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Weak charge-density-wave transition in $LaAgSb_2$ investigated by transport, thermal, and NMR studies

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Abstract

We report a study of the charge-density-wave (CDW) behavior in $LaAgSb_2$ by means of electrical resistivity, Seebeck coefficient, thermal conductivity, specific heat, and nuclear magnetic resonance (NMR) measurements. Except for the Seebeck coefficient, apparent indications of CDW ordering at around 207 K were noticed in the physical quantities investigated. On the other hand, all measured physical properties are insensitive to the second CDW formation ($\sim$184 K), as the transition character is considerably weaker than the high-temperature one. Further, analyses of the thermal conductivity and NMR Knight shift data revealed that the observed variations are essentially of electronic origin. The present findings are in good agreement with the previous results, indicating that the high-temperature CDW ordering is associated with a small gapping of the Fermi surface with a minor periodic displacement of the crystal lattice in $LaAgSb_2$.

1. Introduction

The intriguing charge-density-wave (CDW) transition phenomenon continues to attract attention. Such transitions usually take place in materials with low-dimensional characters in the crystal structures, due to the instability at low temperatures against a periodic lattice distortion [1, 2]. In this respect, the CDW phenomenon is rarely seen in three-dimensional (3D) materials, and only a few 3D systems such as the spinel compound CuV_2S_4 and the ternary silicide $Lu_5Ir_4Si_{10}$ have been reported to possess CDW characteristics [3, 4]. Direct microscopic evidence for the CDW formation in these materials has been further confirmed from the appearance of superlattice reflections by x-ray scattering measurements [3, 5].

Recently, an additional member, $LaAgSb_2$, has been added to the list of 3D CDW systems by Song and co-workers [6], owing to the lack of anisotropic structural units such as linear chains or planes in its crystal structure. This material crystallizes in a tetragonal $ZrCuSi_2$-type crystal structure (space group $P4/nmm$). Within this structure, the La atoms are coordinated

by eight Sb atoms, and the Sb atoms occupy two different sites with nonequivalent ligand coordination [7]. Previous bulk studies on $LaAgSb_2$ have indicated plausible anomalies in the measured physical properties at around 207 K [8], a change in the slope of the electrical resistivity and a cusp in the magnetic susceptibility. An x-ray scattering investigation has further confirmed that both features are the signatures of CDW modulation along the a-axis. In addition, a weak transition near 184 K has also been observed, attributed to another CDW ordering with distortion in the c-axis [7].

In order to obtain a further insight into the electronic states of $LaAgSb_2$ relevant to the CDW transitions, we have performed a detailed study by means of electrical resistivity (ρ), Seebeck coefficient (S), thermal conductivity (κ), specific heat (C_P), and nuclear magnetic resonance (NMR) measurements on the titled compound. A comparison made between our present and earlier results on $LaAgSb_2$ indicates a rather modest change in the Fermi-level density of states (DOS) responsible for the weak nature of CDW ordering.

2. Experiments

Polycrystalline $LaAgSb_2$ was prepared by arc-melting of the constituent elements under argon atmosphere. Due to the high volatility of Sb, we started with excess amount of Sb to compensate the loss of antimony due to evaporation. The resulting ingot was then sealed in a quartz ampoule and annealed at 800 °C for three days. Room-temperature x-ray diffraction analysis taken with Cu Kα radiation confirms a single phase, and the reflection peaks in the diffraction spectrum could be indexed according to the expected $ZrCuSi_2$-type structure.

Electrical resistivity measurement was carried out by the standard four-terminal method. Seebeck coefficient and thermal conductivity measurements were simultaneously performed in a closed-cycle refrigerator using a heat pulse technique. Relative specific heats were performed with a high-resolution ac calorimeter, using chopped light as a heat source. Further details about the experimental techniques for these measurements can be found elsewhere [4]. NMR measurements were carried out using a Varian 300 spectrometer, with a constant field of 7.06 T. A home-built probe was employed for both room-temperature and low-temperature experiments [9]. Since $LaAgSb_2$ is metallic in nature, a powdered sample was used to avoid the skin depth problem of the radio frequency (rf) transmission power. The specimen was put in a plastic vial that showed no observable ^{139}La NMR signal. ^{139}La NMR line shapes were obtained from spin-echo fast Fourier transforms using a standard $\pi/2$–τ–π sequence. The Knight shift (K) here was referred to the ^{139}La resonance frequency of aqueous $LaCl_3$.

