations suggest that the ph-VF scattering rate is proportional to Tx, and the coefficient C increases with increasing T_K. The fitted results, keeping this assumption in mind, are given in Fig. 4(a); and the obtained parameters are listed in Table II. For CePtSn, CeNiSn, and CeRhSb, the broad maxima are well reproduced. Since the pronounced enhancement of κ_{ph} of CeRhAs below $T_3=165$ K obscures the fitting, we have adjusted the κ_{ph} value at T_3. It should be noted again that the lattice modulation in CeRhAs affects $\kappa_{ph}(T)$.

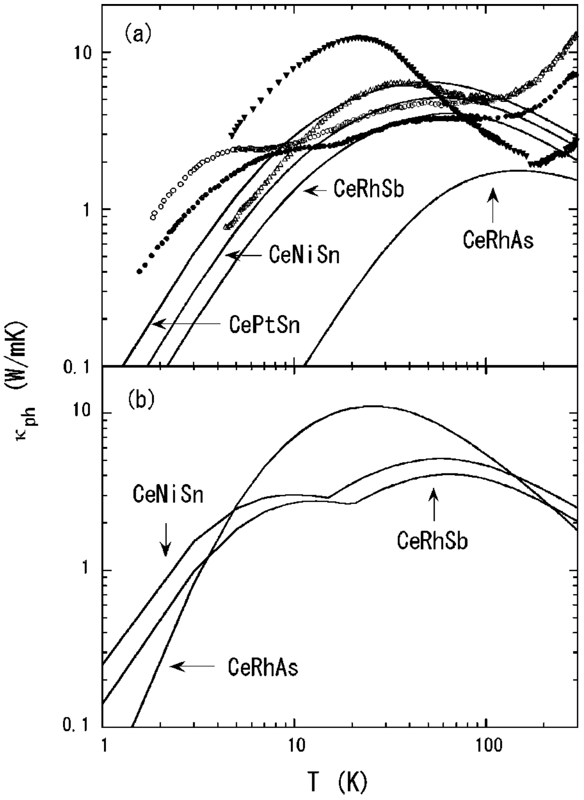

FIG. 4. (a) The temperature dependence of κ_{ph} for CePtSn, CeNiSn, CeRhSb, and CeRhAs. The solid curves represent the fitted results with Eq. (6) for each compound without taking into account the pseudogap formation. (b) The temperature dependence of κ_{ph} calculated by Eq. (6) for CeNiSn, CeRhSb, and CeRhAs by taking into account the pseudogap formation.

In Table II, the ratios T_K/C are the same order of magnitude for the four compounds, implying that C is roughly proportional to T_K. Thus, the reduction of κ_{ph} by the ph-VF

TABLE II. Coefficients in Eq. (7) giving the fitted results shown in Figs. 4(a) and 4(b), and T_K/C.

	$A(\times 10^5$ $\mathrm{K}^{-3}\,\mathrm{s}^{-1})$	$B(\mathrm{s}^{-1})$	$C(\times 10^8$ $\mathrm{K}^{-1}\,\mathrm{s}^{-1})$	$D(\times 10^3$ $\mathrm{K}^{-4}\,\mathrm{s}^{-1})$	T_K/C $(\times 10^{-7}$ $\mathrm{K}^2\,\mathrm{s})$
CePtSn	1.1	0	1.0	4.0	1.0
CeNiSn	1.3	0	1.5	3.5	3.4
CeRhSb	1.6	0	2.0	3.2	4.5
CeRhAs	1.6	4×10^8	50	1.0	2.7

scattering is confirmed. This result would be consistent with an experimental observation of the pronounced softening in acoustic phonon branches of a typical VF compound CeNi compared to those of the La counterpart.[38] The softening of acoustic phonon branches in CeNi means a small gradient in the dispersion curve. Therefore the group velocity of acoustic phonons becomes slower, and thus κ_{ph} would be reduced. The extremely huge C value of CeRhAs may be consistent not only with the high T_K but also with a strong el-ph coupling, leading to the observed lattice modulation. Equation (6) could not reproduce the upturn of κ_{ph}'s of all compounds above 100 K. This may be due to the uncertainty stemming from the rather small difference between κ_{ph} and κ_{el} above 100 K and/or the negligence of the detailed phonon frequency spectrum. We note here that similar upturns in κ_{ph} were observed in several Ce-based VF compounds.[25,39]

