Anomalous boron isotope effects on electronic structure and lattice dynamics of CuB$_2$O$_4$††

Rea Divina Mero, Chun-Hao Lai, Chao-Hung Du and Hsiang-Lin Liu

Copper metaborate had a unique crystal structure and exhibited noteworthy magnetic phase transitions at 21 and 10 K. The electronic structure and lattice dynamics of copper metaborate Cu$^{11}$B$_2$O$_4$ single crystals were investigated and compared with the optical properties of CuB$_2$O$_4$ to assess the boron isotope effect. The optical absorption spectrum at room temperature revealed two charge-transfer bands at approximately 4.30 and 5.21 eV with an extrapolated direct optical band gap of 3.16 ± 0.07 eV. Compared with the data on CuB$_2$O$_4$, the electronic transitions were shifted to lower energies upon the replacement of a heavier boron isotope. The band gap was also determined to be lower in Cu$^{11}$B$_2$O$_4$. Anomalies in the temperature dependence of the optical band gap were observed below 21 K. Furthermore, 38 Raman-active phonon modes were identified in the room-temperature Raman scattering spectrum of Cu$^{11}$B$_2$O$_4$, which were also observed in CuB$_2$O$_4$ with a shift to lower frequencies. No broadening caused by isotopic changes was observed. As the temperature decreased, phonon frequencies shifted to higher wavenumbers and the linewidth decreased. Anomalous softening in the Raman peaks below 21 K was also revealed.

I. Introduction

Isotopes are atoms with the same number of protons and electrons but a different number of neutrons. Isotopes differ in mass but are chemically identical. Early theoretical works have established that only properties dependent on nuclear mass are altered in isotopes. The most obvious instance of such dependence is the mass-dependent effect on the harmonic lattice vibrational frequency, which is represented as $1/\sqrt{m}$. Isotope-dependent properties also include properties that are affected by changes in unit cell volume, atomic hopping mobility, and anharmonicities—for example, thermal conductivity, thermal expansion, melting temperature, nuclear magnetic resonance, and superconducting phase transition temperature. The electronic band structures were once believed to remain identical in isotopes under such changes. However, this belief has been justified only by atomic-spectra data. Evidence has revealed that in the case of molecular spectra, the effect of mass involves differences between isotopes through the mechanism of electron–phonon coupling. The presence of an isotope effect is an effective indicator of phonon-mediated superconductivity in materials and constitutes support for the Bardeen–Cooper–Schrieffer (BSC) theory of superconductivity.

Studies on the isotope effects of different materials are crucial in clarifying these materials’ properties, especially when investigating phonons and their interactions. For instance, isotope labeling in the study of graphene provided direct evidence that the growth mechanism is substrate dependent. Furthermore, isotopic substitution in diamond ($^{12}$C and $^{13}$C) and in diamond-type semiconductors (Si and Ge) was noted to increase the indirect electronic energy gap because of isotopically induced changes in lattice volume and electron–phonon interaction. Isotopic shifts in the superconducting gap and binding energy of high $T_c$ superconductors were used to analyze the nature of the electron–lattice coupling and elucidate the electron pairing mechanism in high $T_c$ superconductors. Isotope shifts were demonstrated to be an essential test of superconductivity.

BCS superconductors with electron–phonon coupling are expected to have a total isotope effect coefficient of 0.5. The isotope effect coefficient $\alpha$, is defined as $\alpha = -d \ln T_c/d \ln M$ where $M$ is the atomic mass. The coefficient $\alpha$ was measured in the superconductor MgB$_2$. An analysis of the magnetization data revealed a large boron isotope effect, which indicated superconductivity in this material. The extrapolated $T_c$ exhibited at least 1 K difference between the $^{11}$B and $^{10}$B samples. The isotope effects from Mg were small compared with the boron isotope effects, which clearly indicated that phonons associated with boron vibrations are crucial in superconductivity. The findings further revealed superconductivity in transition metal diborides (i.e. NbB$_2$) and borocarbides (e.g., YNi$_2$B$_2$C and LiNi$_2$B$_2$C). The natural abundance of stable boron isotopes...
facilitated the assessment of isotopic effects, despite a lack of suitable isotopes for the other elements.

