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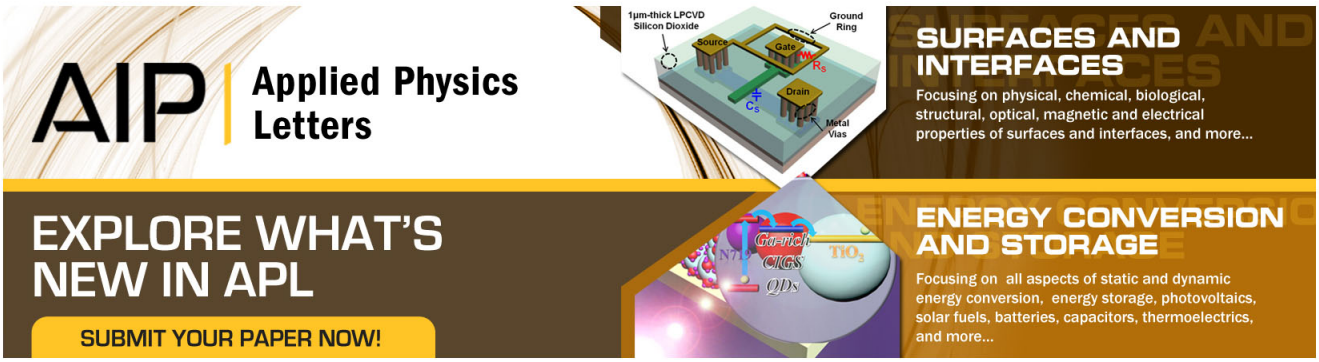

# Origin of ground state anomaly in $LaB_6$ at low temperatures

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The authors investigate the temperature evolution of the electronic structure of $LaB_6$, a widely used material as high brightness cathode, using UV photoemission spectroscopy with state-of-the-art energy resolution (1.4 meV) and band structure calculations in order to probe the origin of low temperature anomaly in its physical properties. Comparison of experimental and theoretical results suggests that electron correlation is not significant in this system and that the electronic states in the vicinity of the Fermi level, $\epsilon_F$, possess mixed character. High resolution spectra at different temperatures $T$ reveal a pseudogap for $T<100$ K, which evolves gradually with the decrease in temperature. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2459779]

Rare-earth hexaborides have drawn significant attention in recent times due to the many exotic properties exhibited by these systems. For example, $CeB_6$ is known to be a dense Kondo system, $SmB_6$ is one of the first Kondo insulator discovered, signature of superconductivity is observed in $LuB_6$ and $(Y,La)B_6$, etc. Recently, an unexpected ferromagnetism with high Curie temperature is observed in La-doped $CaB_6$ compounds.[1] All these properties evidently indicate significant promises in both fundamental issues and technological applications. Among all these hexaborides, $LaB_6$ has got wide applications as a highly efficient thermionic emitter because of its low work function, low rate of evaporation, and a congruently vaporizing nature.[2,3] It is used as an electron beam source for various purposes such as microfabrication of integrated circuits, various spectroscopic tools, x-ray source, etc. Interestingly, $LaB_6$ exhibits superconductivity[4] ($T_c \sim 0.1$ K) and quantum interference effect.[5]

$LaB_6$ forms a cubic structure with La occupying the body centered position of the cube and $B_6$ octahedra at the corners. The temperature dependence of resistivity is linear at high temperatures (up to 1000 K) as that of metals.[6] However, at low temperatures ($T<15$ K), it becomes anomalous, exhibiting an increase in resistivity with the decrease in temperature.[7] Anomaly is also observed in other bulk properties such as thermal conductivity,[8] thermoelectric power,[9] specific heat,[10] etc. Such anomaly has been attributed to various effects such as electron-phonon coupling, phonon drag, different dynamics of La and B sublattices, etc. However, the origin of such effect is still unclear.

In this letter, we report our results on the evolution of the electronic structure with temperature using photoemission spectroscopy. High energy resolution (1.4 meV) enabled us to probe subtle changes in the spectrum near $\epsilon_F$. Spectra above 100 K resemble behavior of a simple metal, consistent with the bulk properties. However, the spectra below 100 K exhibit anomalous evolution with the appearance of a pseudogap at $\epsilon_F$.

