Anomalous transport and thermal properties of NiTi and with Cu and Fe-doped shape memory alloys near the martensitic transition

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The temperature dependent electrical and thermal properties including electrical resistivity ($\rho$), specific heat ($C_p$), Seebeck coefficient ($S$) and thermal conductivity ($\kappa$) have been studied for the polycrystalline NiTi, Ti$_{50}$Ni$_{40}$Cu$_{10}$ and Ti$_{50}$Ni$_{48.5}$Fe$_{1.5}$ shape memory alloys from 10–400 K. It was found that the electrical resistivity and Seebeck coefficient exhibit a typical metallic behavior throughout the temperature range investigated. A significant thermal hysteresis between warming and cooling was observed in all the three alloys which is a manifestation of the first-order nature of martensitic transitions. Our results indicate the presence of two stage martensite transformations, i.e. $B_2$ $\rightarrow$ $B_19'$ for Ti$_{50}$Ni$_{40}$Cu$_{10}$ while $B_2$ $\rightarrow$ $B_19'$ for NiTi and Ti$_{50}$Ni$_{48.5}$Fe$_{1.5}$ alloys. An analysis on the measured thermal conductivity reveals that the anomalous feature in $\kappa$ at the $B_19$ $\rightarrow$ $B_19'$ transformation for Ti$_{50}$Ni$_{40}$Cu$_{10}$ is essentially attributed to the electronic contribution, while an enormously large peak in warming run observed at the $B_19$ $\rightarrow$ $B_2$ transformation is due to the change in lattice thermal conductivity. © 2011 American Institute of Physics.

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I. INTRODUCTION

In recent years, numerous investigations on the martensitic phase transition in NiTi shape memory alloys have been carried out in order to understand and eventually improve the shape memory effect and superelasticity properties of these alloys. These alloys are of significant theoretical interest due to the fascinating underlying mechanisms driving the martensitic transition and associated changes in their electronic structure and phonon spectrum. The NiTi alloy undergoes a first-order structural transition from a high temperature cubic (CsCl-type structure) austenitic phase to a low temperature monoclinic martensitic phase. Appropriate thermo-mechanical treatment and/or doping, a third element can change the transformation sequence into two stage transformations, from $B_2$ to intermediate $R$ phase and then to $B_19'$ upon cooling. It has been reported that a small amount of structural disorder may also affect the $R$ phase stability and which can be understood in terms of Fermi-surface nesting. The lattice anomalies in the phonon dispersion relation and the interplay between the phonon softening and electronic structure are of particular interest in the Ni-Ti system. The electronic band structure studies have confirmed that these electronic instabilities are in the form of singularities in the density of states (DOS), i.e. a sharp variation or a peak around the Fermi level ($E_F$) as well as the Fermi surface nesting. In general, such electronic instabilities tend to cause significant variations in the physical properties and also lead to crystallographic transition or distortion as a result of lattice instability. The theoretically predicted electronic instabilities and the subsequent effects on the electrical and thermal properties have been extensively investigated in NiTi, especially around the martensitic transition. However, electronic effects associated with changes in chemical composition or doping of the element must play an important role on the martensitic transition and a complete understanding must account for the interplay between electronic and disorder effects on the soft phonon instability.