Although isotopic effects are well studied in high $T_c$ superconductors, research on isotopic shifts in phase transition of magnetic materials is scarce. Copper metaborate, CuB$_2$O$_4$ exhibited complex magnetic properties that have been extensively investigated. Canted antiferromagnetic ordering occurred below 21 K followed by a commensurate-to-incommensurate magnetic structure at 10 K.\textsuperscript{12,13} CuB$_2$O$_4$ crystallizes in a unique noncentrosymmetric $I\bar{4}2d$ structure which contains BO$_4$ tetrahedrons with Cu$^{2+}$ ions between them. These Cu$^{2+}$ ions are located in two inequivalent crystallographic positions (see ESI Fig. 1†). Various studies reported that CuB$_2$O$_4$ exhibited the unusual magnetoelectric properties and complex magnetic, electric and optical coupling phenomenon.\textsuperscript{14–17} Notably, CuB$_2$O$_4$ containing $^{11}$B and $^{10}$B isotopes exhibited no significant shifts in the phase transition temperatures, as demonstrated by the nearly identical magnetic susceptibility illustrated in Fig. 1.

This finding contrasted with the large isotope effects identified in high $T_c$ superconductors. Studies on antiferromagnetic cuprates have also revealed negligible oxygen isotope effects in the magnetic phase transition temperatures.\textsuperscript{18,19} The optical features of antiferromagnetic copper metaborate under isotopic substitution remain unexplored. In this paper, the boron isotope effects in copper metaborate were optically and vibrationally investigated. We analyzed the dependence of the electronic transition energy on the boron isotope mass as obtained from spectroscopic ellipsometry. Our measurements revealed notable isotope effects in the charge-transfer excitation energies and the direct band gap. The Raman isotopic shifts accorded with the calculated shifts because of changes in isotopic mass, which enabled the identification of the boron-related vibrations. Anomalies in the band gap, the peak energy of charge-transfer bands, and Raman-active phonon modes of Cu$^{11}$B$_2$O$_4$ were observed at 21 K, confirming the spin–charge–lattice interaction in this material. These results elucidate the intricate lattice dynamics and the influence of the isotope effects on the electronic states, which are vital for the isotope engineering of optoelectronic and photonic devices.

Fig. 1 The temperature dependence of magnetic susceptibility measured in an applied magnetic field of 50 Oe for $H \perp [001]$ of single-crystal Cu$^{11}$B$_2$O$_4$ and CuB$_2$O$_4$.

Fig. 2 Optical absorption spectra of Cu$^{11}$B$_2$O$_4$ and CuB$_2$O$_4$ at room temperature. The dashed lines illustrate the best fit with the Lorentz function. Inset illustrates the direct band gap analysis of Cu$^{11}$B$_2$O$_4$ and CuB$_2$O$_4$ at 300 K.

Fig. 3 Temperature-dependent optical absorption spectra of Cu$^{11}$B$_2$O$_4$. Inset illustrates the temperature-dependent band gap energy. The vertical dashed lines denote the magnetic phase transition temperatures at 10 and 21 K.
II. Experimental details

