

Absence of strong correlation in $\text{Li}_2\text{Pd}_3\text{B}$ T. Yokoya,¹ T. Muro,¹ I. Hase,² H. Takeya,³ K. Hirata,³ and K. Togano⁴¹Japan Synchrotron Radiation Research Institute(JASRI)/Spring-8, 1-1-1 Kouto, Sayo, Hyogo 679-5198, Japan²Nanoelectronics Research Institute, National Institute of Advanced Industrial Science and Technology, 1-1-4 Umezono, Tsukuba, Ibaraki 305-8568, Japan³National Institute for Material Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan⁴Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

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We use x-ray photoemission spectroscopy to study the electronic structure of new superconductor $\text{Li}_2\text{Pd}_3\text{B}$. Binding energies of the Pd $3p$ and $3d$ indicate valency that is intermediate between Pd metal ($0\pm$) and $\text{PdO}(2+)$, or effectively Pd $4d^9$ configuration. Comparison of satellite features in core level spectra of $\text{Li}_2\text{Pd}_3\text{B}$ with that of PdO suggests that a larger hybridization strength of $\text{Li}_2\text{Pd}_3\text{B}$ than that of PdO . The valence band spectrum is in excellent agreement with first principle band structure calculations, allowing us to ascribe the states at the Fermi level responsible for the superconductivity to be mainly Pd $4d$ hybridized with B $2p$ and Li $2p$. These observations indicate that correlation effects play a negligible role for the physical properties of the new superconductor.

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Very recently, Togano *et al.* reported that $\text{Li}_2\text{Pd}_3\text{B}$ is the first Pd-based superconductor among metal rich ternary borides with the transition temperature (T_c) of ~ 8 K.¹ $\text{Li}_2\text{Pd}_3\text{B}$ has been known to have a cubic structure (space group of $P4_332$) consisting of distorted Pd_6 octahedra centered by boron atoms, which share all vertices to form a unique three dimensional framework.² Due to the observation of superconductivity in $\text{Li}_2\text{Pd}_3\text{B}$, it is important to study the electronic structure of this compound.

One of the interesting questions is the role of electron-electron correlation effects in $\text{Li}_2\text{Pd}_3\text{B}$. Electron-electron correlation effects in $3d$ transition metal compounds have been studied extensively due to the fascinating physical properties, believed to originate from the correlation effects, e.g., high temperature superconductivity in cuprates,³ colossal magneto resistance in manganites,⁴ and high thermoelectric power in cobaltates.⁵ On the other hand, in $4d$ transition compounds, while the existence of correlation effects in Pd metal has already been reported in the early 1980s,^{6,7} importance of correlation effects in $4d$ electrons has increased especially after the discovery of superconductivity in Sr_2RuO_4 ,⁸ where superconducting properties due to the correlation effects has been reported. For $\text{Li}_2\text{Pd}_3\text{B}$, very recent theoretical studies⁹ have reported that the electronic properties of this compound are likely to be dominated by strong correlation effects due to the characteristic crystal structure, and proposed a possible realization of the first superconductivity described with a three-dimensional t - J model.

X-ray photoemission spectroscopy (PES) provides direct information on valence band electronic structure and core level spectral features and an estimate of physical parameters such as, charge transfer energy Δ , hybridization strength T , and on-site Coulomb potential U_{dd} .¹⁰ Therefore PES has been widely used for studying electron-electron correlation effects of $3d$ transition metal compounds and even of $4d$ transition metal compounds. In this paper, we show core level and valence band x-ray photoemission studies of the

new superconductor $\text{Li}_2\text{Pd}_3\text{B}$. We found that the satellite features in Pd $3p$ and $3d$ core levels are very small compared with those observed in Pd and PdO . We also found that the valence band spectrum of $\text{Li}_2\text{Pd}_3\text{B}$ can be well described by band structure calculations. These results indicate that electron correlation effects do not play a major role in $\text{Li}_2\text{Pd}_3\text{B}$. In addition, the chemical shift of the core level main peaks indicates that the valency of the Pd atom takes a value between $\text{Pd}(0\pm)$ and $\text{PdO}(2+)$, that is in effective proximity to the $4d^9$ configuration.

