Temperature-dependent optical properties of CuFeO$_2$ through the structural phase transition†

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Delafossite CuFeO$_2$ has recently attracted considerable attention because of its complex phase transitions and practical applications. A thorough understanding of the optical properties of CuFeO$_2$ is essential for its further exploration. In this paper, we investigated the temperature-dependent optical properties of CuFeO$_2$ single crystals through Raman scattering spectroscopy and spectroscopic ellipsometry. The room temperature Raman scattering spectrum exhibited six phonon modes at approximately 352, 509, 692, 1000, 1052, and 1171 cm$^{-1}$. Upon cooling across 11 K, which is the rhombohedral to monoclinic structural phase transition temperature, a softening of the $E_3$-symmetry 352 cm$^{-1}$ mode and a hardening of the $A_{1g}$-symmetry 692 cm$^{-1}$ mode were observed. Moreover, analysis of the temperature-dependent real part of the dielectric function and direct band gap revealed anomalies at 11 K. These results demonstrate a profound connection between the structural phase transition, lattice dynamics, and electronic structure of CuFeO$_2$ and provide key information for CuFeO$_2$-based device design and fabrication.

1. Introduction

In the delafossite CuMO$_2$ ($M$ = IIIA, transition metal elements) series, CuFeO$_2$ is a well-known p-type semiconductor.$^{1,2}$ CuFeO$_2$ has attracted attention as a p-type transparent conducting oxide that could be used for applications of anodes in lithium ion batteries.$^{1-3}$ Recent technological developments in CuFeO$_2$ and other ferrite materials have focused on the energy conversion and storage, photocatalytic degradation of pollutants in water and air, and solar fuels production via water splitting and CO$_2$ reduction.$^{4-9}$ In addition to device applications, the special magnetic structure and structural phase transition of CuFeO$_2$ are an attractive issue in fundamental science. CuFeO$_2$ has two Néel temperatures. The first Néel temperature ($T_{N1}$) of CuFeO$_2$ is near 16 K, where the magnetic structure is changed from paramagnetic to collinear-incommensurate antiferromagnetic without any structural phase transition. The second Néel temperature ($T_{N2}$) is near 11 K, where the magnetic structure is changed to collinear-commensurate antiferromagnetic without any structural phase transition. Further, the lattice structure is changed from the rhombohedral to monoclinic phase below $T_{N2}$.10,11

Numerous studies have examined the structural, magnetic, vibrational and optical properties of CuFeO$_2$. Fig. 1 illustrates the room temperature crystal structure and structural and magnetic phase transitions of CuFeO$_2$. Ye et al.10 and Kimura et al.11 have presented the X-ray and neutron diffraction patterns of CuFeO$_2$ powders and single crystals. At room temperature, CuFeO$_2$ has a rhombohedral structure with the $R3m$ space group, with lattice parameters of $a = b = 5.982$ Å, $c = 17.163$ Å, $\alpha = \beta = 90^\circ$, and $\gamma = 120^\circ$.10,11 In the low temperature phase, it has a monoclinic lattice structure with the $C2/m$ space group, with lattice parameters of $a = 11.574$ Å, $b = 3.040$ Å, $c = 5.982$ Å, and $\beta = 154^\circ$.10 The $c$-axis compression reduced the bond length of Cu–O from 1.83805 Å (17 K) to 1.7863 Å (4 K). The structural phase transition also induced the compression of FeO$_6$ octahedral units. The bond length of Fe–O was split from 2.024 Å (17 K) to 2.0225 and 2.0255 Å (4 K).10 Temperature-dependent magnetic susceptibility revealed that the material became antiferromagnetic below $T_{N1} = 16$ K.12 Furthermore, in neutron diffraction results, CuFeO$_2$ displayed an incommensurate antiferromagnetic structure at approximately $T_{N1} = 16$ K.10,11 A commensurate spiral antiferromagnetic structure was exhibited at temperatures below $T_{N2} = 11$ K, and the crystal structure changed to the monoclinic phase.10,12 The unique magnetoelastic effect of this material enables functional devices to be realized.13-15