The flux method was used to grow Cu_{11}B_{2}O_{4} single crystals. The crystals with a (110) surface used in this study had approximate dimensions of 3 × 3 × 2 mm³. For each batch, crystals were characterized using X-ray powder diffraction (see ESI Fig. 2 and 3) and magnetization measurements (Fig. 1). The X-ray powder diffraction profile, the Rietveld refinement pattern, and the difference pattern for Cu_{11}B_{2}O_{4} confirmed the formation of a single crystal. The lattice constants and the sample's crystallographic data, obtained from the Rietveld refinement, accorded with those reported in the literature on CuB_{2}O_{4}. The magnetization data revealed low-temperature magnetic phase transitions at 21 and 10 K. Above 21 K, Cu_{11}B_{2}O_{4} exhibited paramagnetism. Between 21 and 10 K, the material revealed commensurate antiferromagnetism. Below 10 K, the material transitioned to incommensurate antiferromagnetism. The spectroscopic ellipsometry measurements were performed under angles of incidence of 60°–75° using a J. A. Woollam Co. M-2000U ellipsometer over a spectral range of 0.73–6.42 eV. For temperature-dependent measurements between 4.5 and 300 K, the ellipsometer was equipped with a Janis ST-400 ultrahigh-vacuum cryostat. Only a single angle of incidence was possible because of the 70° angle of the two cryostat windows. The micro-Raman scattering spectra were measured in a backscattering configuration using a laser with an excitation wavelength of 488 nm and a SENTERRA spectrometer with a 1024-pixel-wide charge-coupled detector. The spectral resolution using this spectrometer was typically lower than 0.5 cm⁻¹, and the laser power was lower than 4.0 mW to avoid heating effects. The polarized Raman scattering spectra were obtained in backscattering geometry with incident and scattered lights parallel to the [110] and [110] directions, denoted as Y₀ and Y₀, respectively. Three scattering configurations were thus obtained: Y_0(ZZ)Y_0, Y_0(X'X')Y_0, and Y_0(ZX')Y_0. In this Porto notation, the direction parallel to the crystallographic

Fig. 4  Temperature dependence of the peak energy, linewidth, and normalized intensity of the (a) 4.30 and (b) 5.21 eV optical transitions. The vertical dashed lines denote the magnetic phase transition temperatures at 10 and 21 K.
was determined to be 3.16. The band gap of a normal solid, which holds contributions from direct and indirect transitions, can be estimated from the electronic transitions from the 2p states of the oxygen ions to the 3d states of the copper ions. The direct band gap \( E_g \) of \( \text{Cu}^{11}\text{B}_2\text{O}_4 \) estimated from the absorption coefficient \( a(E) \), was determined to be 3.16 \( \pm \) 0.07 eV, as displayed in the inset of Fig. 2. The band gap of a normal solid, which holds contributions from direct and indirect transitions, can be estimated from the absorption coefficient \( a(E) \) as follows:

\[
a(E) = A(E - E_{g,\text{dir}})^{0.5} + B(E - E_{g,\text{indir}} + E_{ph})^2.
\]

where \( E_{g,\text{dir}} \) and \( E_{g,\text{indir}} \) are the magnitudes of direct and indirect gaps, respectively; \( E_{ph} \) is the emitted (absorbed) phonon energy, and \( A \) and \( B \) are constants.

The temperature-dependent optical absorption spectra of \( \text{Cu}^{11}\text{B}_2\text{O}_4 \) are displayed in Fig. 3. As the temperature decreased, the absorption peaks displayed a gradual increase in their intensity and peak position, whereas the linewidth narrowed. The temperature-dependent band gap is displayed in the inset of Fig. 3. The band gap decreased as the temperature decreased consistent with the anomalous behavior of \( \text{CuB}_2\text{O}_4 \). We find \( \frac{dE_g}{dT} = 6.41 \times 10^{-4} \text{ eV K}^{-1} \) which is a little lower compared to \( \text{CuB}_2\text{O}_4 \) but still in the same order of magnitude with those found for \( \text{MAPbI}_3 \). Below 21 K, the band gap exhibited a gradual increase as the temperature decreased. This anomaly and discontinuity were correlated with the magnetic ordering at this temperature point. These findings demonstrate that the shifts were caused by spin–charge interactions, rather than changes induced by thermal contraction or alterations in the unit cell volume.

