## Boron ${}^{10}B-{}^{11}B$ isotope substitution as a probe of mechanism responsible for the record thermionic emission in LaB<sub>6</sub> with the Jahn–Teller instability

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Materials with a low work function find diverse applications in electronic devices (see, e.g., [1]). Due to the high electronic emissivity, melting point, mechanical and chemical stability, rare earth (RE) hexaborides  $RB_6$ (R is a metal ion) are among the most promising compounds for high-power electronic technology. The crystal structure of RE hexaborides has the bcc CaB<sub>6</sub>-type with Pm3m-O<sup>h</sup><sub>1</sub> symmetry and may be represented as a rigid network of covalent-bound octahedral-shaped B<sub>6</sub> complexes with RE ions embedded in the large size cavities formed by  $B_6$  clusters [2]. It was found that in the higher borides  $RB_{12}$ , development of the Jahn–Teller (JT) instability in the boron  $B_{12}$  clusters leads to emergence of a collective excitation that involves corresponding JT-mode and produces both the rattling vibration of the RE atom and modulation of electronic density in the conduction band [3, 4]. It was suggested that the effects arise from the complex interaction among lattice, orbital and charge carriers subsystems, and that their striking consequence is the conversion of large fraction of conduction electrons into a non-equilibrium state with very strong scattering. This phenomenon was also proposed [5] to cause a record low thermal emission work function of LaB<sub>6</sub> ( $\varphi \approx 2.66 \,\text{eV}$  [6]). Since the boron network is essentially involved in the formation of the collective mode, here our goal was to explore in detail its evolution and in this way the evolution of the conduction electrons state upon isotopic substitution in the boron sublattice of several isotopically substituted  $La({}^{10}B_x{}^{11}B_{1-x})_6$  solid solutions.

High quality single crystals of  $\text{La}({}^{10}\text{B}_{x}{}^{11}\text{B}_{1-x})_{6}$ with x = 0, 0.189 ( $\text{La}^{\text{nat}}\text{B}_{6}$ ), 0.5, 0.75 and 1 were grown as described in [7]. The infrared (IR) reflectivity spectra  $R(\nu)$  were measured at room temperature at frequencies  $\nu = 40-8000 \text{ cm}^{-1}$  employing a Bruker Vertex 80V Fourier-transform spectrometer. With the J. A. Woollam V-VASE ellipsometer, spectra of optical conductivity  $\sigma(\nu)$  and dielectric permittivity  $\varepsilon'(\nu)$  of the samples were directly determined at 3700–35000 cm<sup>-1</sup>. DC conductivity  $\sigma_{\text{DC}}$  and Hall resistivity of the same samples were measured using a standard five-probe method.

Though the obtained reflectivity spectra of all crystals are typical for a good metal, when fitting the spectra we observe significant deviations from the Drude conductivity model [8] above a few hundred  $\rm cm^{-1}$ . We formally model these deviations by introducing, in addition to the Drude free carrier term, a minimal set of Lorenztzian-shaped excitations, see Fig. 1. The results we obtain here for the  $La({}^{10}B_x{}^{11}B_{1-x})_6$ are qualitatively similar to those deduced from the infrared experiments on hexaborides  $\mathrm{Gd}_{x}\mathrm{La}_{1-x}\mathrm{B}_{6}$  [5], and dodecaborides  $LuB_{12}$  [3] and  $Tm_{0.189}Yb_{0.811}B_{12}$  [4]. In [3–5], the origin of the excitations was associated with cooperative-dynamic Jahn-Teller effect in the boron sub-lattices, which produces quasi-local vibrations (rattling modes) of loosely bound RE ions, leading to "modulation", via hybridization of 5d-conduction electrons

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Fig. 1. (Color online) Contributions observed in the infrared conductivity spectra of  $La({}^{10}B_x{}^{11}B_{1-x})_6$  single crystals from Drude-type electrons in the conduction band (Drude electrons) and collective peak (non-equilibrium electrons). The temperature is T = 300 K

and 2p-boron states, of the conduction band along certain crystallographic directions. We believe that similar mechanisms are responsible for the observed peak in the conductivity spectra of  $La({}^{10}B_x{}^{11}B_{1-x})_6$  crystals. More specifically, because of double orbital degeneracy of the highest occupied molecular orbital, the B<sub>6</sub> molecules are JT active and their structure is thus labile due to JT distortions. In such cases, certain intrinsic structural defects lift the degeneracy and lower the B<sub>6</sub> symmetry. We suggest that reinforcement of the structural JT liability in the boron sub-lattice of RB<sub>6</sub> due to cooperative dynamic JT effect may be considered as the cause of large amplitude displacements of La atoms in oversized  $B_{24}$ cages, resulting in both, distortions and symmetry lowering of the *bcc* lattice and emergence of the rattling modes attributed to quantum motion of the La ions in the double-well potentials with the minima separated by  $\sim 0.5$  Å. As a consequence of the quantum motion (zero temperature vibrations) of La-ions, dramatic changes of the 5d-2p hybridization of electron states should occur in hexaborides resulting in (i) the formation of a collective mode (overdamped oscillator) and (ii) the emergence of non-equilibrium (hot) charge carriers.

We suggest that the effect of the discovered nonequilibrium (hot) electrons that make up the majority in LaB<sub>6</sub> (up to  $\approx 70$  %) can be considered as the key factor responsible for the extraordinarily low work function of thermoemission in this compound. Taking into account that the found highest values of the oscillator strength, dielectric contribution and damping of collective peak are observed for La<sup>nat</sup>B<sub>6</sub> which is characterized by strongest disorder in the boron sublattice, we conclude that this disorder is among the important factors determining unique thermoemission characteristics of the LaB<sub>6</sub>. To summarize, the analysis of the optical conductivity spectra of several isotopically mixed  $La({}^{10}B_x{}^{11}B_{1-x})_6$  solid solutions shows that in addition to the Drude free carrier spectral component there exists an intensive collective excitation. We suggest that the presence in the conduction band of non-equilibrium (hot) electrons involved in the formation of this excitation is at the origin of the extraordinary low electronic work function in LaB<sub>6</sub>. The finding provides a fresh look at the mechanisms responsible for highest thermoemission characteristics of materials.

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