3. Results and discussion

The temperature dependence of the electrical resistivity for $LaAgSb_2$ is displayed in figure 1. With lowering temperature, ρ decreases quasi-linearly with a small hump appearing at around 200 K, and such an anomalous feature becomes clear in a $d\rho/dT$ versus T plot (inset of figure 1). The apparent drop in $d\rho/dT$ at 207 K is consistent with the previous observation on the single-crystal sample [6]. The very small rise in ρ at 207 K suggests that the reduction in the conduction electron density is not substantial and one can thus expect only a small Fermi surface (FS) gapping and a weak CDW formation in $LaAgSb_2$. On the other hand, we could not notice any unambiguous variation in $\rho(T)$ or $d\rho/dT$ for the 186 K CDW ordering, which is less pronounced but is still visible in the single-crystal electrical resistivity data along the c-direction. For the present polycrystalline sample, however, the existence of inevitable disorder and/or the lack of anisotropic nature might smear out the low-temperature CDW transition.

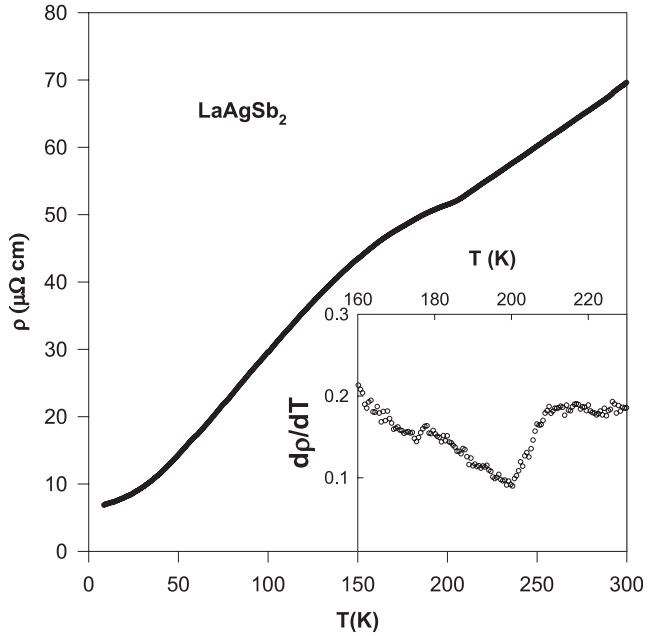

Figure 1. Temperature dependence of the resistivity of $LaAgSb_2$. Inset: a plot of ρ versus T around 200 K.

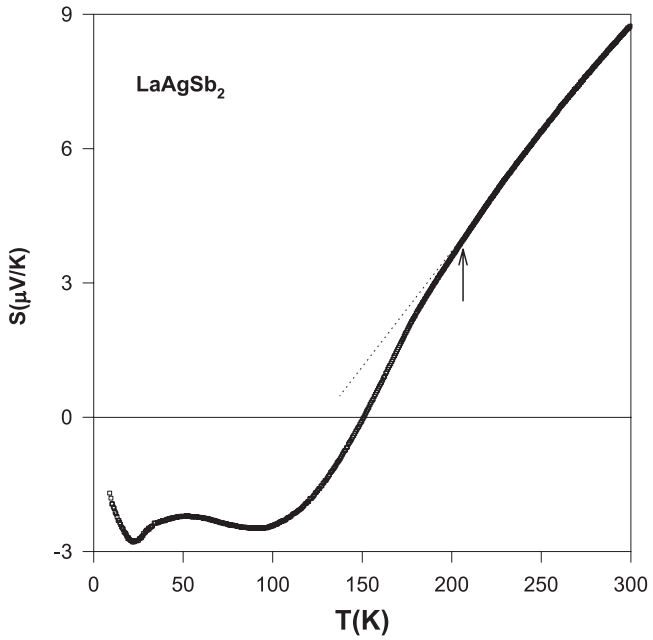

Figure 2. Temperature dependence of the Seebeck coefficient of $LaAgSb_2$. The dashed line and arrow indicate a possible change of the slope in the measured Seebeck coefficient around 200 K.

The plot of the measured Seebeck coefficient as a function of temperature is given in figure 2. On lowering the temperature, S decreases quasi-linearly with temperature, a typical

feature commonly found in nonmagnetic metals. At high temperatures, the sign of S is positive, signifying that the hole-type carriers dominate the high-temperature thermoelectric transport. Around 150 K, S undergoes a sign crossover from positive to negative, followed by a small negative minimum near 25 K. The minimum is commonly ascribed to the phonon-drag effect. It is noted that a similar S characteristic has also been observed in the Ce-based diantimonide compounds [10].