We examined the peak energy, linewidth, and normalized intensity of the fitted Lorentzian peaks displayed in Fig. 4. Above 21 K, the energy peak and linewidth exhibited minimal temperature variation, whereas the peak intensity increased as the temperature decreased. Anomalies near the magnetic phase transition temperature were evident in \( \text{Cu}^{11}\text{B}_2\text{O}_4 \). Below 21 K, the peak position shifted to higher energies and the linewidth decreased for two absorption peaks. These phenomena were similar to those observed in \( \text{CuB}_2\text{O}_4 \). The temperature dependences of \( \text{Cu}^{11}\text{B}_2\text{O}_4 \) and \( \text{CuB}_2\text{O}_4 \) were somewhat similar. The hardening as well as damping and intensity changes of the absorption bands below 21 K were approximately of the same magnitude in both samples. A notable isotope effect was indicated by the shift of the absorption band toward lower energies in \( \text{Cu}^{12}\text{B}_2\text{O}_4 \) (4.30 and 5.21 eV) compared with \( \text{CuB}_2\text{O}_4 \) (4.49 and 5.83), as illustrated in Fig. 2. This isotopic shift is similar to those observed in \( \text{CuB}_2\text{O}_4 \) but still in the same order of magnitude with those found for \( \text{MAPbI}_3 \). The temperature-dependent optical absorption spectra of \( \text{Cu}^{11}\text{B}_2\text{O}_4 \) are displayed in Fig. 3. As the temperature decreased, the peak energy and linewidth exhibited minimal temperature variation, whereas the peak intensity increased as the temperature decreased. Anomalies near the magnetic phase transition temperature were evident in \( \text{Cu}^{11}\text{B}_2\text{O}_4 \). Below 21 K, the band gap exhibited a gradual increase as the temperature decreased. This anomaly and discontinuity were correlated with the magnetic ordering at this temperature point. These findings demonstrate that the shifts were caused by spin–charge interactions, rather than changes induced by thermal contraction or alterations in the unit cell volume.

\[
\left( \frac{\partial E_g}{\partial M_e} \right)_T = \left( \frac{\partial E_g}{\partial M_e} \right)_T^{\text{EP}} + \left( \frac{\partial E_g}{\partial M_e} \right)_T^{\text{TE}}.
\]

The first term is a contribution from the electron–phonon interaction (EP). The second term stems from lattice constant changes and is labeled as TE since it has similar behavior with thermal lattice expansion. Moreover, the second term can be extended in terms of the isotopic mass. The changes in isotopic mass translate to the changes in pressure within the crystal structure and a relative change in the lattice constants. We have observed the negligible changes in the X-ray powder diffraction profiles of \( \text{CuB}_2\text{O}_4 \) and \( \text{Cu}^{13}\text{B}_2\text{O}_4 \) (see ESI Fig. 2†), and thus ruled out the contributions from the second term. We speculate that the negative isotope effect in \( \text{Cu}^{11}\text{B}_2\text{O}_4 \) may arise from the changes in the electronic band structures induced by the d-electron–phonon interactions. The degeneracy of the d states

\[
\left( \frac{\partial E_g}{\partial M_e} \right)_T = \left( \frac{\partial E_g}{\partial M_e} \right)_T^{\text{EP}} + \left( \frac{\partial E_g}{\partial M_e} \right)_T^{\text{TE}}.
\]
of the Cu ions in the upper valence band was partially lifted and mixed with the p states of B ions under a crystal field. This p–d hybridization was verified in CuB₂O₄ and accounted for its magnetoelectric properties. Substitution of a heavier B isotope in Cu₁₁B₂O₄ may enhance the p–d hybridization through the electron–phonon interactions and raise the maximum of the valence band, resulting in a decrease of the band gap. Similar phenomenon has been confirmed in energy band transition studies on other Cu containing compounds such as CuCl, CuBr, and CuInS₂. Further theoretical calculations of the electronic band structures of Cu₁₁B₂O₄ and CuB₂O₄ are needed to clarify the origin of this negative isotope effect.