There have been many reports regarding the effects of ternary alloying elements on martensitic transition and shape memory characteristics in NiTi alloys related to the metallurgical aspects but very few on thermal properties such as Seebeck effect, thermal conductivity etc. In addition to the electrical resistivity, the Seebeck coefficient can be more effectively used to probe the changes in DOS across the martensitic transition. Lee et al. have reported a sharp variation in the Seebeck coefficient near the phase transition in NiTi and suggested that the presence of a peak near the Fermi level may be the cause of the observed lattice instability in NiTi. Although a large number of investigations focused on the electronic and structural properties of the NiTi alloys, to the best of our knowledge, no comprehensive investigation on thermoelectric and/or thermodynamic properties have been reported so far in the case of Cu and Fe doped NiTi systems. The element Cu is unique in the sense that it can be substituted for Ni up to about 25 at.% and still exhibits shape memory effect. By substituting 10 at.% Cu for Ni, the alloy exhibits two stage martensitic transformation; cubic ($B_2$) $\rightarrow$ orthorhombic (B19) $\rightarrow$ monoclinic (B19') while a very small substitution of ~1.5 at.% Fe shows cubic ($B_2$) $\rightarrow$ rhombohedral (R) $\rightarrow$ monoclinic (B19') distortion. In the present work, high-precision measurements of electrical resistivity, Seebeck coefficient, specific heat and thermal conductivity from 10 to 400 K on the equiatomic NiTi as well as Fe (1.5 at.% and Cu (10 at.%) doped for Ni in NiTi

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alloys were carried out. For all measured electrical and thermal properties, pronounced anomalous responses were observed near the martensitic transitions in these alloys. In particular, abrupt peaks were observed in thermal conductivity, presumably associated with the combination of a strong electron-phonon interaction and a substantial rearrangement of DOS near the Fermi level. Investigation of these physical properties will help us to develop a deeper understanding of the underlying physics of the two-stage transformation in the NiTi-based shape memory alloys.

II. EXPERIMENTAL DETAILS

The polycrystalline ingots of binary equiatomic Ti50Ni50 and ternary Ti50Ni48.5Fe1.5 (in at.%) shape memory alloys were prepared by vacuum arc remelter (VAR) in which high purity titanium, nickel, copper and iron were remelted at least six times in high purity Ar atmosphere. The weight loss of as-melted ingots is less than 1 $\times$ 10$^{-4}$. The as-melted ingots were homogenized and then hot-rolled at 900°C to a plate of about 2 mm thicknesses by using a rolling machine (STANAT TA-515-5-SX8) at a constant rolling speed of 10 m/min. Thereafter the plate was solution-treated at 900°C for 1 h and then water-quenched. The oxidation layer of the plate was chemical etched by a solution composed of HF : HNO3 : H2O = 1 : 5 : 20 (in volume) and then polished by #150 sandpaper. After removing the oxidation layer, the plate was cut by a Buehler IsoMet precision cutter into the testing specimens with the longitude along the hot-rolling direction. Electrical resistivity measurements were performed using a standard four-point contact method. Seebeck coefficient and thermal conductivity measurements were simultaneously carried out, by a direct heat pulse technique, in helium closed cycle refrigerator over the temperature range of 10–400 K. Further details about the experimental techniques can be found elsewhere. Transport measurements were made along and perpendicular to the rolling direction and both show similar results. Here only data with the applied electrical and heat currents along the rolling direction of samples are presented.

III. RESULTS AND DISCUSSION

A. Electrical resistivity

The temperature-dependent electrical resistivity $\rho(T)$ for Ni-Ti alloy upon cooling and warming (10–400 K) is shown in Fig. 1. Upon cooling from 400 K, $\rho(T)$ show a sharp rise followed by a sudden fall in the form of two well-defined peaks clearly seen in inset of Fig. 1. As the temperature decreases further, the electrical resistivity of NiTi decreases, representing a typical metallic behavior as also observed in Ni-Mn-Ga alloys. The previous reports on $\rho(T)$ behavior for near-equiatomic samples showed only a single peak in the cooling curve as a result of the transformation from the high-temperature parent phase (B2 phase, cubic) to a low temperature martensite phase (B19′-phase, monoclinic). It is also possible that, for certain compositions and heat treatments, the intermediate phase (R phase, rhombohedral) appears before B19′. In the present study, the noticeable two peaks observed at 298 K and 292 K in $\rho(T)$ correspond to B2 $\rightarrow$ R and R $\rightarrow$ B19′ transformations, respectively. The start/finish temperatures for this intermediate R phase as well as martensite and austenite phases have been represented by $R_s / R_f$, $M_s / M_f$ and $A_s / A_f$ respectively as shown in Fig. 1. On the other hand, the warming curve of $\rho(T)$ shows only one peak which occurs at a higher temperature of around 326 K. Such a finding suggests that the reverse transformation (warming sequence) in NiTi occurs only in one stage, i.e. directly from B19′ $\rightarrow$ B2. Further, the values of $\rho$ at room-temperature and the residual resistivity are considerably low, indicating that our NiTi sample is possibly more ordered than that previously reported. This is in good agreement with the presence of noticeable phonon drag effect in Seebeck coefficient data, which will be discussed in the following section.