The polycrystalline $\text{Li}_2\text{Pd}_3\text{B}$ samples used in the present PES studies were prepared by an arc-melting process in order to attain high-density material, details of which are described in Ref. 1. The polycrystalline samples of Pd and PdO were also measured for comparison. We chose Pd and PdO for the two main reasons, (1) the valency of these compounds can be estimated from the chemical formula, $0\pm$ for Pd and $2+$ for PdO from an ionic picture, and (2) the valence band and core level PES spectra have been reported already for both materials.^{6,7,11} Also, detailed theoretical studies which provide values for the electronic structure parameters were available for PdO .¹² The core level and valence band spectra of Pd and PdO discussed latter are consistent with those reported previously and provide a good reference for the binding energies of core levels and the valence band electronic structure of $\text{Li}_2\text{Pd}_3\text{B}$. PES experiments were carried out on a Scienta SES200 analyzer using synchrotron radiation light (1300 eV) from beam line BL25SU at SPring-8 with an energy resolution of 250 meV. All the spectra were measured at 20 K under a base pressure of 3.6×10^{-8} Pa. Clean surfaces were obtained by *in situ* fractures. The cleanliness of the surfaces were checked by the absence of C $1s$ signals. We did not observe any spectral changes during the measurements of a few hours. The Fermi level (E_F) of the spectra was referenced to that of a gold film mounted close to the samples. Energy calibration has been performed using the known binding energy of Au $4f$ of a

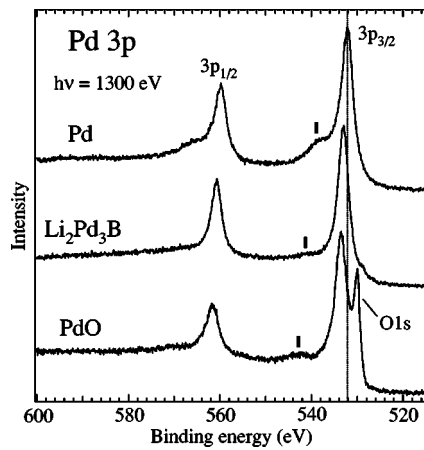


FIG. 1. Pd $3p$ core level spectrum of $\text{Li}_2\text{Pd}_3\text{B}$ compared with those of Pd and PdO measured with 1300 eV and at 20 K. The normalization was performed with the intensity of $3p_{3/2}$ peak.

gold film with respect to the Fermi edge, and it was further confirmed from the good correspondence to the reported binding energies of Pd $3d_{5/2}$ of PdO (336.8 eV).¹¹

To compare the experimental valence band spectra with theoretical studies, we also calculated the band structure of $\text{Li}_2\text{Pd}_3\text{B}$ with the standard full-potential augmented plane wave (FLAPW) method. We have carried out this calculation by using the computer code KANSAI-94 and TSPACE.¹³ For the exchange-correlation potential we adopted the local-density approximation (LDA), according to Gunnarson and Lundqvist.¹⁴ The calculation of the core states and the valence states are self-consistently carried out by the scalar-relativistic scheme.¹⁵ We used the experimentally found lattice constants and space group.² The muffin-tin radius of each atom is 2.2 bohr for Li, 2.0 bohr for Ni, and 1.4 bohr for B. The basis functions with the wave vector $|k+G| < K_{\text{max}} = 6.90a$, where k is a wave vector in the Brillouin zone (BZ) and G is a reciprocal-lattice vector used resulting in about 1360 basis LAPWs.

Figure 1 shows the Pd $3p$ core level spectra of Pd, $\text{Li}_2\text{Pd}_3\text{B}$, and PdO measured at 20 K with 1300 eV photon energy. The sharp peak at 530 eV for PdO is an O $1s$ core level. One may find a very weak structure at 529 eV in the $\text{Li}_2\text{Pd}_3\text{B}$ spectrum, which can be ascribed to an O $1s$ signal from Li_2O impurities. We observe Pd $3p_{1/2}$ and $3p_{3/2}$ spin-orbit splitting peaks with satellite features at higher binding energy, more evident for $3p_{3/2}$. The intensity of the satellite compared with that of the main peak depends on the compounds and shows the smallest intensity for $\text{Li}_2\text{Pd}_3\text{B}$. We also find that the binding energy of the main peak varies systematically. These spectral features can be studied in more detail with Pd $3d$ core level spectra because of the smaller linewidth of the core level spectra of Pd $3d$ than those of Pd $3p$.