Salke et al.16 and Pavunnya et al.17 have studied the temperature-dependent Raman scattering spectra of CuFeO$_2$
single crystals and polycrystalline pellets down to the liquid nitrogen temperature. They determined that the temperature-dependent peak positions of the in-plane Fe–O vibration $E_g$ mode and the out-of-plane Cu–O vibration $A_{1g}$ mode could be predicted using theoretical anharmonic models. Salke et al. further investigated the pressure-dependent Raman scattering spectra of CuFeO$_2$ single crystals up to 23 GPa. They reported that the $E_g$ and $A_{1g}$ modes exhibited hardening with an increase in pressure. When the pressure was higher than 18 GPa, the $E_g$ mode split and exhibited an obvious softening, indicating a structural phase transition. Aktas et al. presented the temperature-dependent Raman scattering spectra of CuFeO$_2$ and CuCrO$_2$ single crystals. They reported that both the $E_g$ and $A_{1g}$ modes exhibited a softening within 1 cm$^{-1}$ below 14 K, which was associated with a pseudo-proper ferroelastic transition occurring in multiferroic materials. Wheatley et al. prepared CuFeO$_2$ thin films with thickness of 21 nm and 75 nm through pulse laser deposition. Using transmittance and diffuse reflectance spectra, they found a direct band gap of approximately 1.3 to 1.4 eV at room temperature. Roble et al. presented the room temperature diffuse reflectance spectroscopy of bulk 3R-CuFeO$_2$. They found a direct band gap of approximately 1.3 eV. Eyert et al. reported the partial densities of states of the rhombohedral phase CuFeO$_2$. They determined that rhombohedral CuFeO$_2$ is a semiconductor with an optical band gap of 1.15 eV; the band gap value of the monoclinic CuFeO$_2$ is 0.05 eV.

Most studies have focused on room temperature optical measurements and were limited to powder samples. The temperature-dependent optical properties of CuFeO$_2$ single crystals have remained unexplored. In this study, we combined Raman scattering spectroscopy and spectroscopic ellipsometry to explore the temperature-dependent lattice dynamics and electronic structure of CuFeO$_2$ single crystals. Furthermore, we investigated the correlation between the temperature-dependent optical response of CuFeO$_2$ and its structural phase transition. Our results reveal the intricate relationship between charge-lattice interactions and structural phase transition in CuFeO$_2$.

II. Experimental methods

The single-phase CuFeO$_2$ powders were prepared by the solid-state reaction method. The starting materials used in the study were reagent-grade Cu$_2$O (99.9%) and Fe$_2$O$_3$ (99.9%). The CuFeO$_2$ was prepared directly from mixing Cu$_2$O and Fe$_2$O$_3$ in stoichiometric ratio and then calcined under N$_2$ atmosphere at 1123 K with following the formula of Cu$_2$O + Fe$_2$O$_3$ = 2CuFeO$_2$. The X-ray powder diffraction was performed to determine the phase purity of synthesized single-phase CuFeO$_2$ powders. Furthermore, the synthesized single-phase CuFeO$_2$ powders were pressed by isostatic compaction to form a cylindrical rod with 6–8 mm in diameter and 80 mm in length. We then sintered the rod at 900 °C in N$_2$ atmosphere with keeping 24 hours to obtain condensed rod and increase its mechanical strength. To grow the CuFeO$_2$ single crystal, we used the floating zone (FZ) method, which transfers this condensed rod into a furnace in FZ, and then crystal growth with the rate of 1 mm h$^{-1}$ in a flow of CO/CO$_2$ gas. As-grown CuFeO$_2$ single crystal is opaque-black color with 5 mm in diameter and 70 mm in length. The obtained crystals in this study that formed on the (001) surface exhibited disk shapes that were 5 mm in diameter and 3 mm in thickness. The single crystals were characterized using X-ray powder diffraction and magnetization measurements. Besides the higher cost and longer growth process, the advantages of using CuFeO$_2$ single crystal for research are high phase purity, excellent crystallinity, and easy to study the anisotropic behavior of the materials compared to CuFeO$_2$ polycrystalline powder. Moreover, X-ray powder diffraction profile revealed that the as-grown and one year aging samples exhibited almost identical pattern, implying the good stability for CuFeO$_2$.

