

Collective infrared excitation in the cage-glass LuB₁₂

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Rare earth borides RB_{12} (R – metal ion) form a family of compounds that are in the focus of both, fundamental and applied research [1, 2]. The R ions are centered in the large cuboctahedral B_{24} cages formed by six neighboring B_{12} units. Large difference between the size of the B_{24} cage and the radius of the metal ion leads to the formation of loosely bound state of the heavy ion in the rigid B_{24} cage resulting in low energy (14–18 meV [3]) dispersion-less phonon modes. Sorting through various metals leads to wide variety of phenomena observed in the compounds making them promising for applications and stimulating studies of their fundamental physical properties. We apply infrared (IR) spectroscopy for the search of low-energy excitations and, thus, for the study of the nature of the ground state in LuB₁₂ which is the most representative member of the dodecaborades family. High quality single crystals Lu^{*N*}B₁₂ (N : natural, 10 and 11) were grown by inductive zone melting technique [4]. At frequencies $\nu = 40\text{--}8000\text{ cm}^{-1}$, room temperature reflection coefficient $R(\nu)$ spectra were measured using Vertex 80V Fourier-transform spectrometer. With the J.A. Woollam V-VASE ellipsometer, optical parameters of the samples were determined at $3700\text{ cm}^{-1}\text{--}35000\text{ cm}^{-1}$, and reflection coefficients were calculated and merged with the infrared reflectivity spectra. The data from [5] were used to extend the spectra up to $\approx 400000\text{ cm}^{-1}$. The obtained broad-band $R(\nu)$ spectra were analyzed together with the DC conductivity of the same samples measured using four-terminal scheme. No significant difference in the spectra of the Lu^{nat}B₁₂, Lu¹⁰B₁₂, and Lu¹¹B₁₂ samples were detected. Below we present the analysis of the spectra obtained for the Lu^{nat}B₁₂ crystal.

As is seen from Fig. 1a, typically metal-like reflectivity spectrum of Lu^{nat}B₁₂ cannot be described within the

Drude conductivity model alone (dashed line). This indicates that there are additional mechanisms governing the electronic properties of the compound. We model these mechanisms (solid line in Fig. 1a) with Lorentzian terms expressed as $\sigma^*(\nu) = \frac{0.5\Delta\varepsilon\nu_0^2\nu}{\nu\gamma + i(\nu_0^2 - \nu^2)}$ ($\Delta\varepsilon$ is dielectric contribution, ν_0 is resonance frequency, γ is damping constant). Fig. 1b presents the obtained conductivity spectrum of Lu^{nat}B₁₂ (solid line) together with five additive contributions. The L3 and L4 resonances are characterized by reasonable dielectric contributions, $\Delta\varepsilon \approx 2\text{--}5$, and moderate damping constants, $\gamma/\nu_0 \approx 0.7\text{--}0.8$, and thus could be associated with electronic transitions between the conduction band states near Fermi level. On the contrary, the excitations L1 and L2 are rather unusual in having unexpectedly large dielectric contributions $\Delta\varepsilon$, especially the L1 peak ($\Delta\varepsilon \approx 8000 \pm 4000$). We believe that these terms do not represent separate mechanisms but rather are two components needed to formally reproduce the measured reflectivity spectrum with the excitation that has a non-Lorentzian lineshape, see lines in Fig. 1b labeled with “L1+L2”. It is known that the splitting of triply degenerate highest occupied molecular orbitals of the B₁₂ molecule is at the origin of its Jahn–Teller (JT) activity and correspondent distortions [6]. In general, the JT distortions are non-polar. However, their IR activity have *via* coupling to a polar mode. In [6] arguments are presented in favor of cooperative dynamic JT effect in the boron sublattice of LuB₁₂ that induces the rattling mode of lutetium ion in the double-well potential. Coupling to this quasilocal mode can activate the IR activity of the JT vibrations. Due to hybridization of 5d orbitals of lutetium and 2p states of boron, the charge carriers in the conduction band are also expected to be involved in the formation of the collective excitation.

