Superconductivity and the electronic phase diagram of \( \text{LaPt}_{2-x}\text{Ge}_{2+x} \)

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Abstract

In many cases, unconventional superconductivity are realized by suppressing another order parameter, such as charge density wave (CDW) or spin density wave (SDW). This suggests that the fluctuations of these order parameters play an important role in producing superconductivity. \( \text{LaPt}_{2}\text{Ge}_2 \) undergoes a structural phase transition (SPT) at 394 K accompanied by a double period modulation in the \( a \)-axis direction, and superconducts at \( T_c = 0.41 \) K. We performed band calculations and found a partial Fermi surface nesting corresponding to the double period modulation, which indicates that the SPT of this compound is due to CDW. By changing the stoichiometry between Pt and Ge, we succeeded in suppressing the CDW transition temperature (\( T_{\text{CDW}} \)) and increasing \( T_c \) in \( \text{LaPt}_{2-x}\text{Ge}_{2+x} \). Comparison of \(^{139}\text{La} \) and \(^{195}\text{Pt} \)-NMR data reveals strong fluctuations associated with CDW around \( T_{\text{CDW}} \). From \(^{139}\text{La} \)-NQR measurements at zero field, we found that an isotropic superconducting gap is realized in \( \text{LaPt}_{2-x}\text{Ge}_{2+x} \) (\( x = 0.20 \)). We discuss the relationship between superconductivity and the CDW order/fluctuations.

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I. INTRODUCTION

Most of ternary compounds in the formula of $MT_2X_2$ ($M$ = rare earth or alkaline earth metals, $T$ = transition metals, $X$ = Si or Ge) including some Fe-based superconductors crystallize in the body centered tetragonal ThCr$_2$Si$_2$ type structure (Fig. 1(a)). On the other hand, some $MT_2X_2$ with $T$ = Ir or Pt crystallize in the primitive tetragonal CaBe$_2$Ge$_2$ type structure (Fig. 1(b)). The CaBe$_2$Ge$_2$ type structure is closely related to the ThCr$_2$Si$_2$ type structure. The ThCr$_2$Si$_2$ type structure has two [X-T-X] layers along the $c$-axis while in the CaBe$_2$Ge$_2$ type structure, one of them is replaced by [T-X-T] layer. Some of non-magnetic CaBe$_2$Ge$_2$ type compounds (SrPt$_2$As$_2$$_{1,7}$ and LaPt$_2$Si$_2$$_{6,8,9}$) show a coexistence of superconductivity and charge density wave (CDW). In these compounds, the CDW occurs in the [X-T-X] layers.

Fluctuations associated with CDW or spin density wave (SDW) have attracted much attention in recent years, since they may be responsible for superconductivity that is realized near a CDW or SDW phase. In the high-$T_c$ cuprates, spin fluctuations arising from the nearby antiferromagnetism have been studied extensively. Recently, CDW has also attracted attention in relation to the unusual normal state in the cuprates$^{10}$. In the Fe pnictides, both spin fluctuations and orbital or structural fluctuations are believed to be important. For example, underdoped BaFe$_{2-x}$M$_x$As$_2$ ($M$ = Co, Ni) are metallic and show a tetragonal-to-orthorhombic structural phase transition (SPT) followed by an SDW order$^{11,12}$. Superconductivity appears after suppressing these orders, and fluctuations associated with SPT and SDW have been observed$^{12}$. Compounds such as SrPt$_2$As$_2$ and LaPt$_2$Si$_2$ showing a coexistence of superconductivity and CDW can be recognized as non-magnetic versions of Fe-based superconductors, because both CDW and SDW originate from a Fermi surface nesting and the crystal structure is very similar.

LaPt$_2$Ge$_2$ is a superconductor with $T_c = 0.41$ K$^{13,11}$ and shows a SPT at 385.8 K$^{15}$. As shown in Figs. 2(a) and 2(b), The crystal structure of the high temperature phase is a tetragonal CaBe$_2$Ge$_2$ type (space group: $P4/nmm$) while that of the low temperature phase is a monoclinically distorted CaBe$_2$Ge$_2$ type ($P2_1/c$)$^{11,15}$. The monoclinic phase has a doubled unit cell in the $a$-axis direction. As shown in Figs. 2(c) and 2(d), the monoclinic distortion is mainly in the [Ge(1)-Pt(2)-Ge(1)] layer, while there is almost no distortion in the [Pt(1)-Ge(2)-Pt(1)] layer. The origin of the SPT, and its relationship to superconductivity
is unknown.