It is known that the Seebeck coefficient is a sensitive probe for the phenomenon associated with significant changes in the DOS, such as CDW ordering and crystallographic transition/distortion induced by the electronic instabilities [4, 11]. Therefore, one would expect to see distinctive features in the vicinity of the CDW transition, particularly for the first CDW ordering temperature (207 K) in the present case of $LaAgSb_2$. However, only a feeble change of the slope around 200 K has been noticed (see the dashed line and the arrow in figure 2), which is very likely due to the complex factors governing the sign, magnitude, and the temperature-dependent variation of S. Unlike the electrical resistivity, the magnitude and the sign of S are related to the position of the Fermi level (E_F), in addition to the type of charge carrier and its density [12]. In fact, the above argument holds reasonably well for nonmagnetic systems at sufficiently high temperatures, where the effects of phonon drag and magnetic impurity scattering can be neglected. As a result of partial gapping of the Fermi surface/reduction in the conduction electron density, an increase in S would be expected. In the present case, the expected increase in S might be masked by the marginal changes in the DOS around E_F. Such a possibility is likely for the multiply connected Fermi surfaces with more than one band crossing the Fermi level [6, 13].

Since S varies rather linearly with the temperature above 200 K, indicating that the diffusive Seebeck coefficient dominates the observed S at high temperatures, one can extract the value of E_F through the classical formula $|S| = \frac{\pi^2 k_B^2 T}{2eE_F}$, assuming a one-band model with an energy-independent relaxation time. The value of $E_F = 0.72$ eV, obtained by fitting the data between 200 and 300 K, is consistent with the metallic nature of $LaAgSb_2$.

The temperature dependence of the measured thermal conductivity for $LaAgSb_2$ is plotted in figure 3. The overall temperature-dependent characteristic $\kappa(T)$ is similar to those observed in metals and semimetals: a weak linear decrease with temperature followed by a broad hump at around 25 K. The low-temperature peak is a typical feature for the reduction of thermal scattering in metals at low temperatures. Unlike the Seebeck coefficient, a visible variation at around 205 K was found, as demonstrated in the inset of figure 3. Since this anomaly occurs at a temperature close to the hump in the electrical resistivity, it is thus reasonable to connect this peculiar feature with the formation of CDW. As expected, no indication of the second CDW ordering temperature (184 K) has been found in κ. An earlier study on the temperature dependence of the lattice parameters has revealed only a small change along the c-axis in the vicinity of the first CDW ordering [6]. Also, the magnitude of the CDW displacement for the first transition is an order of magnitude larger than the second one [6]. Further, a complicated variation in the interatomic distances between the various groups of atoms La–Ag, La–Sb and Sb–Sb has also been noticed [7]. As a consequence, only a very weak variation in the phonon heat conduction (lattice contribution) is accompanied by the first CDW ordering and essentially no visible change for the low-temperature one, as indeed observed.

In order to have a better understanding about the electronic and lattice contribution towards the total measured thermal conductivity, we have separated the measured thermal conductivity into lattice and electronic thermal conductivity by using the Wiedemann–Franz ($\kappa_e = L_0 T/\rho$, where κ_e is the electronic thermal conductivity and ρ is the electrical resistivity) law. The phonon/lattice contribution κ_L to the total thermal conductivity is obtained by subtracting the electronic contribution κ_e from the measured thermal conductivity. The plot of κ_e and κ_L versus

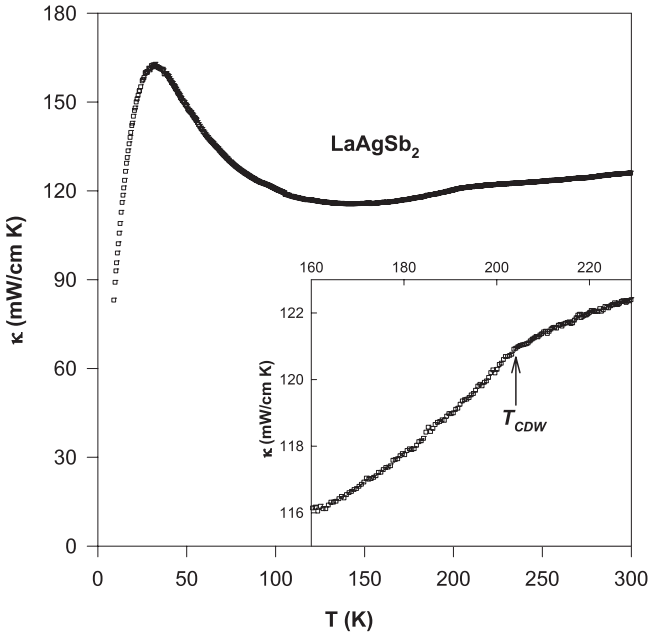

Figure 3. Temperature dependence of the thermal conductivity of $LaAgSb_2$. Inset: a magnified plot of the thermal conductivity in the vicinity of the CDW transition.