Micro-Raman scattering measurements were performed in a backscattering geometry using a 785 nm laser. The linearly polarized light was focused into a 3 µm-diameter spot on the sample surface. The Raman scattering signal was collected and dispersed using a SENTERRA spectrometer equipped with a 1024-pixel-wide charge-coupled detector. The spectral resolution achieved using these instruments were typically less than 0.5 cm$^{-1}$. To avoid heating effects, the laser power was set to 0.1 mW. The polarized Raman scattering spectra were taken in scattering geometry of Z(YY)Z and Z(YX)Z. In this Porto notation, the first and the last letter represent the propagation directions of the incident and the scattered light, whereas the letters in parentheses indicate the electric field polarizations of the incident and scattered light, respectively. X, Y, Z, and Z were parallel to the [100], [010], [001], and [001] crystal directions,
respectively. When the polarizations of the incident and the scattered light are carefully controlled, the selection rules for the Raman scattering from phonon modes allow accurate mode assignments.24 We placed the sample in a continuous-flow helium cryostat, which can control the temperature to be in the range of 5–300 K.25

Temperature-dependent spectroscopic ellipsometric spectra were obtained using a J. A. Woollam Co. M-2000U ellipsometer under a Janis ST-400 vacuum cryostat with a pressure under 10−8 torr. The data were collected in the spectra range between 0.73 and 6.42 eV with temperatures between 4.5 and 300 K.25,26 The raw ellipsometry variables \( \Psi \) and \( \Delta \) are related to the complex Fresnel reflection coefficients for light polarized parallel \((R_p)\) and perpendicular \((R_s)\) to the plane of incidence.

\[
\tan \Psi e^{i\Delta} = \frac{R_p}{R_s}
\]  

For isotropic bulk materials, the dielectric function can be transformed by the raw ellipsometry variables \( \Psi \) and \( \Delta \). However, the surface roughness would cause a small absorption below the absorption edge.27 The complex dielectric function was determined from fitting the ellipsometric variables by building a three medium optical model consisting of an air ambient structure/surface roughness/single crystal.25,26 The surface roughness can be described by a Bruggeman effective medium approximation by assuming 50% vacuum and 50% bulk.28 The surface roughness was approximately 1 nm in CuFeO\(_2\).

III. Results and discussion

A. Vibrational properties

The room temperature polarized Raman scattering spectra of CuFeO\(_2\) are presented in Fig. 2. Polarized Raman scattering studies allow one to obtain the symmetry properties and assignments of different Raman-active phonon modes. In the 

\( Z(YYZ) \) configuration, we observed two main peaks at approximately 352 and 692 cm\(^{-1}\). In addition, a broad peak was observed at approximately 509 cm\(^{-1}\), which was attributed to the Cu vacancy induced phonon mode.26 We also observed low-intensity broad phonon modes near 1000, 1052, and 1171 cm\(^{-1}\), which should be ascribed to multiphonon bands.29–31 According to factor group analysis, CuFeO\(_2\) has a rhombohedral structure (space group \( R\bar{3}m \)) containing one formula unit per primitive cell. The irreducible representation of the phonon modes at the center of the Brillouin zone is given by \( \Gamma = A_{1g} + E_g + 3A_{2u} + 3E_u \).16 These modes were classified as Raman active \((A_{1g} + E_g)\), infrared active \((2A_{2u} + 2E_u)\), and acoustic \((A_{2u} + E_u)\). In the \( Z(YYZ) \) configuration, the intensity of the 352 cm\(^{-1}\) mode became much stronger than that in the \( Z(YYZ) \) configuration, indicating that it is of the \( E_g \) character.12–14 By contract, the 692 cm\(^{-1}\) and multiphonon modes almost vanished, indicating that they exhibit \( A_{1g} \) symmetry.16–18 Our room temperature experimental results are consistent with those of previous studies.16–18