In this work, we address this issue by band calculations, material synthesis and nuclear magnetic resonance (NMR) measurements. We find that the SPT is due to CDW order. By suppressing the CDW order, $T_c$ is enhanced. We have also performed nuclear quadrupole resonance (NQR) measurements to study the superconducting gap. We will also discuss about the fluctuations associated with the CDW/SPT.

FIG. 1: (Color online) Crystal structure of the ThCr$_2$Si$_2$ type (a) and CaBe$_2$Ge$_2$ type (b). The blue rectangle and the pink oval represent the [X-T-X] and the [T-X-T] layers, respectively.

FIG. 2: (Color online) Crystal structure of the tetragonal (a) and monoclinic (b) phases, [Pt(1)-Ge(2)-Pt(1)] (c) and [Ge(1)-Pt(2)-Ge(1)] (d) layers of the monoclinic phase. The solid rectangle represents the unit cell.
II. METHODS

The full relativistic band calculations including spin-orbit coupling (SOC) were performed with all-electron full-potential linear augmented plane wave (FLAPW) method implemented in HiLAPW\textsuperscript{16}. Details of numerical procedures were described in the previous work\textsuperscript{16}. Polycrystalline samples of LaPt$_{2-x}$Ge$_{2+x}$ were synthesized by melting the elements of La (99.9\%), Pt (99.99\%), and Ge (99.99\%) in an arc furnace under high purity (99.9999\%) Ar atmosphere. The resultant ingot was turned over and re-melted several times to ensure good homogeneity. The weight loss during the arc melting was less than 1\%. Subsequently, the samples were wrapped in Ta foil, sealed in a quartz tube filled with He gas, annealed at 1000 °C for 3 days and then slowly cooled to room temperature over a period of 3 days. The samples were characterized by powder X-ray diffraction using Rigaku RINT-TTR III at room temperature. The XRD patterns were analyzed by RIETAN-FP program\textsuperscript{17}. The crystal structure is drawn by using VESTA program\textsuperscript{18}. The resistivity was measured by using a dc four-terminal method in the temperature range of 1.4 ∼ 480 K. For ac susceptibility and NMR/NQR measurements, a part of the ingot was powdered. The $T_c$ was determined by measuring the inductance of a coil filled with a sample which is a typical setup for NMR/NQR measurements. The measurements below 1.4 K was carried out with a $^3$He-$^4$He dilution refrigerator. NMR/NQR were carried out by using a phase-coherent spectrometer. The NMR spectrum was obtained by integrating the spin echo intensity by changing the resonance frequency ($f$) at the fixed magnetic field of 12.951 T. The spin-lattice relaxation rate ($1/T_1$) was measured by using a single saturating pulse, and determined by fitting the recovery curve of the nuclear magnetization to the theoretical function\textsuperscript{19,20}. $(M_0 - M(t))/M_0 = \exp(-t/T_1)$ for $^{195}$Pt-NMR, $(M_0 - M(t))/M_0 = (1/84) \exp(-t/T_1) + (3/44) \exp(-6t/T_1) + (75/364) \exp(-15t/T_1) + (1225/1716) \exp(-28t/T_1)$ for $^{139}$La-NMR (center peak) and $(M_0 - M(t))/M_0 = 0.931265 \exp(-16.934663t/T_1) + 0.001432 \exp(-7.919195t/T_1) + 0.067304 \exp(-3t/T_1)$ for $^{139}$La-NQR ($\eta = 0.71, m = \pm3/2 \leftrightarrow \pm5/2$ transition), where $M_0$ and $M(t)$ are the nuclear magnetization in the thermal equilibrium and at a time $t$ after the saturating pulse.
III. RESULTS