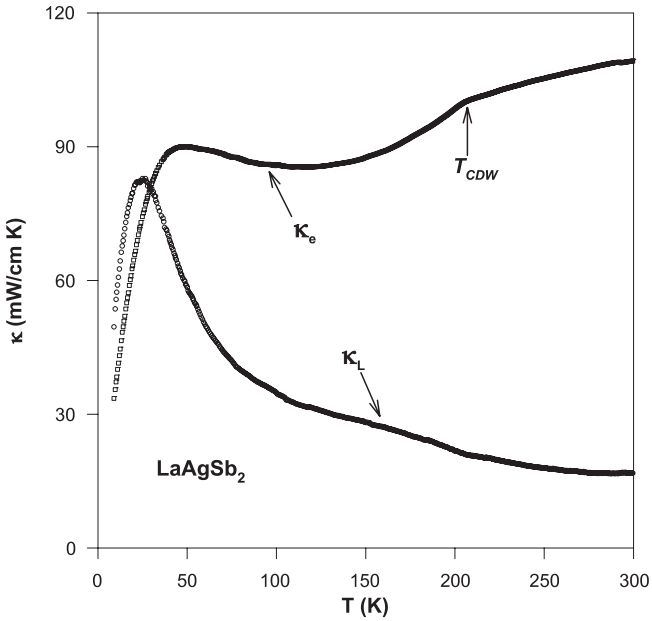

Figure 4. The estimated electronic (κ_e) and lattice (κ_L) contributions to the total thermal conductivity in $LaAgSb_2$.

T is shown in figure 4. From this separation, it is clearly seen that the observed feature in κ near the CDW ordering is essentially electronic in origin. We thus conclude that the decrease in κ at around 207 K is due to the change in κ_e as a result of a slight decrease in the conduction electron

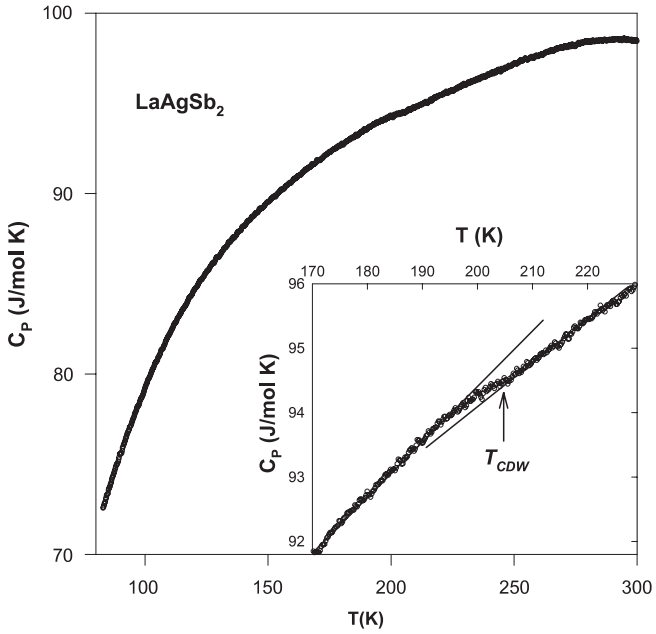

Figure 5. Temperature dependence of the specific heat of $LaAgSb_2$. The inset shows C_P versus T near the CDW transition.

density/gapping of the Fermi surface. Also, the absence of any resolvable anomaly in the lattice thermal conductivity agrees with the small periodic displacement of the crystal lattice [6, 7]. It is worthwhile mentioning that a well-defined peak in κ near the CDW transition has been reported in the ternary rare-earth silicides $R_5Ir_4Si_{10}$ (R = Dy–Lu) [14]. The peak feature has been ascribed to the heat carried by the soft phonon and mode occupation, associated with the strongly coupled nature of the CDW transition in this class of material. In view of the fact that the thermal conductivity peak in $LaAgSb_2$ is not evident, this thus suggests that $LaAgSb_2$ could be described as a weakly coupled CDW system.