The temperature-dependent unpolarized Raman scattering spectra of CuFeO\(_2\) are depicted in Fig. 3. With a decrease in temperature, the peak positions of all phonon modes shifted to higher frequencies, their resonance linewidth narrowed, and their intensity increased. Six Lorentzian oscillators were used to fit the Raman scattering spectrum at 5 K (inset of Fig. 3). Fig. 4 illustrates the frequencies, linewidths, and normalized intensities of the \( E_g \) and \( A_{1g} \) phonon modes as a function of temperature. The oscillation strength of the \( E_g \) and \( A_{1g} \) phonon modes increased as temperature decreased, but remained constant when the temperature was lower than 100 K. In a normal anharmonic solid, when temperature decreases, the
phonon frequency should increase and linewidth decrease. The temperature-dependent phonon frequency and linewidth can be written as

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

and

$$\gamma(T) = \gamma_0 + B \left[ 1 + \frac{2}{\exp(\Theta/T) - 1} \right]$$  \hspace{1cm} (3)

where $\Theta$ is the Debye temperature and $\omega_0$ and $\gamma_0$ are the frequency of the optical phonon mode and the linewidth at 0 K, respectively.\(^{32}\) The parameters $A$ and $B$ are the anharmonic coefficients. The values of $\omega_0$ ($\approx 353.7$ cm\(^{-1}\)), $\gamma_0$ ($\approx 5.2$ cm\(^{-1}\)), $A$ ($\approx -6.0$ cm\(^{-1}\)), and $B$ ($\approx 4.6$ cm\(^{-1}\)) were determined to analyze the anharmonic contributions to the 352 cm\(^{-1}\) $E_g$ mode. For the 692 cm\(^{-1}\) $A_{1g}$ mode, the values of $\omega_0$ ($\approx 696.7$ cm\(^{-1}\)), $\gamma_0$ ($\approx 14$ cm\(^{-1}\)), $A$ ($\approx -1.4$ cm\(^{-1}\)), and $B$ ($\approx 9.6$ cm\(^{-1}\)) were determined. The average Debye temperature was 357 K, which was lower than that of other delafossite materials (CuCrO\(_2\), $\Theta = 830$ K).\(^{31}\) Parameter $A$ was negative, indicating that the peak frequency shifted higher as temperature decreased. By contrast, parameter $B$ was positive, indicating that the linewidth became narrower as temperature decreased. Theoretical predictions based on eqn (2) and (3) are the solid lines in Fig. 4(a) and (b). Fig. S1\(^+\) presents the temperature-dependent Raman scattering spectra of the multiphonon modes of CuFeO\(_2\). Fig. S2\(^+\) further displays the frequency, damping, and normalized intensity of the multiphonon modes as a function of temperature. As temperature decreased, the phonon frequency exhibited hardening and the linewidth narrowed. The temperature-dependent variation of all phonon frequencies and linewidths can be fitted well using the anharmonic model.

When the temperature was below 11 K, which was denoted as structural phase transition in Fig. 1, the $E_g$ mode exhibited a softening and the $A_{1g}$ mode exhibited a hardening. Our results differ from those of the previous studies, in which both the $E_g$ and $A_{1g}$ modes exhibited a redshift below 14 K.\(^{18}\) Previous neutron diffraction studies indicated that the lattice constant $a$ of the monoclinic phase was nearly three times larger than that of rhombohedral phase, whereas the lattice constant $b$ remained almost the same. By contrast, the lattice constant $c$ of the monoclinic phase was two times smaller than that of the rhombohedral phase.\(^{10}\) The $E_g$ mode exhibited a softening with a 0.9 cm\(^{-1}\) deviation from the theoretical predictions of the anharmonic model. By contrast, the $A_{1g}$ mode exhibited a hardening with a 0.8 cm\(^{-1}\) deviation from the theoretical predictions of the anharmonic model. The effects of the structural phase transition in CuFeO\(_2\) caused in-plane vibration softening and out-of-plane vibration hardening.