A. Electronic structure calculations

In the band calculation, we used the crystal structure determined for single crystal LaPt$_2$Ge$_2$ by Imre et al.\textsuperscript{15}. Figures 3(a) and 3(b) show the band structure and the Fermi surface of the tetragonal phase, respectively. These results are very similar to those of LaPt$_2$Si$_2$.\textsuperscript{4} The Fermi surface consists of five sheets, and there are two 2D-like sheets around M point. The outer Fermi surface clearly shows a partial nesting represented by a red arrow. The nesting vector is $q_{\text{CDW}} = 0.42 \pm 0.03$ which is close to the actual modulation vector of $q_{\text{CDW}} = 0.515$. Figures 3(c) and 3(d) display the total and partial density of states ($N(E)$), respectively. Comparison between the tetragonal and monoclinic phases shows that the total $N(E)$ at the Fermi level ($E_F$) of the monoclinic phase is 18% smaller than that of the tetragonal phase. This result together with the existence of Fermi surface nesting and the double period modulation in the $a$-axis indicate that the SPT of LaPt$_2$Ge$_2$ is due to CDW. Looking in detail, the partial $N(E_F)$ at Pt(1) for the tetragonal and monoclinic phases are very similar. The partial $N(E_F)$ at Pt(2) is larger than that at Pt(1) in the tetragonal phase, while is reduced to a value almost same as that at Pt(1) in the monoclinic phase, indicating that the CDW appears in [Ge(1)-Pt(2)-Ge(1)] layer.
FIG. 3: (Color online) Band structure (a) and Fermi surface (b) of the tetragonal phase. The red arrows represent a nesting vector. Total and partial $N(E)$ of the tetragonal (c) and monoclinic (d) phases. The Fermi level is taken at the origin in (a), (c), and (d).
B. Basic physical properties of LaPt$_{2-x}$Ge$_{2+x}$

No impurity peaks were observed in the XRD pattern in the range of $0 \leq x \leq 0.30$. The extra Ge in non-stoichiometric LaPt$_{2-x}$Ge$_{2+x}$ ($x > 0$) is assumed to occupy deficient Pt sites because Pt and Ge sites are equivalent in the CaBe$_2$Ge$_2$ type structure. Figure 4 shows the $x$ dependence of the lattice parameters for LaPt$_{2-x}$Ge$_{2+x}$ at room temperature. With increasing $x$, the $c$-axis length increases linearly up to $x = 0.20$. Beyond $x = 0.20$, the $c$-axis length is saturated which suggests that the solubility limit is $x = 0.20$. On the other hand, the length $a$ and $b$ decrease. For $x \geq 0.06$, $a$ and $b$ become constant since the compounds are in the tetragonal structure.

Figure 5(a) shows the temperature dependence of the electrical resistivity for LaPt$_{2-x}$Ge$_{2+x}$. The electrical resistivity for $x = 0$ showed a kink at $T_{CDW} = 394$ K due to the onset of CDW. This is in good agreement with the value of $T_{CDW} = 385.8$ K reported by Imre et al.\textsuperscript{15}. With increasing $x$, $T_{CDW}$ decreased. For $x = 0.15$, the anomaly due to the CDW disappeared. Figure 5(b) shows the magnified view of the low temperature range. Superconductivity was observed in all samples except for $x = 0$. As seen in Fig. 5(b), the $T_c$ increased with increasing $x$. The sample with $x = 0.20$ showed the highest $T_c$.

Figure 6 shows the temperature dependence of the ac susceptibility measured by the NMR/NQR coil for LaPt$_{2-x}$Ge$_{2+x}$. All samples showed a large decrease in the ac susceptibility below $T_c$. 


FIG. 4: (Color online) $x$ dependence of the lattice parameters $a$, $b$ and $c$ for LaPt$_{2-x}$Ge$_{2+x}$. The monoclinic structures are interpreted in the notation of tetragonal structure.
FIG. 5: (Color online) (a) Temperature dependence of the electrical resistivity for LaPt$_{2-x}$Ge$_{2+x}$. The solid arrows indicate $T_{\text{CDW}}$. (b) Magnified view of the low temperature range. The solid arrows indicate $T_c$. 
FIG. 6: (Color online) Temperature dependence of the ac susceptibility for LaPt$_{2-x}$Ge$_{2+x}$. The solid arrows indicate $T_c$.

C. CDW transition probed by $^{195}$Pt- and $^{139}$La-NMR

We performed both $^{195}$Pt- and $^{139}$La-NMR measurements for the $x = 0.06$ and $x = 0.20$ samples at a fixed magnetic field of 12.951 T. Because $^{139}$La has nuclear spin 7/2, fluctuations due to both the hyperfine field and the electric field gradient can be probed by the spin-lattice relaxation. By contrast, $^{195}$Pt-NMR can only see the former, since $^{195}$Pt has nuclear spin 1/2.

Figure 7(a) shows the $^{195}$Pt-NMR spectra at $T = 200$ K. The spectrum of $x = 0.06$ is sharper than that of $x = 0.20$, probably it is because the grains in $x = 0.06$ are well orientated to the magnetic field towards the high susceptibility direction. The grains in $x = 0.20$ are orientated only partially, resulting in spectrum close to a powder pattern. The degree of orientation depends on the anisotropy of the susceptibility, the size of the domains and the size of the grains. We speculate that the domains of $x = 0.06$ has grown much larger than that of $x = 0.20$ because $x = 0.06$ is closer to the stoichiometry.

