Temperature-dependent local structure and superconductivity of $BaPd_2As_2$ and $SrPd_2As_2$

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The local structures of 122-type paradium arsenides, namely $BaPd_2As_2$ and $SrPd_2As_2$, are examined by As K-edge extended x-ray absorption fine structure measurements to find a possible correlation between the variation of their superconducting transition temperature and the local structure. The local atomic distances are found to be consistent with average distances measured by diffraction techniques. The temperature dependence of mean square relative displacements reveal that, while $BaPd_2As_2$ is characterized by a local As-Pd soft mode, albeit with larger atomic disorder, $SrPd_2As_2$ shows anomalous As-Pd correlations with a kink at ∼160 K due to hardening by raising temperature. We have discussed implications of these results and possible mechanisms of differing superconducting transition temperature in relation with the structural instability.

I. INTRODUCTION

Superconductivity in condensed matter generally appears or gets enhanced by a concomitant suppression of the other orders, recognized as the interplay between different degrees of freedoms [1,2]. In such cases, the knowledge of relation between crystal structure and superconductivity is of prime importance since this relationship largely affects other electronic degrees of freedoms. Iron-based superconductors are a good example in which interplay between structural transition and superconductivity exists and the structural parameters have direct interplay with spin, charge, and orbital fluctuations, important for the superconductivity [3]. Incidentally, such an intriguing interplay is strictly related to the As chemistry, therefore interaction between arsenic *4p* and iron *3d* electrons and bonding of As atoms [4]. The so-called "122" compounds [5,6] forming a body-centered tetragonal $ThCr_2Si_2$-type structure (space group $I4/mmm$) at room temperature have been main systems to study these correlations [7,8]. In general, the 122-type structure exhibits a structural phase transition from the tetragonal structure to an orhorhombic on cooling [9]. However, some compounds such as $CaFe_2As_2$ show other types of structural transition, namely a collapsed tetragonal (CT) phase transition under small external pressure, characterized by a discontinuous change in the material's lattice parameters and volume [10,11]. The CT phase is nonmagnetic and lacks magnetic fluctuations with suppressed supercon-

ductivity [11,12]. The driving mechanism of the CT phase has been attributed to the strong interlayer interaction through As-As covalent bonding [12,13].

As a matter of fact, superconductivity also appears in the nonmagnetic CT phase of 122 materials when Fe atoms are completely substituted by other metals, although the superconducting transition temperature (T_c) remains relatively low [14–23]. Recently, an interesting relationship between the Debye temperature and T_c has been found in Pd-based 122 type of CT arsenide [23]. The compounds with lower Debye temperature tend to show higher T_c. For instance, $BaPd_2As_2$ shows superconductivity below ∼3.5 K with the Debye temperature being ∼140 K while T_c of $SrPd_2As_2$ is ∼1 K with the Debye temperature of ∼300 K. The estimated specific heat γ values of these compounds are very close to each other [23], suggesting that the density of states of the two compounds can be comparable. Hence it has been discussed that the presence of soft phonon may enhance electron-phonon interaction (λ) in the phonon-mediated superconductivity. In this context it should be important to know which local lattice mode may be important to drive this electron-phonon interaction in these materials.

In this work we report a comparative temperature-dependent study of the local structure of $BaPd_2As_2$ and $SrPd_2As_2$ by means of As K-edge extended x-ray absorption fine structure (EXAFS). We have found a marked difference in the temperature dependence of the mean square relative displacements (MSRD) of the As-Pd bond in these two compounds. While the general trend of Einstein temperature (Θ_E) in the two systems is consistent with that of the Debye temperature, we find that the MSRD of the As-Pd bond in $BaPd_2As_2$ can be described by a single Einstein temperature,

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whereas that in $SrPd_2As_2$ shows crossoverlike behavior ~ 160 K from lower to higher Einstein temperature. We have also found that, although the T_c of $BaPd_2As_2$ is more than three times higher than that of $SrPd_2As_2$, the static disorder in the latter is much lower than that in the former. The results are consistent with structural instability induced phonon softening to trigger strong coupling superconductivity in $BaPd_2As_2$.