B. Vibrational properties

Fig. 5 displays the room-temperature unpolarized Raman scattering spectrum of Cu₁₁B₂O₄. The phonon peaks were fitted using a standard Lorentzian profile. The spectrum comprised 38 first-order Raman-active phonon modes, which is the same number of phonon modes observed in CuB₂O₄. We previously identified 12A₁, 12B₂, and 14E modes in polarized Raman scattering measurements of CuB₂O₄. The inset of Fig. 5 illustrates the polarized Raman scattering spectra of Cu₁₁B₂O₄ in different configurations. The phonon peaks and their assigned symmetries are summarized in Table 1. We assigned the phonon peaks of Cu₁₁B₂O₄ to the same atomic vibrations assigned to CuB₂O₄. Low-frequency modes below 200 cm⁻¹ were rotational vibrations of Cu ions. Peaks higher than 200 cm⁻¹ but lower than 400 cm⁻¹ were modes associated with changes in the bond angles that tilted and bent the BO₄ tetrahedra. These phonon peaks were coupled to the Cu–O vibrations, which were distributed over the entire frequency range. The highest vibrations from Cu–O stretching modes were observed in the range of 400–900 cm⁻¹. The Cu–O

| Phonon frequency (cm⁻¹) | Symmetry | Δω (cm⁻¹) (ω₁₄₆ – ω₁₁₂) | ω₁₁₂/ω₁₄₆ | Assignment |
|------------------------|----------|--------------------------|-------------|------------|
| ω₁     142             | E        | 1                        | 0.990       | Cu atom oscillations |
| ω₂     151             | B₂       | 1                        | 0.993       |             |
| ω₃     192             | E        | 2                        | 0.992       |             |
| ω₄     209             | B₂       | 2                        | 0.993       |             |
| ω₅     222             | E        | 1                        | 0.994       | BO₄ tetrahedron tilting and bending coupled to Cu–O vibrations |
| ω₆     250             | A₁       | 2                        | 0.993       |             |
| ω₇     264             | B₂       | 1                        | 0.995       |             |
| ω₈     284             | B₂       | 1                        | 0.995       |             |
| ω₉     318             | B₂       | 2                        | 0.995       |             |
| ω₁₀    333             | A₁       | 2                        | 0.994       |             |
| ω₁₁    391             | E        | 1                        | 0.997       |             |
| ω₁₂    401             | A₁       | 1                        | 0.997       | Cu–O stretching/Jahn–Teller modes |
| ω₁₃    426             | B₂       | 1                        | 0.997       |             |
| ω₁₄    443             | E        | 2                        | 0.997       |             |
| ω₁₅    471             | A₁       | 2                        | 0.997       |             |
| ω₁₆    491             | B₂       | 1                        | 0.998       |             |
| ω₁₇    505             | E        | 1                        | 0.998       |             |
| ω₁₈    539             | E        | 3                        | 0.995       |             |
| ω₁₉    572             | E        | 2                        | 0.997       |             |
| ω₂₀    587             | B₂       | 2                        | 0.996       |             |
| ω₂₁    596             | A₁       | 2                        | 0.997       |             |
| ω₂₂    614             | B₂       | 2                        | 0.996       |             |
| ω₂₃    677             | E        | 3                        | 0.995       |             |
| ω₂₄    692             | B₂       | 4                        | 0.995       |             |
| ω₂₅    704             | A₁       | 2                        | 0.997       |             |
| ω₂₆    726             | A₁       | 2                        | 0.997       |             |
| ω₂₇    744             | B₂       | 3                        | 0.996       | Mixed Cu–O, B–O vibrations |
| ω₂₈    785             | A₁       | 2                        | 0.998       |             |
| ω₂₉    885             | E        | 3                        | 0.996       |             |
| ω₃₀    896             | A₁       | 4                        | 0.996       |             |
| ω₃₁    907             | E        | 4                        | 0.995       | Pure B–O stretching |
| ω₃₂    926             | B₂       | 39                       | 0.959       |             |
| ω₃₃    959             | E        | 23                       | 0.977       |             |
| ω₃₄    974             | E        | 21                       | 0.979       |             |
| ω₃₅    988             | A₁       | 23                       | 0.977       |             |
| ω₃₆    1004            | B₂       | 59                       | 0.944       |             |
| ω₃₇    1057            | A₁       | 58                       | 0.948       |             |
| ω₃₈    1107            | A₁       | 16                       | 0.985       |             |
stretched modes in the range 700–900 cm⁻¹ were mixed with the B–O vibrations, whereas modes above 900 cm⁻¹ were considered to have occurred mainly from B–O stretching vibrations. Our experimental results of the phonon modes demonstrated good agreement with the theoretical ab initio calculations by Pisarev et al. 22 The data on the isotope boron effects, summarized in Table 1, elucidates the coupling involved in the phonon vibrations occurring primarily between Cu and B.