A high quality sample, $LaB_6$ was prepared by arc-melting technique using high purity B crystalline powder and predried $La_2O_3$ in pure argon atmosphere. After a few meltings with additional B, good quality $LaB_6$ formed. The sample was characterized using the powder x-ray diffraction (XRD). The sharp and intense XRD patterns and absence of impurity feature ensure high quality of the sample. The estimated lattice parameter, 4.157 Å, is identical to the literature value. No magnetic phase transition was observed on these samples. Photoemission measurements down to 15 K were carried out using a state-of-the-art photoelectron spectrometer equipped with SES2002 Gammadata Scienta analyzer and monochromatic photon sources. The energy resolution was 1.4 meV for He I and 300 meV for x-ray photoemission measurements. The sample surface was cleaned by scraping in a vacuum of $3\times10^{-11}$ torr and reproducibility was confirmed after each trial of scraping. Low temperature measurements were performed using an open cycle He cryostat and the sample temperature was measured by mounting the sensor close to the sample.

The electronic band structure calculations were carried out using state-of-the-art full potential linearized augmented plane wave (FLAPW) method within the local density approximations using WIEN2K software.[11] The lattice parameters were obtained from the analysis of XRD patterns. The muffin-tin radii for La and B were set to 1.376 and 0.847 Å, respectively. The convergence was achieved considering 512 $k$ points within the first Brillouin zone. The error bar for the energy convergence was set to $<0.25$ meV/f.u. and the charge convergence was achieved to be less than $10^{-3}$ electronic charge.

In Fig. 1, we show the calculated density of states (DOS) and compare with the experimental valence band spectrum obtained using He I excitation source. The spectrum at 30 K in Fig. 1(a) exhibits a flat intensity down to about 2 eV binding energy and an intense peak spreading over 2–5.5 eV. The experimental spectrum corresponds well to the calculated total DOS shown in Fig. 1(b). The higher binding energy region is primarily contributed by the B $2p$ partial DOS as evident from Fig. 1(c). La $5d$ and $4f$ shown in Fig. 1(d) exhibit negligible contributions at these energies. However, the flat intensity in the vicinity of $\epsilon_F$ has almost comparable contributions from B $2p$, La $5d$, and La $4f$ states, indicating strong mixing of these electronic states. The spectrum close to $\epsilon_F$ exhibits a sharp Fermi cutoff with significantly large intensity and large bandwidth. Thus, the corresponding electronic states have an essentially itinerant character with neg-

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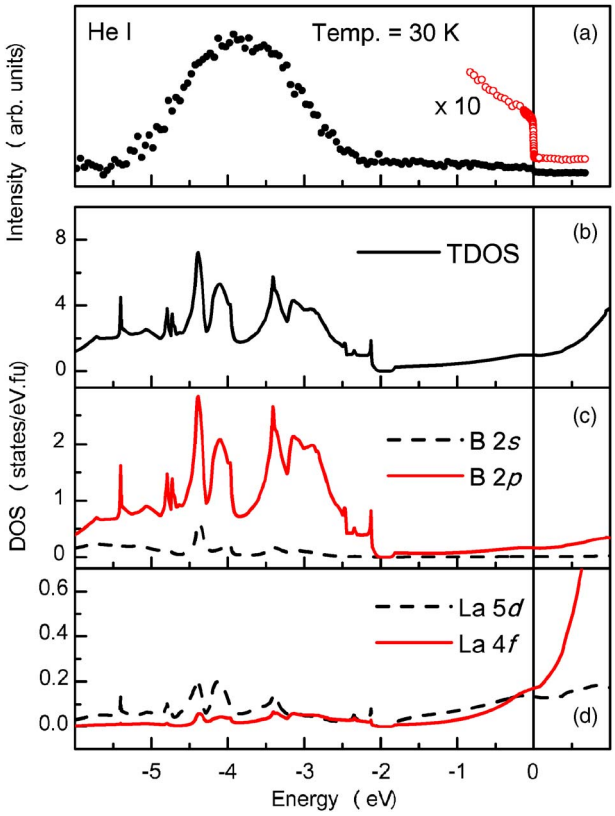


FIG. 1. (Color online) (a) He I spectrum at 30 K. Open circles represent shifted and rescaled intensity near $\epsilon_F$. FLAPW results of (b) total DOS, (c) B 2*s* and 2*p* partial DOSs, and (d) La 5*d* and 4*f* partial DOSs.