II. METHODS

Polycrystalline samples of $BaPd_2As_2$ and $SrPd_2As_2$ were synthesized by heating starting materials in sealed quartz tubes. It is known that $BaPd_2As_2$ has three polymorphs, namely $ThCr_2Si_2$-type, $CeMg_2Si_2$-type, and alternately stacked $CaBe_2Ge_2$- and $CeMg_2Si_2$-type structures [24,25]. Among them, $ThCr_2Si_2$ type exhibits superconductivity [21,23] while the $CeMg_2Si_2$ type does not [23]. In this study, the sample of $BaPd_2As_2$ with the $ThCr_2Si_2$-type structure was selectively synthesized by controlling the synthesis conditions [23], and a T_c value of 3.85 K was evaluated through the magnetization measurement. On the other hand, the T_c value of $SrPd_2As_2$ was not evaluated because of its low T_c (=0.92 K) [20].

Arsenic K-edge (11 868 eV) x-ray absorption measurements were performed at the Spline beamline [26] of the European Synchrotron Radiation Facility, where the synchrotron radiation was monochromatized using a double crystal Si(111) monochromator. The spectra were acquired sequentially on the two samples as a function of temperature in transmission mode using three ionization chambers mounted in series for simultaneous measurements on the sample and a reference. Finely powdered samples of $BaPd_2As_2$ and $SrPd_2As_2$ were mixed uniformly in an organic matrix and pressed into pellets of 13 mm diameter for obtaining the edge jumps to be about 1. Several absorption scans at each temperature (3–5 scans) were measured to ensure high signal to noise ratio and spectral reproducibility. The sample temperature during the measurements was controlled and monitored within an accuracy of ± 1 K. As K-edge x-ray absorption spectra were also measured on $CaPd_2As_2$ (see the Supplemental Material [27]), a related compound, using the LISA beamline of the European Synchrotron Radiation Facility following a similar experimental approach. The EXAFS oscillations were extracted from the absorption spectra using standard procedure based on spline fits [28].

III. RESULTS

Figure 1 shows the temperature dependence of Fourier transform (FT) magnitudes of k^2-weighted EXAFS oscillations extracted from As K-edge x-ray absorption spectra measured on $BaPd_2As_2$ (a) and $SrPd_2As_2$ (b). Insets show the corresponding EXAFS oscillations. The data are not corrected by photoelectron phase shifts and hence represent raw experimental data. The EXAFS oscillations are visible up to high k range (~ 16 Å^{-1}) even at 300 K. In both compounds, the first FT peak appears at ~ 2.5 Å that corresponds to Pd-As and As-As bonds, and the second peak at 3.2–3.4 Å corresponds to As-Ba or As-Sr distance. It is clear from the
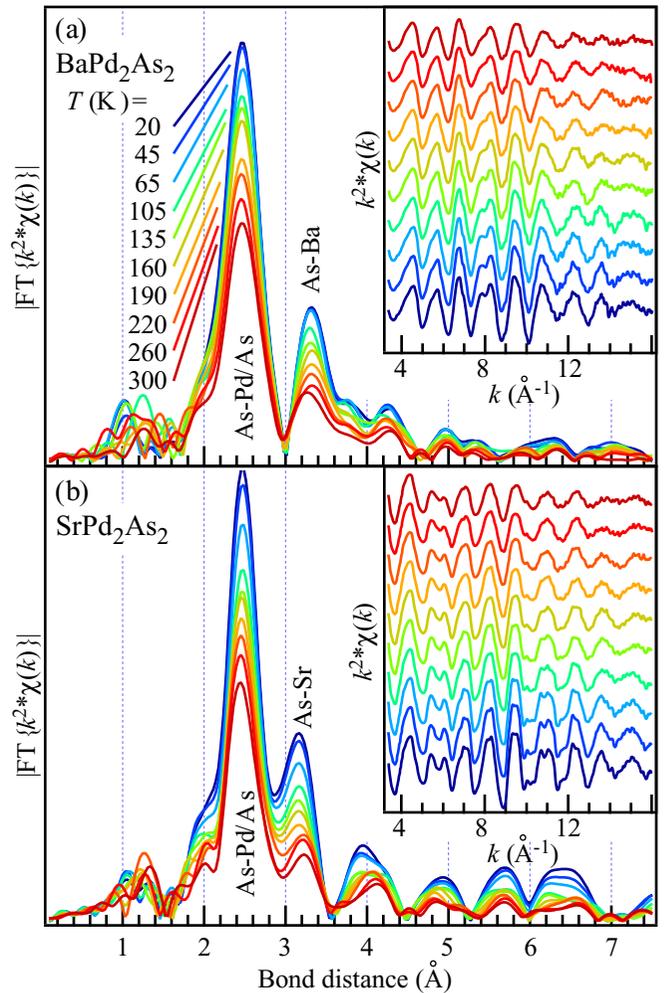
FIG. 1. Temperature dependence of Fourier transform magnitudes of k^2-weighted As K-edge EXAFS on (a) $BaPd_2As_2$ and (b) $SrPd_2As_2$. Inset shows the corresponding EXAFS oscillations. The data are not corrected by the phase shifts.