In Fig. 2, the $\rho(T)$ curves for cooling and warming (10–400 K) sequences of Ti50Ni48.5Cu10 (Fig. 2(a)) and Ti50Ni48.5Fe1.5 (Fig. 2(b)) alloys are shown. In the case of Ti50Ni48.5Cu10, two stage martensitic transformations (B2 $\rightarrow$ B19 $\rightarrow$ B19′) on cooling is clearly seen (see Fig. 2(a)), which was not previously reported. The start and finish temperatures for the forward transformations are shown by primed such as M′$_s$ and M′$_f$ and those for reverse transformations are A′$_s$ and A′$_f$ for B2 $\leftrightarrow$ B19′ transformations. The transformations for B19 $\leftrightarrow$ B19′ are shown by non-primed ones. Figure 2(a) shows that B2 $\rightarrow$ B19, the first stage transformation takes place completely over a narrow temperature range while for the B19 $\rightarrow$ B19′, the second stage transformation takes place over a much wider temperature range from ~298 K to 100 K. Although the martensite transformations are diffusionless transformations, there is a rearrangement of the lattice during the transformation which does produce a change in the
quantum states of the electron near the Fermi surface. The internal strain effects including lattice defects and continuous monoclinic distortion are considered as the origin of the anomalous behaviors in $\rho(T)$ during these transformations. Previous TEM studies on internal defects in B19 and B19' martensites shown that B19 is twinless whereas B19' has an internally twinned structure. This suggests that when the B2 $\rightarrow$ B19 transformations are taking place, there is neither stacking faults nor formation of twins which results in a relatively weak resistivity change. The large resistivity change observed for the B19 $\rightarrow$ B19' second stage transformation, however, can be attributed to lattice invariant shear induced twin defects and continuous monoclinic distortion behavior.

Figure 2(b) shows the temperature-dependent electrical resistivity for Ti$_{50}$Ni$_{48.5}$Fe$_{1.5}$ alloy during cooling and warming (10–350 K). While cooling, Ti$_{50}$Ni$_{48.5}$Fe$_{1.5}$ alloy undergoes two stage transformations as B2 $\rightarrow$ R $\rightarrow$ B19' as that of TiNi alloy. It is noted that, with the addition of a small amount of Fe, the martensitic transformation temperature ($T_M$) decreases considerably. Upon cooling, the first transformation (B2 $\rightarrow$ R) is characterized by a sharp increase in $\rho(T)$ with maximum $\rho$ value of 131 $\mu\Omega$-cm at 267 K and a small thermal hysteresis of $\sim$10 K is noticed. The second transformation, characterized by a large hysteresis, represents the subsequent transformation from R phase to B19' phase. Previous reports suggested that the R $\rightarrow$ B19' transformation shows stacking faults as well as formation of twins that results in an increase in resistivity up to 135 $\mu\Omega$-cm at 232 K during the transformation below $M_s$ and then decreases with decrease in temperature. From the above discussion, it is clear that the crystal structures, accommodation twin variants, twin defects, and crystal distortion play important role in the temperature variation of electric resistivity during the phase transformation for parent NiTi as well as Fe and Cu doped alloys. The addition of Cu and Fe decreases the martensitic transformation temperature through intermediate phases.