The temperature dependence of the specific heat for $LaAgSb_2$ is shown in figure 5. Notice that the ac technique does not give the absolute value of specific heat due to unknown amount of power absorbed from the light source. Therefore, we have normalized our ac data to the previously reported data at 150 K to obtain an absolute value of the specific heat [15]. Similar to the results from other presently investigated transport properties and earlier reported specific heat measurement, no anomaly has been detected to indicate any magnetic ordering/transition or other type of effects at low temperatures [15]. However, a magnified plot of C_P near 200 K (the inset of figure 5) reveals a weak anomaly across the first CDW temperature, as evidenced by a distinct variation in the slope. On the other hand, no noticeable variation could be resolved near the second CDW transition. Such an observation is consistent with the results of the electrical resistivity as well as the thermal conductivity.

In a simplified approach, there are three major contributions to the specific heat, namely vibrational (lattice phonon), electronic and magnetic. From the thermal conductivity results and the nonmagnetic nature of $LaAgSb_2$, the observed variation in the vicinity of 207 K is presumably due to the changes in the electronic DOS as a result of the decrease in the free-electron density/gapping of the Fermi surface. In addition, the weak anomalous feature in the specific heat data also point out the weakly coupled nature of the CDW ordering in $LaAgSb_2$.

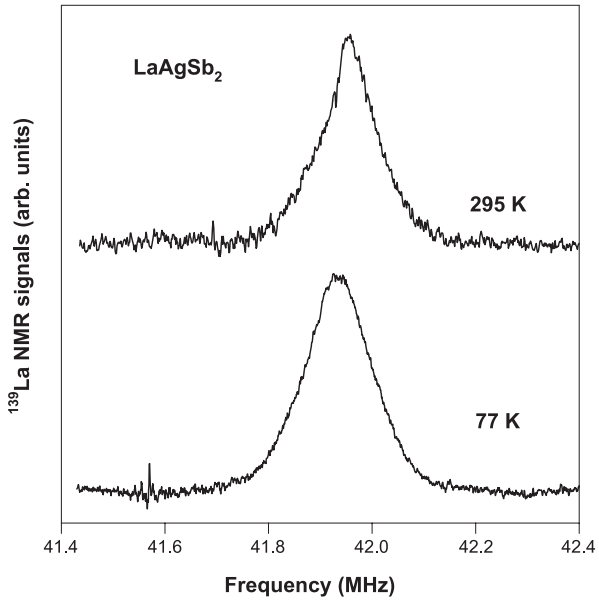

Figure 6. ^{139}La central transition spectra of $LaAgSb_2$ measured at 295 and 77 K, respectively.

For nonmagnetic metals, the NMR Knight shift is generally associated with the carrier density in the vicinity of the Fermi surface. To provide a microscopic picture for the change of the Fermi surface due to CDW formation in $LaAgSb_2$, we thus measured the ^{139}La NMR Knight shift above and below the transition temperature. The obtained ^{139}La NMR spectra at 295 and 77 K are shown in figure 6. The absence of significant broadening at 77 K confirms that the anomalous magnetic feature at 207 K is not due to magnetic ordering. For the case of ^{139}La, we report the shift of the peak of the central transition. The determined K values are -1.273% and -1.327% for 295 and 77 K, respectively. The Knight shift change for the La site between 295 and 77 K indicates the electronic structure modifications, although the variation is a rather small one ($\Delta K = -0.054\%$).

The Knight shift here can be expressed as $K = K_s + K_d$. The first term is the s-contact Knight shift, which is positive due to the positive hyperfine field of s electrons. The second part is called the d-spin shift, which is negative because the core polarization by d states contributes to a negative shift [16]. According to the Knight shift data of $LaAgSb_2$, K_s should be relatively small, and the dominant K_d produces negative K values above and below the transition temperature. Below the CDW transition temperature, the negative value of K slightly increases, indicative of the decrease in K_s. Thus the result of $\Delta K = -0.054\%$ can be reasonably connected to the reduction of the Fermi-level s-character electrons, attributed to the CDW formation.

4. Conclusions

We have studied the electronic properties of the $LaAgSb_2$ compound relevant to the CDW transitions. The measured quantities (ρ, κ, C_P, and K) exhibit moderate variations across the CDW ordering temperature of 207 K. The absence of a notable anomaly in the Seebeck coefficient has been attributed to the complexity of the Fermi surfaces. In addition, analyses of the thermal conductivity and ^{139}La NMR Knight shift data indicate that the observed changes

during the phase transition are very small and are essentially of electronic origin. In these respects, it reinforces the conclusion that $LaAgSb_2$ is a weak CDW system associated with a small gapping of Fermi surfaces.

Acknowledgments

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