figure that the local bond distances in $SrPd_2As_2$ are shorter than those in $BaPd_2As_2$, which is in general agreement with those estimated from x-ray diffraction measurements [25,29]. The peaks appearing at $\geqslant 4$ Å would originate from multiple scattering as well as distant atom contributions. The FT peak amplitudes $\geqslant 4$ Å tend to be higher in $SrPd_2As_2$ than in $BaPd_2As_2$, indicating smaller overall disorder in $SrPd_2As_2$.

To quantify the local lattice parameters, the measured EXAFS oscillations were modeled with three shells involving the nearest neighbor As-Pd, As-As, and As-Ba/Sr distances. The EXAFS modeling was carried out in the single scattering approximation using the standard EXAFS equation [28]. The EXCURVE 9.275 code [30] was used for the model fits in which calculated amplitude and phase factors were used. In the starting model the structural parameters deduced from x-ray diffraction measurements were used [25,29]. In these model fits, the passive electrons reduction factor S_0^2 was set to 0.9, while the number of neighboring atoms N_i were fixed to their nominal values (4 for As-Pd, 1 for As-As, 4 for As-Ba/Sr). The photoelectron energy zero (E_0) was fixed after fit trials on several scans. The fitting k range was
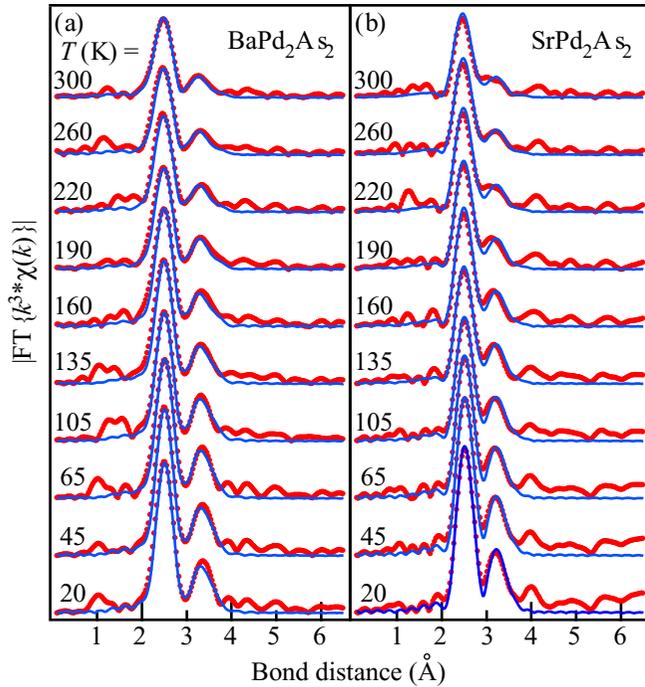
FIG. 2. Fourier transform magnitudes of k^3-weighted As K-edge EXAFS on (a) $BaPd_2As_2$ and (b) $SrPd_2As_2$ after phase shift corrections. Red dots represent experimental data and blue lines show the model fits.

3.4–16 Å^{-1}. The number of independent data points, $2\Delta k \Delta R/\pi$, for the present EXAFS model fits ($\Delta R = 2.0$ Å) was ~16 in which eventually six parameters were varied. It should be mentioned that apart from sequential measurements and the same data treatments, the EXAFS model fit approach was the same for the two systems for a direct comparison of the derived physical parameters. The uncertainties in the physical parameters were determined by creating correlation maps and by analyzing independent scans. Figure 2 shows the temperature-dependent FT of k^3-weighted As K-edge EXAFS of $BaPd_2As_2$ (a) and $SrPd_2As_2$ (b) after phase shift correction along with the three-shell model fits. The spectra are displayed as red dots with offset for each temperature, and the vertical scale of Figs. 2(a) and 2(b) are kept to be the same for a realistic comparison.