There is a thermodynamic requirement that intermediate martensite phase must have smaller transformation strain energy than the final product. However, whether or not the intermediate phase is present or which intermediate phase (R or B19) would appear actually depends on the competition in the intrinsic and extrinsic energies during the transformation. Here, the intrinsic energy is governed by lattice dynamics (phonon softening), while the extrinsic energies arise from resistance to lattice distortion (i.e. transformation) by precipitation or dislocations.

B. Seebeck coefficient

The temperature dependence of Seebeck coefficient $S(T)$ for NiTi is shown in Fig. 3. The positive value of measured Seebeck coefficient indicates that the majority charge carriers are holes. The $S(T)$ characteristics shows a sharp rise in both cooling and warming runs at 305 K and 340 K, respectively, with a hysteresis of about 35 K. Overall, the austenite and martensite start and finish temperatures can be much more clearly defined in the Seebeck coefficient data. It is noted that, on cooling, the Seebeck coefficient shows a sharp dip at about 306 K which indicates the appearance of the intermediate R phase, consistent with that observed by resistivity measurements.

Below the transitions, $S(T)$ follows the typical metallic diffusive behavior and around 50 K a visible hump (indicated by arrow) is noticed. Such a feature is presumably due to the phonon drag effect. The phonon drag effect was nearly suppressed in the earlier report on NiTi and its absence has been attributed to the effect of disorder. Furthermore, the anomaly around the phase transition is much sharper and well pronounced, thus, we argue that the present NiTi alloy is more ordered than the reported thermally and mechanically treated NiTi alloys. Nevertheless, the relatively weak phonon drag peak in the present study indicates the presence of still some amount of disorder.
It is well known that Seebeck coefficient is very sensitive to the slight changes in the position of Fermi energy ($E_F$) across the DOS. The sharp variations in $S$ near martensitic transition indicate a significant modification of the Fermi surface DOS during the phase transition. Another interesting comparison is the $S(T)$ behavior between NiTi and the ferromagnetic shape memory alloy Ni$_2$MnGa, where $S(T)$ for Ni$_2$MnGa shows pronounced peak within a narrow temperature interval of about 5 K with less thermal hysteresis near the martensitic transition.$^{28}$ In all those above mentioned shape memory alloys, the presence of a peak near $E_F$ and Fermi surface nesting have been clearly established through many experimental and theoretical investigations. Nevertheless, the exact driving force for the observed anomalies, whether the presence of peak in DOS or Fermi surface nesting is an intriguing issue and warrants further investigations.

Figure 4 displays the warming and cooling curves for the temperature-dependent Seebeck coefficient for Ti$_50$Ni$_{40}$Cu$_{10}$ (Fig. 4(a)) and Ti$_50$Ni$_{48.5}$Fe$_{1.5}$ (Fig. 4(b)) compositions. The Seebeck coefficient is positive for the entire temperature range under investigation, revealing that the majority charge carriers are also holes irrespective of the doping of Cu or Fe in the parent NiTi. Below the transitions, similar to that of NiTi, $S(T)$ follows the typical metallic diffusive behavior and a visible phonon drag hump below 50 K (indicated by arrows) is noticed for both doped samples. In case of Ti$_50$Ni$_{40}$Cu$_{10}$ composition, the Seebeck coefficient increases with increasing temperature and develops a broad maximum at around 240 K and a local minimum near 280 K (see Fig. 4(a)). Such a variation is associated with the change in the resistivity data for the B19$'$ → B19 transformation. A change in slope and a hump in this temperature range are also observed for thermal conductivity and specific heat measurements, which will be discussed in later sections. As the temperature is increased further, a sharp fall was observed in the vicinity of the B19 → B2 transformation with a thermal hysteresis of 10 K. The inset of Fig. 4(b) clearly shows upturns in the $S(T)$ curve at ~284 K for B2 → R transformation and at ~242 K for R → B19$'$ transformation and these two stage transitions are strongly hysteretic. As discussed above, the anomalous features in Seebeck coefficient are mainly arising from the significant modifications of the Fermi surface as these alloys undergo martensite transitions. Lee et al.$^3$ have speculated that a peak in the DOS located slightly below the Fermi level, as predicted by band structure calculations for NiTi, could be a contributing factor. It is known that peaks in the DOS near Fermi level may cause lattice instabilities, thus raising the possibilities for the occurrence of structural transitions. The contributions from both electronic and lattice degree of freedoms are essential in explaining the physical properties of these NiTi-based shape memory alloys, as we will further discuss in the thermal conductivity section.