The spectrum of $x = 0.06$ shows two peaks at high temperatures (Fig. 7(b)). This is because there are two Pt sites in LaPt$_2$Ge$_2$. Since Pt(2) is mainly affected by the CDW, we identified the high frequency peak having large $T$-dependence as Pt(2), and the low frequency peak as Pt(1). For $x = 0.20$, two Pt sites can not be distinguished because of the
powder pattern.

The temperature dependence of the Knight shift (K) obtained from these spectra is shown in Fig. 8(a). The K reflects $N(E_F)$, through $K = K_o + K_s$ and $K_s = A\mu_B N(E_F)$. Here $K_o$ and $K_s$ are $T$-independent orbital part and $T$-dependent spin part, respectively, and $A$ and $\mu_B$ are the hyperfine coupling constant and the Bohr magneton, respectively. For Pt(2), a large decrease in the $K$ due to the change in the $N(E_F)$ was observed around $T_{CDW}$, while for Pt(1), no change due to the CDW was observed.

The quantity $1/T_1 T$ also reflects the $N(E_F)$ through the relation $1/T_1 T = A^2 \pi k_B \gamma_n^2 h N^2(E_F) + (1/T_1 T)_F$. Here, $\gamma_n$ is a nuclear gyromagnetic ratio, and the $T$-dependent $(1/T_1 T)_F$ is due to magnetic or electric fluctuations whose frequency is equal to the NMR frequency $f$. For $x = 0.06$, the temperature dependence of $1/T_1 T$ (Fig. 8(b)) and $K$ is consistent. For Pt(2), the $1/T_1 T$ decreased around $T_{CDW}$ because of the decrease in the $N(E_F)$ and became almost the same as that of Pt(1). While for Pt(1) site, no change due to the CDW was observed. These results are consistent with the band calculations. For $x = 0.20$ where it is difficult to distinguish Pt(1) and Pt(2) in the spectrum (Fig. 7), the $T_1$ was measured at the left peek where the Pt(1) signal is dominant. No clear change was observed in the temperature dependence of the $1/T_1 T$.

Figure 9 shows the temperature dependence of the $1/T_1 T$ measured by $^{139}$La-NMR. For $x = 0.06$, the $1/T_1 T$ increased upon cooling to $T_{CDW}$, and then decreased rapidly because of the onset of CDW. Similar behavior was observed for $x = 0.20$. These results are in sharp contrast with those for $^{195}$Pt-NMR. Such upturn in $^{139}$La-NMR $1/T_1 T$ can be understood as due to fluctuations associated with CDW that couple to the electric quadrupole moment of $^{139}$La nuclei.
FIG. 7: (Color online) (a) $^{195}$Pt-NMR spectra for LaPt$_{2-x}$Ge$_{2+x}$ ($x = 0.06$ and 0.20) at 200 K. (b) $^{195}$Pt-NMR spectra for LaPt$_{2-x}$Ge$_{2+x}$ ($x = 0.06$) at various temperatures.
FIG. 8: (Color online) (a) Temperature dependence of the $^{195}$Pt-NMR Knight shift for LaPt$_{2-x}$Ge$_{2+x}$ ($x = 0.06$). (b) Temperature dependence of the $^{195}$Pt-NMR $1/T_1 T$ for LaPt$_{2-x}$Ge$_{2+x}$ ($x = 0.06$ and 0.20).
FIG. 9: (Color online) Temperature dependence of the $^{139}\text{La-NMR } 1/T_1T$ for LaPt$_{2-x}$Ge$_{2+x}$ ($x = 0.06$ and $0.20$).

D. Phase diagram for LaPt$_{2-x}$Ge$_{2+x}$

Figure 10 shows the phase diagram for LaPt$_{2-x}$Ge$_{2+x}$ obtained in the present work. In this phase diagram, the $T_{\text{CDW}}$ was determined by two ways: by the minimum of the electrical resistivity ($x \leq 0.1$) or by the maximum of the $^{139}\text{La-NMR } 1/T_1T$ ($x = 0.20$). The $T_{\text{CDW}}$ decreased linearly and the $T_c$ increased with increasing $x$. The maximum $T_c$ was 1.95 K in $x = 0.20$. The CDW critical point ($T_{\text{CDW}} = 0$) is estimated to be $x_c = 0.22$ by extrapolating the data for $x \leq 0.2$. 
FIG. 10: (Color online) Phase diagram for LaPt$_{2-x}$Ge$_{2+x}$ obtained by the present work. The red circles represent the $T_{CDW}$ determined by a minimum of the electrical resistivity ($x < 0.20$) or a maximum of the $^{139}$La-NMR $1/T_1T$ ($x = 0.20$). The filled blue squares represent the $T_c$ determined as the onset temperature of the ac susceptibility. The $T_c$ is multiplied by 20 for clarity.