Let us consider the effect of the pseudogap formation on κ_{ph}. We assume that the coefficient C depends on T as $C(T)=C_0+C_1(T/T^*)^2$ below T^* due to the lacking of the precise information of the temperature dependence of the pseudogap. This temperature dependence of C is an analogy of the model proposed to explain the enhancement of $\kappa(T)$ below a charge-density-wave transition temperature.[40] The term C_0 reflects the presence of $D_{res}(E_F)$, which is assumed to be zero for CeRhAs. In order to reproduce $\kappa_{ph}(T)$ below about 4 K, C_0's are taken to be 13% and 15% of $C(T^*)$ for CeNiSn and CeRhSb, respectively. The thus calculated curves render fairly well the qualitative behavior of $\kappa_{ph}(T)$, as illustrated in Fig. 4(b). This model therefore confirms that the prolonged phonon lifetime due to the reduction of the el-ph scattering rate actually enhances κ_{ph}. In the case of CeRhAs with T^* of 370 K, the T^{-1} dependence of $\kappa_{ph}(T)$ below T^* is observed since $\mathrm{pmfp}_{(ph\text{-}ph)}<\mathrm{pmfp}_{(el\text{-}ph)}$ below T^*. On the other hand, in CeNiSn and CeRhSb with T^* of 15–20 K, the relation of $\mathrm{pmfp}_{(ph\text{-}ph)}>\mathrm{pmfp}_{(el\text{-}ph)}$ below T^* leads to the T^2 dependence in $\kappa_{ph}(T)$ at low temperatures. Therefore it may be asserted that the large difference between the enhancement of κ_{ph} below T^* in CeRhAs and that in CeNiSn or CeRhSb is caused by a competition between the $\mathrm{pmfp}_{(ph\text{-}ph)}$ and the $\mathrm{pmfp}_{(el\text{-}ph)}$. As noted above, the effect of both the VF and the pseudogap formation on κ_{ph} is taken into account by a modification of the el-ph coupling constant. In order to confirm the proposed model, more systematic studies of $\kappa(T)$ on isostructural VF compounds without pseudogaps are necessary.

IV. SUMMARY

We have performed measurements of the thermal conductivity for isostructural compounds CePtSn, CeNiSn, CeRhSb, and CeRhAs with ϵ-TiNiSi-type structure in order to study the effects of both the VF and the pseudogap formation on κ_{ph}. In this series of compounds with no atomic disorder, the phonon-scattering processes, except the ph-VF one, are expected to be almost the same. Furthermore, κ_{ph} is much larger than κ_{el}, especially below 100 K. It is noteworthy that these facts assure us of the systematic and precise discussion about the effects of the VF and the pseudogap formation on κ_{ph}. In fact, it is evidenced that κ_{ph} is progressively reduced with increasing T_K due to the enhancement of the ph-VF scattering rate. This assertion may be concluded for CeRhAs above T_3, but the effect of the lattice modulation cannot be neglected. A PGEC state is not realized in all these compounds. The enhancement of κ_{ph} due to the pseudogap formation is also manifested in this study. In CeRhAs with $T^*=370$ K, the pronounced enhancement of κ_{ph} is observed. On the other hand, the smaller enhancement of κ_{ph} occurs in CeNiSn or CeRhSb with T^* of 15–20 K. Such a different behavior may originate from the competition between the $\mathrm{pmfp}_{(el\text{-}ph)}$ and the $\mathrm{pmfp}_{(ph\text{-}ph)}$, i.e., $\mathrm{pmfp}_{(ph\text{-}ph)}<\mathrm{pmfp}_{(el\text{-}ph)}$ in CeRhAs, and $\mathrm{pmfp}_{(ph\text{-}ph)}>\mathrm{pmfp}_{(el\text{-}ph)}$ in CeNiSn or CeRhSb below T^*, respectively. The research on the significant reduction of κ_{ph} by the ph-VF scattering has only just begun, and this study is expected to serve as one of the clues in searching for novel thermoelectric materials with low thermal conductivity.

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