It is noted that measured $S(T)$ for all three studied alloys are rather linear at high temperatures (in the B2 phase). For ordinary metals, the Seebeck coefficient is expected to be linear in temperature and can be associated with Mott’s formula $S = \frac{2e}{kB} \frac{\partial \rho}{\partial T}$, assuming a one-band model with an energy-independent relaxation time. Here, $E_F$ is the Fermi energy and $k_B$ is the Boltzmann constant. By fitting the data in the high-$T$ austenitic phase, we obtained $S(T)/T = 2.15 \times 10^{-2}$ (μV/K$^2$), $1.92 \times 10^{-2}$ (μV/K$^2$), and $1.74 \times 10^{-2}$ (μV/K$^2$) for NiTi, Ti$_50$Ni$_{40}$Cu$_{10}$, and Ti$_50$Ni$_{48.5}$Fe$_{1.5}$, respectively. Thus, the $E_F$ values of 2.73 eV (Ni-Ti), 3.06 (Ni-Ti-Cu), and 3.37 eV (Ni-Ti-Fe) were estimated from this simple model, in good agreement with the metallic nature for these alloys. It is seen that the doping of Cu and Fe results in a change in $E_F$ and the electronic properties of the NiTi alloy, which in turn has a strong influence on the martensitic transition as we did observe experimentally.

C. Specific heat

Specific heat measurement is known as a sensitive probe of phase transitions involving entropy change. The plot of the measured specific heat ($C_P$) of NiTi is illustrated in Fig. 5. From the $C_P(T)$ characteristics of cooling and warming runs, the substantial variations across the phase transition with a large hysteresis between 250–340 K indicates the presence of a strong first-order transition in NiTi. Similar to $\rho$, the cooling run shows a much pronounced variation than that of the warming run. The excess specific heat $\Delta C_P$ across the transition was estimated to be as large as about 30% on cooling run and about 14% on heating run. However, we have not observed any noticeable anomaly for the existence of the intermediate phase in our $C_P(T)$ data as observed in $\rho(T)$ and $S(T)$. Since $C_P$ is mostly a measure of phonon excitations while $\rho(T)$ and $S(T)$ are probes of electronic characteristics of solids, we thus speculate that the transformation of intermediate phase in NiTi has larger extent of modifications in the electronic structure but a smaller changes in the phonon spectrum.