E. Superconducting gap probed by $^{139}$La-NQR

Figure 11 shows the temperature dependence of the $^{139}$La-NQR $1/T_1$ for the $x = 0.20$ sample which shows the highest $T_c = 1.95$ K. The $1/T_1$ was measured at the $m = \pm 3/2 \leftrightarrow \pm 5/2$ transition. As seen in Fig. 11, the $1/T_1$ is proportional to $T$ in the temperature range of $T_c < T < 4.2$ K which is consistent with the $^{139}$La-NMR $1/T_1T$. Just below $T_c$, the $1/T_1$ showed a small Hebel-Slichter peak and then decreased rapidly. Thus we concluded that the superconducting gap of $x = 0.20$ sample is isotropically opened. The gap size is estimated to be $2\Delta(0)/k_BT_c = 4.0 \pm 0.2$, which is slightly larger than the BCS value ($2\Delta(0)/k_BT_c = 3.53$).
FIG. 11: (Color online) Temperature dependence of the $1/T_1$ for LaPt$_{2-x}$Ge$_{2+x}$ ($x = 0.20$) obtained by $^{139}$La-NQR. The inset is a $1/T_1$ on a logarithmic scale vs $T_c/T$ plot. The solid line below $T_c$ means that $1/T_1 \propto \exp (-\Delta/k_B T)$. From the slope, $2\Delta/k_BT_c = 4.0 \pm 0.2$ is obtained.

IV. DISCUSSION

The relationship between CDW and superconductivity has been investigated in systems by intercalation (Cu$_x$TiSe$_2^{21}$, Cu$_x$TaS$_2^{22}$), substitution (Lu$_5$Ir$_4$(Si$_{1-x}$Ge$_x$)$_{10}^{23}$) or applying pressure (2H-NbSe$_2^{24}$, NbSe$_3^{25}$). The general feature of these systems is that suppressing CDW results in increasing $T_c$. The phase diagram of LaPt$_{2-x}$Ge$_{2+x}$ also has this feature. It is natural to think that the $T_c$ increases because of the increase in $N(E_F)$ by suppressing CDW. To verify this idea, we used a rough approximation by fixing the Debye temperature $\theta_D$ and the attractive interaction $V$ to estimate the increase in $T_c$ from $x = 0$ ($T_c = 0.41$ K). We used McMillan formula$^{26}$ for this estimation,

$$T_c = \frac{\Theta_D}{1.45} \exp \left( -\frac{1.04 (1 - \lambda)}{\lambda - \mu^* (1 - 0.62\lambda)} \right)$$

(1)

with $\theta_D = 310$ K$^{27}$, $\mu^* = 0.13^{26}$ and $\lambda = VN(E_F)$, where $N(E_F)$ was obtained by band calculations. As a result, we obtained $T_c = 1.47$ K for the tetragonal phase. This value is smaller than $T_c = 1.95$ K obtained for $x = 0.20$, but accounts for the majority of the increase in $T_c$. In cuprates and Fe-based superconductors, the magnetic fluctuations or structural/orbital
fluctuations are believed to play an important role in producing superconductivity. From comparison between $^{195}$Pt- and $^{139}$La-NMR, we found moderate fluctuations around $T_{\text{CDW}}$. Such fluctuations may contribute to the rest of increase in $T_c$.

V. SUMMARY

We performed band calculations for LaPt$_2$Ge$_2$ and showed that the structural phase transition is due to CDW. Secondly, we synthesized non-stoichiometric LaPt$_{2-x}$Ge$_{2+x}$ samples and performed electrical resistivity, ac-susceptibility, $^{195}$Pt and $^{139}$La NMR/NQR measurements. We found that the CDW transition temperature ($T_{\text{CDW}}$) decreases and superconducting transition temperature ($T_c$) increases from 0.41 K to 1.95 K with increasing $x$. From $^{139}$La- and $^{195}$Pt-NMR, we found a reduction of $N(E_F)$ and moderate fluctuations associated with CDW/structure transition. From $^{139}$La-NQR measurements at zero field, we found that an isotropic superconducting gap is realized in LaPt$_{2-x}$Ge$_{2+x}$ ($x = 0.20$). The change in $N(E_F)$ accounts for the majority of the increase in $T_c$.

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