Figure 3 shows the temperature dependence of bond distances from As atoms for $BaPd_2As_2$ (a) and $SrPd_2As_2$ (b). In both compounds, all the bond distances at room temperature appear in an overall agreement with those reported by x-ray diffraction [25,29]. As we change the alkaline earth metal from Ba to Sr, all bond distances tend to contract. This is qualitatively reasonable, considering their ionic radius ~1.61 Å for Ba and ~1.44 Å for Sr in XII coordination [31]. Among three obtained bonds, the As-As distance showed the largest decrease of about 5%. The As-As distance in $BaPd_2As_2$ (~2.6 Å) is comparable to those of collapsed phase of 122-type iron-arsenides. As we substitute Ba with Sr, the lattice constant shrinks and the As-As distance is further compressed.

We show in Fig. 4 the temperature dependence of MSRD, where we have found interesting differences between two ma-
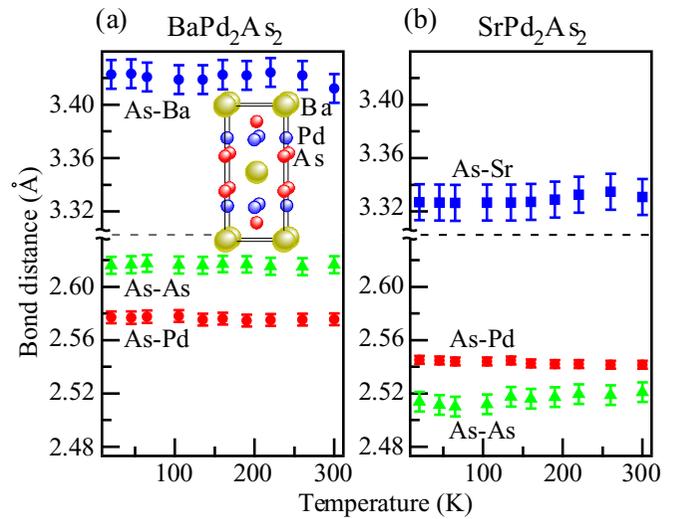
FIG. 3. Experimentally determined local bond distances around the As atom of (a) $BaPd_2As_2$ and (b) $SrPd_2As_2$. Inset in (a) shows the crystal structure.

terials. While MSRD of As-Pd bond in $BaPd_2As_2$ [Fig. 4(a)] monotonically increases by raising temperature, that in $SrPd_2As_2$ [Fig. 4(b)] shows a kink structure ~160 K. On the other hand, the MSRDs of As-Ba/Sr bonds in two compounds show similar behavior including their magnitude. For As-As we show the estimated values only for the highest temperature as a representative since we found that it has relatively large error partially due to the small number of neighboring atoms with signal largely overlapped with As-Pd signal. We have evaluated the Einstein temperatures Θ_E of As-Pd bond using the correlated Einstein model [32]: $\sigma^2 = \sigma_0^2 + \sigma^2(T)$, where σ_0^2 is static configurational disorder and $\sigma^2(T)$ describes the dynamic part. The obtained Θ_E value of As-Pd atomic pairs
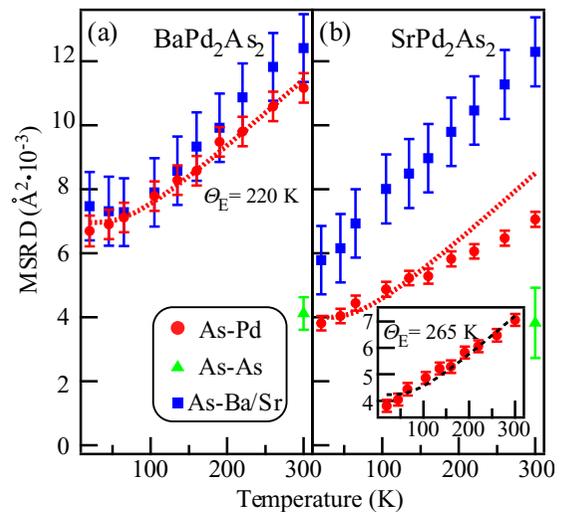
FIG. 4. MSRDs of As-Pd (red circle), As-As (green triangle), and As-Ba/Sr (blue square) on (a) $BaPd_2As_2$ and (b) $SrPd_2As_2$. Red dotted lines denote results of the Einstein model fit for As-Pd bond. In (b), the fit was performed in a temperature range of 20–160 K with the same Einstein frequency with (a) (220 K). Inset of (b) shows the fit result with Einstein frequency as a free parameter.