The Raman scattering spectrum of Cu¹⁰B₂O₄ was shifted to lower frequencies by at least one wavenumber compared with the Raman scattering spectrum of CuB₂O₄, as illustrated in Fig. 5. The softening of the frequencies of the heavier isotope mass was expected based on the simple harmonic model. In this case, Cu¹⁰B₂O₄ contains the heavier ¹¹B isotope compared with the ¹⁰B isotope in CuB₂O₄. The simple harmonic model is expressed as follows:

\[ \omega_{11B} = \omega_{10B} \sqrt{\frac{m_{10}}{m_{10} + \Delta m}} \]  

(3)

where \( \omega_{11B} \) represents the Raman frequency of the ¹¹B enriched sample, \( \omega_{10B} \) represents the frequency of the ¹⁰B sample, \( m_0 \) is the mass of the ¹⁰B, and \( \Delta m \) is the mass difference between the ¹¹B and ¹⁰B isotopes. Using this model, we calculated a ratio of \( \frac{\omega_{11B}}{\omega_{10B}} = 0.95 \) which accords with the observed redshift in the high-frequency Raman modes (Table 1). For frequencies below 900 cm⁻¹, we obtained \( \frac{\omega_{11B}}{\omega_{10B}} \) ratio of approximately 0.99. For frequencies above 900 cm⁻¹, the ratio was approximately 0.95 for \( \omega_{11B} \) and \( \omega_{17B} \), with the largest possible shift of 59 cm⁻¹. These modes are thus confirmed to be pure B vibrations. Modes below 200 cm⁻¹ exhibited the smallest shift in frequency because these peaks mostly originated from the Cu atom vibrations. The shifts in frequency, which were 200–900 cm⁻¹, exhibited differences of approximately 1–2 cm⁻¹. This finding indicates that the boron atoms influence these vibrational modes. High-frequency peaks above 900 cm⁻¹ exhibited more obvious softening in the phonon frequencies shifting by at least 16 cm⁻¹. We observed a clear double peak constituted by \( \omega_{17B} \) (1057 cm⁻¹) and \( \omega_{38B} \) (1107 cm⁻¹) because of the nonuniform shift in the peaks, which contrasted with the overlapping peaks observed in CuB₂O₄. The phonon frequency \( \omega_{18B} \) most likely resulted from oxygen stretching vibrations. We surmise this because it is not heavily shifted with isotopic substitution, similar to other phonon modes in this range.

The temperature-dependent unpolarized Raman scattering spectra of Cu¹¹B₂O₄ are displayed in Fig. 6. For normal anharmonic solids, the phonon frequency should increase and the linewidth should decrease as the temperature decreased. The Raman scattering spectrum at 10 K was fitted with 38 Lorentz oscillators (inset of Fig. 6). The phonon modes of the ¹¹B enriched sample were redshifted. However, no significant changes in the linewidth were observed, and temperature-dependent behavior was similar to that of CuB₂O₄. An examination of the intense peak at 333 and 443 cm⁻¹ is displayed in Fig. 7. Data for all other phonon modes were reported in ESI Fig. 4.‡ Above 21 K, the peak frequencies and linewidth behaved according to the anharmonic model represented by the thin solid lines in Fig. 7. The anharmonic model is expressed as follows: ²⁴

\[ \omega(T) = \omega_0 + A \left( 1 + \frac{2}{\exp\left( \frac{\Theta}{T} \right) - 1} \right) \]  