The specific heat jump $\Delta C_P$ and entropy change $\Delta S$ near the transition can be estimated by subtracting a smooth lattice background fitted far away from the transition, drawn as a solid curve in Fig. 5. The estimated $\Delta C_P/T$ for warming
and cooling curves is shown in inset of Fig. 5. The entropy change, evaluated by integrating the area under \( \Delta C_p/T \) versus \( T \) curve, \( \Delta S = 1.18 \, R \) and \( 1.84 \, R \) (\( R \) is the ideal gas constant) for warming and cooling runs, respectively, are obtained. Such a large amount of entropy change found in TiNi is presumably associated with the strong electron-phonon coupling and the existence of soft phonon modes during the martensitic transformation. In Fig. 6, we illustrate the temperature dependence of specific heat for Ti\(_{50}\)Ni\(_{40}\)Cu\(_{10}\) (Fig. 6(a)) and Ti\(_{50}\)Ni\(_{48.5}\)Fe\(_{1.5}\) (Fig. 6(b)) alloys. Figure 6(a) clearly shows two stage martensite transformations occurring in Ti\(_{50}\)Ni\(_{40}\)Cu\(_{10}\) alloys in the \( C_p \) data for both warming and cooling runs. It should be noted that specific heat peaks for the B2 \( \leftrightarrow \) B19 transformation is very sharp while the B19 \( \leftrightarrow \) B19’ transformation is weaker and spread over a wider temperature range (see Fig. 6(a)), being consistent with the previously reported DSC measurements. We argue that the mechanism of these \( C_p \) anomalies must be related to the energy barriers for a complete transformation in the nucleation stage. It has been proposed that the magnitude of the martensitic shear strain is proportional to the energy of nucleation. The atomic shuffle and martensitic shear strain required for the B19 \( \leftrightarrow \) B19’ transformation are expected to be much smaller than that for the B2 \( \leftrightarrow \) B19 transformation. This suggests that the energy barrier for the nucleation of B2 \( \leftrightarrow \) B19 transformation is higher than that of the B19 \( \leftrightarrow \) B19’ transformation, as we did observe in our specific heat measurements for Ti\(_{50}\)Ni\(_{40}\)Cu\(_{10}\). We do not estimate the entropy changes associated with B2 \( \leftrightarrow \) B19 and B19 \( \leftrightarrow \) B19’ transformations because the two transitions are very close to each other, making the background difficult to define without appropriate models for its shape. However, in view of the fact that the B2 \( \leftrightarrow \) B19 transformation shows a sharp peak over a very narrow temperature range while the B19 \( \leftrightarrow \) B19’ transformation exhibits a weak hump over a rather wide temperature interval, the entropy changes involved during these transitions are comparable.

The plot of the measured \( C_p(T) \) of Ti\(_{50}\)Ni\(_{48.5}\)Fe\(_{1.5}\) is illustrated in Fig. 6(b). Similar to that for the NiTi alloy, only one pronounced specific heat peak but at a lower temperature was found. It is also noted that \( \Delta C_p \) shows a wider spread in temperature around the martensite transition while cooling but is similar in magnitude for both warming and cooling runs. The entropy change of Ti\(_{50}\)Ni\(_{48.5}\)Fe\(_{1.5}\) associated with the transition was estimated by the same procedure as in the NiTi case. Thus, we attain the entropy change \( \Delta S = 0.59 \, R \) for warming (0.91 \( R \) for cooling), and this value is considerably smaller than that obtained for NiTi. Such a finding leads us to the conclusion that a small amount of Fe addition not only decreases the martensitic transformation temperature of NiTi alloy but also weakens the driving force of the transition.

**D. Thermal conductivity**

The thermal conductivity as a function of temperature \( \kappa(T) \) with warming and cooling cycles for NiTi is shown in Fig. 7. The magnitude of room temperature thermal conductivity is approximately 140 mW/cm K, comparable to the earlier reported fully dense NiTi sample.\(^{29}\) It was found that \( \kappa \) increases with rising temperature and exhibits a distinct jump with \( \Delta \kappa/\kappa \sim 34\% \) (warming run) near the martensitic transition. The significant thermal hysteresis between warming and cooling near \( T_M \) is a manifestation of the first-order nature of the transition. It is noticed that the warming run has a much pronounced anomaly than that of the cooling run, in contrast to the electrical resistivity and specific heat data. Below 50 K, \( \kappa_L \) increases rapidly with increasing temperature. This follows from the kinetic equation for lattice thermal conductivity which is given as \( \kappa_L = C_v \nu l \),\(^{30}\) where \( C_v \) is the phonon specific heat, \( \nu \) represents the phonon drift velocity and \( l \) is the mean free path. At low \( T \), the phonon specific heat \( C_v \) has the strongest temperature dependence (\( C_v \propto T^3 \)
than the other physical parameters, accounting for the temperature variation of the observed $\kappa$ below 50 K for NiTi.