In Fig. 2, we show the Pd $3d$ core level spectrum of $\text{Li}_2\text{Pd}_3\text{B}$, together with those of Pd and PdO, measured at 20 K with 1300 eV photon energy. Consistent with the Pd $3p$ spectra, all the three spectra show weak satellite features at higher binding energies to the main peaks of the Pd $3d_{5/2}$ and $3d_{3/2}$ spin-orbit doublet. The spectral line shape of the main

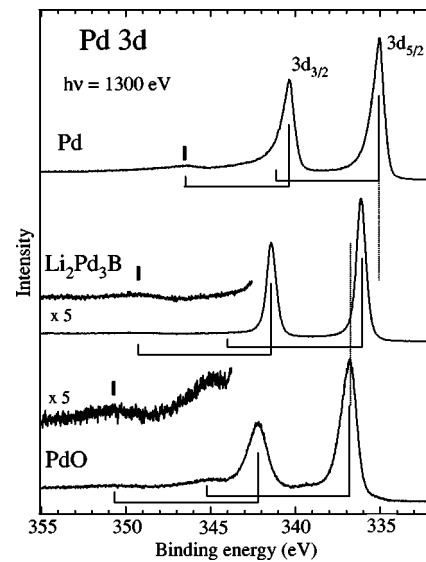


FIG. 2. Pd $3d$ core level spectrum of $\text{Li}_2\text{Pd}_3\text{B}$ compared with those of Pd and PdO measured with 1300 eV and at 20 K. The normalization was performed with the intensity of $3d_{5/2}$ peak.

peaks of $\text{Li}_2\text{Pd}_3\text{B}$ is very narrow and weakly asymmetric compared to that of Pd exhibiting an asymmetric tail at higher binding energy. Such an asymmetry of a core level spectrum are known to originate from a large density of states (DOS) at E_F .¹⁶ Indeed, Pd metal has a very large DOS at E_F , as reported previously¹⁸ and also observed in the present study as shown later. Therefore weak asymmetry of $\text{Li}_2\text{Pd}_3\text{B}$ indicates a marked decrease of the DOS at E_F compared with that of Pd metal. The symmetric line shape of PdO is consistent with the existence of a semiconducting gap at E_F in PdO. The narrower linewidth of $\text{Li}_2\text{Pd}_3\text{B}$ than that of PdO, which is ascribed to the localized nature of the core level as confirmed by theoretical studies,¹² implies the metallic nature of $\text{Li}_2\text{Pd}_3\text{B}$, consistent with transport measurements.¹ The narrow linewidth of $\text{Li}_2\text{Pd}_3\text{B}$, which can be fitted with a single Voigt function, also indicates that the different Pd-Pd bond lengths² do not influence the real valency of Pd.

We also found that the binding energy of the main peak shifts to higher binding energy in the sequence of Pd (335.1 eV), $\text{Li}_2\text{Pd}_3\text{B}$ (336.1 eV), and PdO (336.8 eV). The shift of a core level main peak reflects the chemical environment of an atom, and Pd and PdO are reference materials having Pd valence of $0\pm$ and $2+$, respectively. Therefore the location of the peak of $\text{Li}_2\text{Pd}_3\text{B}$ between those of Pd and PdO indicates that the valency of Pd atoms in $\text{Li}_2\text{Pd}_3\text{B}$ takes a value between $0\pm$ and $2+$, suggesting monovalency. It is noted that monovalent Pd is considered unstable in Pd compounds,¹⁷ though it is reported in clinoptilolite, which is the most abundant natural zeolite.¹⁸ In addition to a simple valence description, it is noted that the intermediate binding energy of Pd $3d$ core level for $\text{Li}_2\text{Pd}_3\text{B}$ is consistent with poorer screening in intermetallic $\text{Li}_2\text{Pd}_3\text{B}$ compared to Pd metal, and better screening compared to insulating PdO.