in BaPd$_2$As$_2$ was ∼220 K. For SrPd$_2$As$_2$, first we tried to fit the temperature-dependent MSRD of As-Pd using a single Einstein temperature [see, e.g., inset of Fig. 4(b)] and obtained a value of ∼265 K with σ_0^2∼2.2 × 10^{-3} Å^2, but the fitting was unsatisfactory especially at low-T side due to the presence of a kink structure in MSRD. Instead, we have found that the data in the low temperature range (20–160 K) can be well described by the same Einstein temperature with that of BaPd$_2$As$_2$ as shown in Fig. 4(b). As temperature raises more than ∼160 K, the MSRD of the As-Pd bond in SrPd$_2$As$_2$ deviates from the expected behavior of Θ_E = 220 K and it turns to a harder local mode. Indeed, the estimated Θ_E for T > 160 K was ∼295 K. In addition, the evaluated σ_0^2 values for the As-Pd correlations were found to be ∼4.5 × 10^{-3} Å^2 for BaPd$_2$As$_2$, ∼1.6 × 10^{-3} Å^2 for the low-T part of SrPd$_2$As$_2$, and ∼2.9 × 10^{-3} Å^2 for the high-T part of SrPd$_2$As$_2$.

IV. DISCUSSION

Here we discuss the possible implications of the present results. First, the MSRDs of As-Ba/Sr bonds in two compounds turned out to be quite similar for the two systems with small differences in the configurational disorder, larger in BaPd$_2$As$_2$. Therefore, the local mode involving alkaline earth metals may not have a direct impact on superconductivity of this system. On the other hand, we found two differences in MSRDs of the As-Pd bonds in BaPd$_2$As$_2$ and SrPd$_2$As$_2$: (i) the σ_0^2, describing static configurational disorder at low T and (ii) the Einstein temperature in high-T region. It seems that at the local scale, As-Pd correlations in SrPd$_2$As$_2$ goes through a lower Θ_E to higher Θ_E, i.e., a tendency from softer to harder local mode involving As-Pd correlations. The latter appears consistent with the measured trend of the Debye temperature by the specific heat. We stress that the static disorder (σ_0^2) in BaPd$_2$As$_2$ with T_c = 3.85 K is more than twice that in SrPd$_2$As$_2$ with T_c∼1 K. Naively one expects that higher disorder should suppress the transition temperature, but apparently this is not the case. Therefore, the configurational disorder may not be coming from any impurity but it should be associated with some kind of structural instability. Incidentally, as mentioned earlier, BaPd$_2$As$_2$ is known to have polymorphs [23–25], while SrPd$_2$As$_2$ stabilizes in the ThCr$_2$Si$_2$ structure. The first-principles calculations [33] suggest that nonsuperconducting CeMg$_2$Si$_2$ type is more stable than superconducting ThCr$_2$Si$_2$-type structure in BaPd$_2$As$_2$. The polymorphism is expected to induce larger configurational disorder and hence softer As-Pd bonds as described by lower Einstein temperature in BaPd$_2$As$_2$. On the other hand, SrPd$_2$As$_2$ does not have such polymorphism but it

goes through a local configurational transition at ∼160 K. Therefore, the superconductivity in BaPd$_2$As$_2$ is likely to be due to structural instability induced softening, which may lead to a strong electron-phonon coupling. It should be mentioned that the isostructural CaPd$_2$As$_2$ is superconducting with a T_c of 1.27 K and a Debye temperature of ∼276 K [20], and can be considered intermediate between BaPd$_2$As$_2$ and SrPd$_2$As$_2$ systems. The Einstein temperature of As-Pd bond in CaPd$_2$As$_2$, determined by temperature-dependent As K-edge EXAFS, is found to be ∼250 K (see the Supplemental Material [27]), consistent with the above arguments. Furthermore, the substitution of phosphorus for arsenic atoms suppresses the structural transition and raises T_c in a sister compound BaNi$_2$As$_{2-x}$P$_x$ [19]. It would be interesting to examine if a similar mechanism is valid for the increased T_c also in BaNi$_2$As$_{2-x}$P$_x$, which has to be clarified in future work.

V. CONCLUSION

In summary, we have studied the local structure of 122-type palladium-arsenides with different T_c's. A systematic temperature-dependent study has permitted us to underline marked differences in the mean square relative displacement of As-Pd bonds for both static disorder as well as in bond stiffness determined by the the related Einstein temperatures. BaPd$_2$As$_2$ has a relatively large static configurational disorder with a single Einstein temperature, while SrPd$_2$As$_2$ contains less static disorder with an anomalous change in the Einstein temperature, from softer to harder by raising temperature. We have argued that structural instability in BaPd$_2$As$_2$ is the likely reason for the existence of the soft phonon producing strong-coupling superconductivity.

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