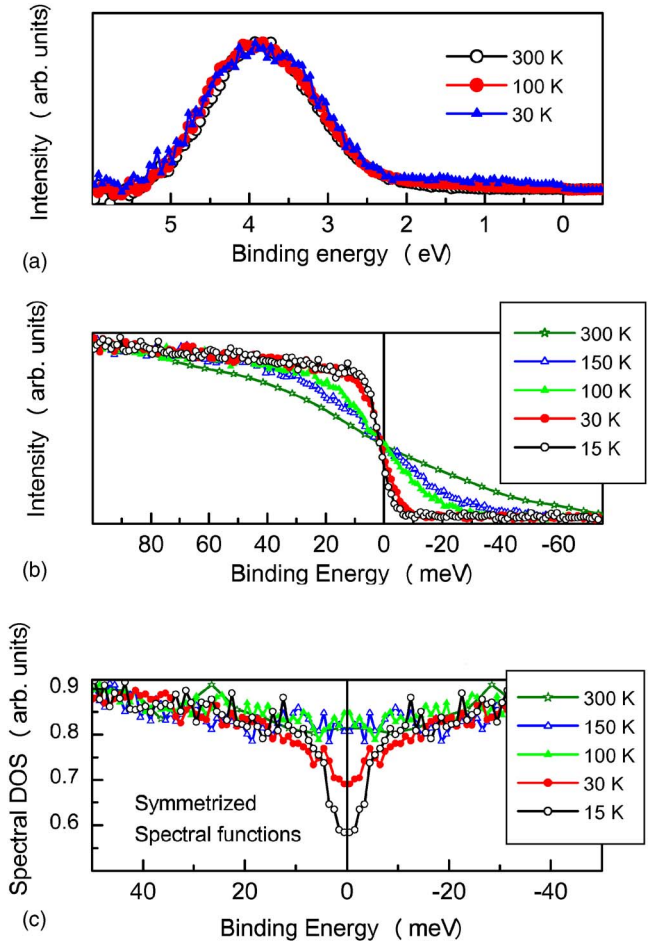


FIG. 2. (Color online) (a) He I valence band spectra at different temperatures. (b) High resolution spectra in the vicinity of $\epsilon_F$. (c) SDOS obtained by symmetrizing the spectra shown in (b).

ligible influence from electron-electron Coulomb repulsions.

The temperature evolution of the valence band is shown in Fig. 2(a) by overlapping the spectra collected at 30, 100, and 300 K. A normalization of the intensity at about 4 eV leads to an identical shape of the spectra at all the temperatures. This indicates that the spectral features at higher binding energies remain almost the same. However, there is a gradual decrease in intensity in the flat part (binding energy $<2$ eV) with the increase in temperature. The electronic transport involves electrons close to the Fermi level. Thus, we investigate the temperature evolution of the spectra in the vicinity of $\epsilon_F$ with very high energy resolution. All the spectra are normalized at 100 meV binding energy and shown in Fig. 2(b). All the spectra above 100 K cross each other at $\epsilon_F$, indicating a behavior expected for a Fermi-liquid system. Interestingly, the spectra below 100 K exhibit a gradual decrease in intensity at $\epsilon_F$ with the decrease in temperature. In order to probe the effect of temperature more efficiently, we have calculated the spectral density of states (SDOS) using the symmetrization method as described below.

Photoemission intensity can be expressed as[12,13] $I(\epsilon) = \int g(\epsilon_1)F(\epsilon_1,T)L^e(\epsilon_1,\epsilon_2)L^h(\epsilon_2,\epsilon_3)G(\epsilon_3,\epsilon)d\epsilon_1 d\epsilon_2 d\epsilon_3$, where $g$ and $F$ are the SDOS and Fermi distribution function, respectively. The Lorentzians, $L^e$ and $L^h$, represent the electron and hole lifetime broadenings, which are insignificant near $\epsilon_F$. The Gaussian $G$ represents the instrumental resolution broadening. Since the energy resolution is very high in the UV photoemission measurements, the broadening due to $G$ is also negligible. Thus, considering the flat DOS near $\epsilon_F$ [$|\epsilon - \epsilon_F| < 100$ meV; see Fig. 1(b)], $S(\epsilon) = I(\epsilon) + I(-\epsilon)$ provides a good representation of the SDOS, $g(\epsilon)$. The thus obtained SDOSs are shown in Fig. 2(c). The SDOSs at higher temperatures ($T > 100$ K) exhibit similar line shape and intensity as expected for a simple metal. However, evolution of SDOS below 100 K is unusual, exhibiting a sharp dip at 30 K. The dip increases further at 15 K as evident in the figure.