Since the thermal conductivity measurements provide valuable information about the various scattering processes of thermal carriers, the present data would offer an opportunity to probe the interplay between the lattice and charge degrees of freedom in these shape memory alloys. In general, the total thermal conductivity for a metal can be expressed as a sum of lattice $\kappa_L$ and electronic $\kappa_e$ terms: $\kappa = \kappa_L + \kappa_e$. The electronic contribution can be estimated by means of Wiedemann-Franz Law: $\kappa_e/\rho = L_0$. Here $\rho$ is the dc electrical resistivity and $L_0 = 2.45 \times 10^{-8}$ W$\mu$K$^{-2}$ is the Lorentz number. We thus calculated the $\kappa_e$ using the Wiedemann-Franz Law and the measured heating curve of $\rho$ data. As illustrated in Fig. 7, the solid line represents calculated $\kappa_e$ for warming curve of NiTi, and the electronic thermal conductivity is found to be about two-thirds of the total thermal conductivity. It is also seen that, except near $T_M$, the electronic thermal conductivity follows the temperature variation of total thermal conductivity quite closely. From this estimation, it is clear that the anomalous jump in $\kappa$ in the vicinity of the martensite transition cannot be explained by the electronic contribution, but must be due to the change of the lattice thermal conductivity $\kappa_L$, as we will discuss in detail later.

Figure 8 shows the temperature dependence of thermal conductivity for Ti$_{50}$Ni$_{40}$Cu$_{10}$ (Fig. 8(a)) and Ti$_{50}$Ni$_{48.5}$Fe$_{1.5}$ (Fig. 8(b)) alloys. It is seen that the overall temperature variations (except near the transitions) and the values of room temperature thermal conductivity are rather similar to that of the NiTi, irrespective of the compositions. We have also calculated the electronic contributions to the total thermal conductivities for warming data as shown as solid lines in Fig. 8 for both Cu and Fe-doped samples. There are two prominent features as seen in Fig. 8(a) for the Ti$_{50}$Ni$_{40}$Cu$_{10}$ alloy. Firstly, a decrease in $\kappa$ across the B19 $\rightarrow$ B19' transformation is noted. From the separation of electronic contribution from the total thermal conductivity, we have a clear confirmation that the feature in $\kappa$ near 280 K for Ti$_{50}$Ni$_{40}$Cu$_{10}$ is essentially caused by the reduction of electronic contribution that corresponds to the increase in the electrical resistivity (see Fig. 2(a)). Secondly, an enormously large thermal conductivity peak (see inset of Fig. 8(a)) with $\Delta\kappa/\kappa \sim 200\%$ (warming run) across the B19 $\rightarrow$ B2 transformation within a narrow temperature range of 10 K was observed. In this case, the change in $\kappa_e$ alone cannot account for this abrupt feature in the total thermal conductivity near 328 K. Instead, the observed anomalous peak in $\kappa$ in the vicinity of the martensite transition must be due to the change of lattice thermal conductivity $\kappa_L$. Such an unusual phenomenon, to the best of our knowledge, is unique to the martensitic transition in the NiTi shape memory alloys and definitely warrants further investigation. For the Ti$_{50}$Ni$_{48.5}$Fe$_{1.5}$ alloy, both warming and cooling run of $\kappa(T)$ clearly show the two stage B2 $\leftrightarrow$ R $\leftrightarrow$ B19' transformations and the R $\leftrightarrow$ B19' transformation is strongly hysteretic (see Fig. 8(b)). Also, huge peaks in $\kappa$ near the B2 $\rightarrow$ R ($\Delta\kappa/\kappa \sim 80\%$) and B19' $\rightarrow$ R transformations ($\Delta\kappa/\kappa \sim 40\%$) were observed. Apparently, the phonons must play an important role for these anomalous peaks observed in Ti$_{50}$Ni$_{48.5}$Fe$_{1.5}$.