(4)

\[ \gamma(T) = \gamma_0 + B \left( 1 + \frac{2}{\exp\left( \frac{\Theta}{T} \right) - 1} \right) \]  

(5)

where \( \omega_0 \) is the intrinsic frequency of the optical phonon mode, \( \gamma_0 \) is the linewidth broadening caused by defects, \( \Theta \) is the Debye temperature, and \( A \) and \( B \) are the anharmonic coefficients. The values of the fitting parameters are summarized in Table 2. Negative values of \( A \) indicate that the phonon frequency increased as the temperature decreased, whereas positive values of \( B \) for the linewidth indicates the contrary. The Debye temperature obtained for different phonon frequencies was within 400–600 K in the same range observed for CuB₂O₄. The anharmonic model revealed that the Raman phonon modes were mostly temperature independent at low temperature. Below the magnetic ordering temperature (21 K), deviations from the anharmonic model remained evident for all intense peaks. A gradual softening of up to 0.3 cm⁻¹ was observed in Cu¹¹B₂O₄.
Soften in the phonon peaks at the magnetic phase transition temperature usually indicates the spin–phonon interactions. The sensitivity of the phonon frequency to correlations of spins of nearest-neighbor pairs can be expressed as follows:\(^\text{34}\)

\[
\Delta \omega(T) = \lambda \langle S_i \times S_j \rangle
\]  

where \(\lambda\) is the spin–phonon coupling constant and \(\langle S_i \times S_j \rangle\) is the nearest neighbor spin correlation. The \(\langle S_i \times S_j \rangle\) can be estimated from \(4 \left( \frac{M_{\text{sub}}(T)}{M_s} \right)^2\) where \(M_{\text{sub}}(T)\) is the sublattice magnetization per magnetic ion and \(M_s\) is the saturation magnetization. The factor of 4 was based on the number of nearest neighbors.\(^\text{34}\) As displayed in Fig. 8, the sublattice magnetization data\(^\text{13}\) obtained from a prior study scaled well with the shift in phonon frequency. Using this correlation, we extracted the spin–phonon coupling constant \(\lambda\) for Cu–O stretching phonon modes tabulated in Table 3.

A slightly higher value of the spin–phonon coupling constant was obtained for Cu\textsuperscript{11}B\textsubscript{2}O\textsubscript{4} compared with the values obtained for CuB\textsubscript{2}O\textsubscript{4}. This slight difference coincides with the quantitative estimate of the spin–phonon coupling \(\lambda\) using a simplified
The lattice model proposed by Sushkov et al., which can be calculated as follows:

\[
\lambda = \frac{2\alpha^2 J}{m_\omega}
\]  

(7)

where \( m \) is the mass of the magnetic ion, \( \omega \) is the mode frequency, \( J \) is the nearest neighbor exchange coupling constant, and \( \alpha \) can be calculated using \( \alpha = 2z/3a_B \) (\( a_B \) is the Bohr radius and \( z \) is the nearest neighbor coordination number). Eqn (7) is inversely related to the phonon frequencies.

The phonon frequencies of Cu\(_{11}\)B\(_2\)O\(_4\) were redshifted from those of CuB\(_2\)O\(_4\), which causes the spin–phonon coupling to increase. Considering only the nearest neighbors (\( z = 4 \)), we obtained \( \alpha = 5.04 \) Å\(^{-1}\). Moreover, we estimated the exchange coupling constant using

\[
J = 3k_B\Theta_{cw}/zS(S + 1)
\]  

(8)

where \( k_B \) is the Boltzmann constant, \( \Theta_{cw} \) is the Currie–Weiss temperature, and \( S \) is the spin angular moment. We used \( z = 4 \), \( S = 1/2 \), and \( \Theta_{cw} = 21 \) K to get \( J = 0.95 \) meV. Therefore, we obtained a quantitative spin–phonon coupling constant \( \lambda \approx 0.037 \) cm\(^{-1}\) which is slightly higher than the values obtained for CuB\(_2\)O\(_4\) (\( \lambda \approx 0.035 \) cm\(^{-1}\)) and scales well with the empirical spin–phonon coupling \( \lambda \) tabulated in Table 3.