We can estimate the concentration of conduction electrons involved in the free carrier conductivity and

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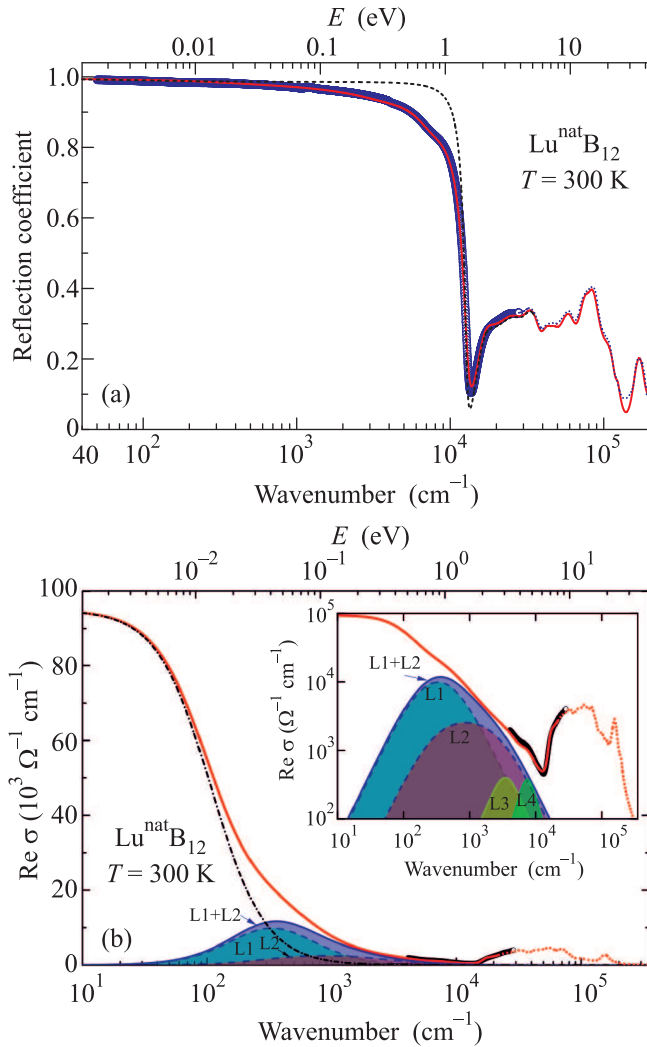


Fig. 1. (Color online) (a) – Room temperature reflectivity spectrum of the Lu^{nat}B₁₂ single crystal. Solid line: fit using the Drude conductivity model and four Lorentzians. Dashed line: fit using the Drude conductivity model alone. (b) – Dynamic conductivity of the Lu^{nat}B₁₂ single crystal obtained by fitting the reflectivity spectrum (solid line in panel (a)). The Drude free-carrier contribution to the conductivity is shown separately with a dashed line. The insert shows four Lorentzian contributions in details

in the formation of the collective excitation, using an expression $\nu_{\text{pl}}^2 = ne^2(\pi m^*)^{-1} = f$ for the plasma frequency ν_{pl} and oscillator strength f (here n is concentration of free electrons, e – their charge, m^* – effective mass). With the Drude plasma frequency $\nu_{\text{pl}} = 21700 \text{ cm}^{-1}$ and $m^* = 0.5m_0$ [7], we obtain $n_{\text{D}} = 2.6 \cdot 10^{21} \text{ cm}^{-3}$. From the combined oscillator strength of L1 and L2 terms, $f_{\text{L1+L2}} = 1.3 \cdot 10^9 \text{ cm}^{-2}$, we get the concentration of the charge carriers participating in the formation of the collective excitation $n_{\text{L1+L2}} = 7.2 \cdot 10^{21} \text{ cm}^{-3}$, and the total concentration of charges in the

conduction band $n_{\text{tot}} = n_{\text{D}} + n_{\text{L1+L2}} = 9.8 \cdot 10^{21} \text{ cm}^{-3}$. The obtained value coincides with the concentration of Lu-ions $n(\text{Lu}) = 9.6 \cdot 10^{21} \text{ cm}^{-3}$ in LuB₁₂ assuming that every lutetium ion delivers one electron in the conduction band. According to the above estimates, about $\approx 70\%$ of charges in the conduction band are involved in the formation of the collective excitation. Similar estimates for Lu¹⁰B₁₂ and Lu¹¹B₁₂ give the percentage of $\approx 70\%$ and $\approx 80\%$, respectively.

In conclusion, room temperature infrared (40–35000 cm^{-1}) spectra are measured of high quality crystals Lu^NB₁₂, N : natural, 10, 11. Broad non-Lorentzian shaped excitation with characteristic frequency in the range 200–1000 cm^{-1} and unusually large dielectric contribution $\Delta\epsilon = 8000$ has to be considered in order to model the measured spectra. No effect of isotopic composition on parameters of the excitation is detected. It is suggested that the origin of the excitation is connected with a collective dynamic Jahn–Teller mode of the boron (B₁₂) clusters that is coupled to rattling vibrations of caged lutetium ions and charge carriers in the conduction band.

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