The observation of a dip at $\epsilon_F$ indicates the appearance of a pseudogap at low temperatures. In order to investigate if such dip is related to any structural change and/or change in Madelung potential at La and/or B sites, we plot the B 1*s* and La $3d_{5/2}$ core level spectra in Fig. 3 at different temperatures employing high energy resolution. La $3d_{5/2}$ spectra in Fig. 3(a) exhibit an intense feature around 838 eV binding energy. The line shape is similar to that observed before using high quality single crystalline samples.[14] The small asymmetry at higher binding energies may be related to a trace of surface oxygen. B 1*s* spectrum in Fig. 3(b) exhibits a single feature with full width at half maximum $<1$ eV, again confirming the high quality of the samples. Interestingly, the spectra at low temperatures exhibit similar line shape in both La $3d_{5/2}$ and B 1*s* spectra. This suggests that the appearance of the pseudogap at low temperatures may have a different origin.

A pseudogap has been observed in various other systems, such as normal phase of high temperature superconductors,[15] charge density wave systems,[12] etc. In these systems, it was predicted that electron-phonon coupling plays a significant role in the occurrence of a

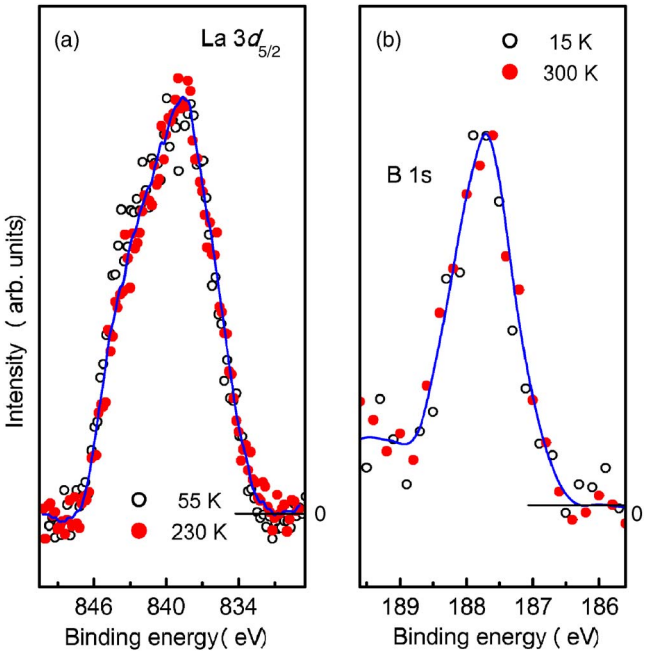


FIG. 3. (Color online) (a) La $3d_{5/2}$ and (b) B 1*s* spectra of $LaB_6$, excited by monochromatic Al $K\alpha$ radiation, at different temperatures. Solid line represents a guide for the eyes.

pseudogap.[16] In $LaB_6$, the boron lattice forms a rigid framework via covalent bonding among the $B_6$ octahedra at the corners of the cube. This leaves a large void space at the body center (radius ~3 Å) to accommodate La ion, which has a relatively small ionic radius (~1.3 Å). This leads to a possibility of large excursions of La ions from their equilibrium positions at finite temperatures. Since, the electronic states in the vicinity of $\epsilon_F$ have a strongly mixed character (almost comparable contributions from B 2*p*, La 5*d*, and La 4*f* states), scattering of electrons due to the lattice vibrations will have significant influence in the bulk properties. Thermal conductivity[8] and thermoelectric power[9] below 15 K indeed exhibit anomaly, which has been predicted to be due to electron scattering from low frequency phonons. Phonon spectra of $LaB_6$ exhibit peaks with a high density of states at low energies[17–19] corresponding to translational and rotational modes of nondeforming $B_6$ units. Thus, low energy phonon modes are probably responsible for the observed pseudogap and the anomalous physical properties of $LaB_6$ at low temperatures. While these results provide significant insight in understanding the low temperature anomaly in $LaB_6$, further studies are required to probe the origin of the pseudogap.

In summary, we have investigated the electronic structure of $LaB_6$ down to 15 K using very high resolution photoemission spectroscopy and the state-of-the-art band structure calculations. Photoemission spectra appear to be very similar to the calculated results, which suggests that the electron correlation effects are not significant. Electronic states close to $\epsilon_F$ have mixed character. Evolution of the spectral DOS exhibits a pseudogap below 100 K as observed in other materials such as high temperature superconductors, charge density wave systems, etc.

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