From the energy separation between the main peak and the satellite feature as well as the intensity of the satellite feature, important parameters describing physical properties

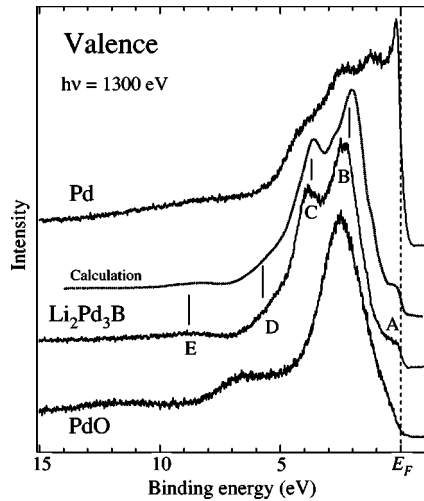


FIG. 3. Valence band spectrum of $\text{Li}_2\text{Pd}_3\text{B}$ compared with those of Pd and PdO measured with 1300 eV and at 20 K. The normalization was performed with the highest peak intensity in each spectrum. Valence band spectrum of $\text{Li}_2\text{Pd}_3\text{B}$ is compared with the band structure calculations broadened by an energy-dependent Lorentzian as well as a Gaussian (a dotted line, see text).

can be extracted.^{11,12} Here we compare the spectral features of $\text{Li}_2\text{Pd}_3\text{B}$ with those of PdO, where theoretical studies for the satellites have been already reported. For PdO, the satellites in the core level and valence bands are ascribed to charge transfer satellites due to a strong hybridization between Pd and O.¹² The satellite features in the Pd 3d PES spectrum of PdO could be described with an impurity Anderson model with a Pd 4d-O 2p charge transfer energy Δ of 5.5 eV, an on-site 4d correlation energy U_{dd} of 4.5 eV (a corresponding Coulomb potential between a core hole and a valence d electron of $Q=U_{dd}/0.7$), and a 4d-2p transfer integral $pd\sigma$ of 2.1 eV corresponding to the effective hybridization strength T [given by $\text{sqrt}(6) \times pd\sigma$] = 5.1 eV.¹² Using available theoretical results reporting a relation between the separation energy and intensity of satellites with respect to $2Q/T$ (Ref. 19) as a general trend, we understand that the very small satellite intensity in $\text{Li}_2\text{Pd}_3\text{B}$ compared to PdO suggests a smaller $2Q/T$ value for $\text{Li}_2\text{Pd}_3\text{B}$ than for PdO. This leads to a larger T value for $\text{Li}_2\text{Pd}_3\text{B}$ than for PdO assuming the same Q value for both compounds, consistent with the covalent bonding of Pd and B in $\text{Li}_2\text{Pd}_3\text{B}$ from the structural analysis.²

Figure 3 shows the valence band spectrum of $\text{Li}_2\text{Pd}_3\text{B}$, compared with Pd and PdO, normalized with the highest intensities of the valence bands. The valence band spectrum of $\text{Li}_2\text{Pd}_3\text{B}$ has smaller intensity features around E_F with a clear Fermi edge structure, two prominent peaks around 2.5 and 4.5 eV with a shoulder around 5.5 eV, and a weak feature around 9 eV. We label those features as A, B, C, D, E, respectively, as shown in Fig. 3. The valence band spectrum of Pd has the highest intensity at E_F with a Fermi edge and with a satellite feature around 8.5 eV ascribed to the two-hole bound states originating from electron correlation effects as confirmed from resonance PES studies.⁶ The valence band spectrum of PdO has structures around 2.5 eV and 6.5 eV with negligible intensity at E_F and a weak satellite

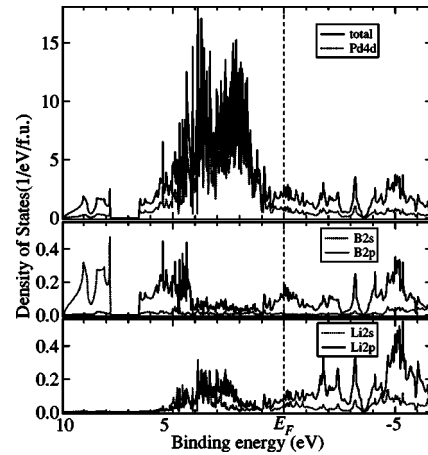


FIG. 4. Calculated total and partial DOS of $\text{Li}_2\text{Pd}_3\text{B}$.

feature around 12 eV. The intensity at E_F of $\text{Li}_2\text{Pd}_3\text{B}$ is smaller than that of Pd, while PdO is a semiconductor without a Fermi edge. Thus the valence band spectral intensities at E_F are consistent with the line shapes of the core-level spectra.