### IV. Summary

We used spectroscopic ellipsometry and Raman scattering spectroscopy to study the electronic structure and lattice dynamics of Cu\(_{11}\)B\(_2\)O\(_4\) single crystals. We assessed the boron isotope effects by comparing the results obtained with the results for CuB\(_2\)O\(_4\). The room-temperature optical absorption spectrum of Cu\(_{11}\)B\(_2\)O\(_4\) revealed the occurrence of charge-transfer transitions from the 2p states of O to the 3d states of Cu at approximately 4.30 and 5.21 eV, which were lower than the values measured for CuB\(_2\)O\(_4\). The direct optical band gap was determined to lower in Cu\(_{11}\)B\(_2\)O\(_4\) (extrapolated at 3.16 ± 0.07 eV). The temperature-dependent band gap and the peak energy of charge-transfer bands exhibited anomalies through the canted antiferromagnetic ordering temperature at 21 K. The

### Table 3 Spin–phonon coupling constant of Cu\(_{11}\)B\(_2\)O\(_4\) obtained for Cu–O stretching related modes

| Mode frequency (cm\(^{-1}\)) | \( \lambda \) (cm\(^{-1}\)) |
|-----------------------------|---------------------------|
| \( \omega_{11} \)       | 0.032                     |
| \( \omega_{12} \)       | 0.033                     |
| \( \omega_{13} \)       | 0.038                     |
| \( \omega_{14} \)       | 0.038                     |
| \( \omega_{15} \)       | 0.032                     |
| \( \omega_{16} \)       | 0.030                     |
| \( \omega_{17} \)       | 0.030                     |
| \( \omega_{18} \)       | 0.030                     |
| \( \omega_{19} \)       | 0.030                     |
| \( \omega_{20} \)       | 0.030                     |
| \( \omega_{21} \)       | 0.030                     |
| \( \omega_{22} \)       | 0.030                     |
| \( \omega_{23} \)       | 0.030                     |
| \( \omega_{24} \)       | 0.030                     |
| \( \omega_{25} \)       | 0.030                     |
| \( \omega_{26} \)       | 0.030                     |
| \( \omega_{27} \)       | 0.030                     |
| \( \omega_{28} \)       | 0.030                     |
| \( \omega_{29} \)       | 0.030                     |
| \( \omega_{30} \)       | 0.030                     |

Fig. 8 Temperature dependence of the shift in the phonon frequency of (a) 333 and (b) 443 cm\(^{-1}\) modes plotted against the normalized square of the magnetic susceptibility. The vertical dashed line denotes the magnetic phase transition temperatures at 21 K.
Raman frequencies of Cu$^{11}$B$_2$O$_4$ shifted lower, whereas the linewidth exhibited no significant change. The extent of the isotopic shift in frequencies accorded with the inverse square root dependence of the mean atomic mass. The temperature dependence of the phonon frequency, linewidth, and normalized intensity exhibited anomalies near 21 K. The temperature dependence of the Cu–O stretching modes also exhibited an anomalous softening at a temperature of less than 21 K. The spin–phonon coupling constant, $\lambda$, were slightly higher than Cu$_2$O$_4$, estimated to be 0.030–0.038 cm$^{-1}$.

Author contributions

H. L. L. conceived the research and was responsible for the experimental design. R. D. M. conducted the experiments. C. H. L. and C. H. D. were responsible for the sample preparation. R. D. M. and H. L. L. drafted the paper. All contributing authors have discussed the results and provided the comments regarding the manuscript.

Data availability statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflicts of interest

The authors declare no competing interests.

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