Now we are in the position to discuss the possible origins for the observed anomalous peaks in $\kappa$ in these alloys, which cannot be simply explained by changes in electron or phonon scattering process. It is worth mentioning that the specific heat and thermal conductivity also show anomalous peaks in the charge-density-wave (CDW) materials. The appearance of Kohn anomaly and the excess heat carried by soft phonons were suggested as possible origins for such an anomalous feature in these thermal properties. Again, by the generalized simple equation, $\kappa_L = C_\nu v_l$, it is expected that the magnitude of anomalous peak in thermal conductivity should be in proportion to that of specific heat jump if the phonon drift velocity and mean free path are not greatly...

**FIG. 7.** (Color online) Thermal conductivity as a function of temperature for NiTi on cooling and warming runs. The solid line represents calculated electronic thermal conductivity ($\kappa_e$) from heating electrical resistivity data. Inset shows the close-up plot for thermal conductivity for cooling and warming runs.

**FIG. 8.** (Color online) Thermal conductivity as a function of temperature for (a) Ti$_{50}$Ni$_{50}$Cu$_{10}$ and (b) Ti$_{50}$Ni$_{48.5}$Fe$_{1.5}$ alloys on cooling and warming runs. The solid lines represent calculated electronic thermal conductivities. Inset shows the blowup plot near the phase transition for Ti$_{50}$Ni$_{40}$Cu$_{10}$ alloy.
influenced at the transitions. Our results seem to support this scenario, since large thermal conductivity peak (34%) and specific heat peak (14%) were found in NiTi alloys.

Nevertheless, in our present study, it is noticed that the thermal conductivity peak is usually larger than the specific heat peak, particularly in the case of Ti50Ni48.5Fe1.5 during the B2 → B19 transformation. Such an observation suggests that in addition to a large number of soft phonon modes in the transition region which provide substantial excess specific heat, there must be presence of other excitations for the heat transport. Possible candidate for such quasiparticles is polarons arising from the strong structural distortion during the martensitic transformation. These structure induced polarons may also contribute to the thermal conduction resulting to the giant peaks near TM in thermal conductivity for these alloys. Further investigations are needed to verify this speculation.

IV. CONCLUSIONS

A systematic investigation of temperature-dependent transport and thermal properties including electrical resistivity (ρ), specific heat (Cp), Seebeck coefficient (S) and thermal conductivity (κ) was performed on polycrystalline NiTi, Ti50Ni40Cu10, and Ti50Ni48.5Fe1.5 shape memory alloys. Pronounced anomalous features and significant thermal hysteresis were observed in all the measured quantities near the martensitic transitions. From the ρ(T) data, it is clear that the crystal structures, accommodation twin variants, twin defects, crystal distortion play important role in the change in the resistivity at the transformation temperature for parent NiTi as well as Fe and Cu doped alloys. In addition, two stage transformations have been clearly identified for all NiTi as well as Fe and Cu doped alloys. The anomalous features in the measured physical properties suggest that the modifications in the Fermi surface and strong electron-phonon interaction play important roles at the martensitic transition in these NiTi-based shape memory alloys. Furthermore, an estimate from the Wiedemann-Franz law demonstrates that the observed peak in thermal conductivity near martensitic transition is mainly associated with the lattice phonons rather than the charge carriers in these alloys. Although the peak features near TM in thermal conductivity and specific heat are presumably due to the contribution from the soft phonons, other excitations such as structural polarons may come into play to the heat transport. In particular, the observed giant thermal conductivity peak near martensitic phase transition in the Cu-doped NiTi system is extremely unusual and certainly warrants further investigations.

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