For $\text{Li}_2\text{Pd}_3\text{B}$, we also found a weak higher binding energy feature around 9 eV in the valence band spectrum, like the satellites in Pd and PdO. The weak features in Pd and PdO valence band spectra are not present in one-electron band structure calculations.^{11,20} To confirm the origin of the 9 eV feature of $\text{Li}_2\text{Pd}_3\text{B}$, we compare the experimental valence band spectra of $\text{Li}_2\text{Pd}_3\text{B}$ with a calculated spectrum added with an integrated background, as shown in Fig. 3. The calculated spectrum (a dotted line) was obtained by carrying out an energy-dependent Lorentzian broadening²¹ and a Gaussian broadening (FWHM of 0.25 eV) of the band structure calculation results after taking ionization cross sections²² into account. We find that the prominent valence band features, the small intensity around the E_F region, as well as the weak feature around 9 eV can all be reproduced with the broadened calculated DOS fairly well. This indicates that the weak feature at 9 eV of $\text{Li}_2\text{Pd}_3\text{B}$ is derived from the structure in DOS and has a different origin compared to satellites in Pd and PdO. To investigate the character of observed electronic structures, we look at the calculated partial DOS shown in Fig. 4. We find A is hybridized states of Pd 4d, B 2p, and Li 2p with larger Pd 4d contribution, and the structures B and C are dominant Pd 4d states. The structure D has Pd 4d and B2p characters. The weak feature E is B 2s states hybridized with Pd 4d states. The states at E_F per formula unit of $\text{Li}_2\text{Pd}_3\text{B}$ is 32.6 (states/Ry/f.u.), smaller than that of MgCNi_3 , which is a superconductor with CNi_6 octahedra (qualitatively similar to the BPd_6 octahedra in $\text{Li}_2\text{Pd}_3\text{B}$) and is reported to have a sharp peak in DOS near E_F giving rise to a ferromagnetic instability.²³ The smaller DOS at E_F of $\text{Li}_2\text{Pd}_3\text{B}$ suggests weaker ferromagnetic correlations. The good agreement with the experimental and calculated valence bands indicates that the electronic structure of $\text{Li}_2\text{Pd}_3\text{B}$ can be well described by the one particle approximation, and therefore electron correlation effects may not play an important role for physical properties. Therefore, the superconductivity of $\text{Li}_2\text{Pd}_3\text{B}$ is most likely phonon mediated. We hope

the present results motivates further thermodynamic and transport measurements to confirm the origin of superconductivity in this Pd-based superconductor.

In conclusion, we have performed x-ray photoemission spectroscopy of the new superconductor $\text{Li}_2\text{Pd}_3\text{B}$ to study the electronic structure and possible correlation effects proposed theoretically. The Pd $3p$ and $3d$ core level spectra show a satellite feature at 7.8 eV higher binding energy from the main peak with very small intensity compared with that of Pd metal and PdO. The valence band spectrum shows a prominent two-peak structure at 2.5 and 4.5 eV with smaller intensity near E_F and a weak feature around 9 eV, consistent with the first-principles band structure calculations. The comparison also shows that states near E_F , which is respon-

sible for the superconductivity, are derived from Pd $4d$ orbitals hybridized with B $2p$ states. These results indicate correlation effects play a negligible role in the new superconductor. In addition, the location of the core level main peaks of $\text{Li}_2\text{Pd}_3\text{B}$ between those of Pd and PdO suggests that the valency of Pd atoms in $\text{Li}_2\text{Pd}_3\text{B}$ takes a value between $0\pm$ and $2+$.

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