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**Fig. 4** Temperature-dependent frequency, linewidth, and normalized intensity of the (a) $E_g$ and (b) $A_{1g}$ phonon modes of CuFeO\(_2\). The fitting results of the anharmonic model are represented in the solid lines. The vertical dashed lines denote the phase transition temperatures at 11 and 16 K.
absorption coefficient $\alpha(E)$ includes contributions from both direct and indirect band gap transitions. The optical absorption coefficient is given by

$$\alpha(E) = A (E - E_{g, \text{dir}})^{0.5} + B (E - E_{g, \text{ind}} + E_{ph})^2$$

where $E_{g, \text{dir}}$ and $E_{g, \text{ind}}$ are the magnitudes of the direct and indirect gaps, respectively; $E_{ph}$ is the emitted (absorbed) phonon energy; and $A$ and $B$ are constants. This model, which assumes a simple band shape, enables the extraction of the direct energy gap when $\alpha^2$ is plotted as a function of photon energy. The inset of Fig. 5(b) illustrates the direct band gap of 1.43 ± 0.01 eV. Our result is similar to that of previous UV-Vis absorption spectrum analyses and theoretical calculations. To confirm that the CuFeO$_2$ single crystal is a direct band gap material, Fig. S4† presents the room temperature photoluminescence spectrum of CuFeO$_2$ determined using a 325 nm excitation laser. The strong photoluminescence signal at approximately 1.3 eV indicated that CuFeO$_2$ has a direct band gap.

Fig. 6(a) and (b) depict the temperature-dependent complex dielectric function of CuFeO$_2$. When temperature decreased, the real part $\varepsilon_1$ decreased in the near-infrared region. Additionally, the real part dielectric function at 1 eV was discontinuous below 11 K. A discontinuous dielectric function due to

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B. Electronic excitations

Fig. 5(a) presents the room temperature real $\varepsilon_1$ and imaginary $\varepsilon_2$ parts of the dielectric function $\varepsilon(\omega)$ of CuFeO$_2$ through ellipsometric analysis. The room temperature experimental ellipsometric and best-fit calculated data of CuFeO$_2$ are presented in Fig. S3.† The dispersion response of the frequency-dependent $\varepsilon_1$ is typical of a semiconductor. Optical transitions are identified in the spectra according to resonance and antiresonance features that appeared at the same energy in $\varepsilon_1$ and $\varepsilon_2$, respectively. Specifically, the imaginary part spectrum $\varepsilon_2$ of CuFeO$_2$ was dominated by several optical transitions. Fig. 5(b) illustrates the room temperature optical absorption coefficient spectrum of CuFeO$_2$. We calculated the optical absorption coefficient using the equation $\alpha = \frac{20\nu}{e} \sqrt{\frac{1}{2} (\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2) - \varepsilon_1(\omega)^2}$. The optical absorption spectrum was modeled reasonably well using the Lorentzian oscillator. Optical absorption started to gradually increase above 0.7 eV, reached a maximum value at approximately 4.3 eV, and then leveled off. The first absorption peak near 1.76 eV was assigned to the on-site iron ion 3d $t_{2g}$ to 3d $e_g$ transition. The second absorption peak near 2.51 eV was assigned to the copper 3d to iron 3d $e_g$ transition. The absorption peaks at approximately 3.70, 4.33, and 5.06 eV were associated with the charge-transfer transitions from the 2p orbital of oxygen to the 3d orbital of copper or iron. In a normal solid, the optical
a structural phase transition has been observed in transition metal oxides, such as BaTiO$_3$. When temperature decreased, the intensity of the imaginary part $\varepsilon_2$ slightly increased at photon energies higher than 3 eV. By contrast, the intensity slightly decreased at photon energies lower than 3 eV. The optical transition peaks at approximately 2.5 and 3.7 eV exhibited a blueshift with decreasing temperature.

The temperature-dependent optical absorption coefficient spectra are presented in Fig. 7. The inset of Fig. 7 highlights the temperature-dependent band gap energy. The band gap became higher when temperature decreased. The band gap of typical inorganic semiconductors as a function of temperature can effectively be described in terms of the Bose–Einstein model:

$$E_G(T) = E_G(0) - \frac{2\alpha_T}{\exp(\theta_T/T) - 1}$$  \hspace{1cm} (5)

where $E_G(0)$ is the band gap energy at 0 K, $\alpha_T$ is the intensity of the phonon–electron interactions, and $\theta_T$ is the average phonon temperature. Our fitting results indicated that the band gap at 0 K should be 1.43 eV. The parameters $\alpha_T$ and $\theta_T$ were 6 meV and 273 K, respectively. These fitting results are similar to those of other multiferroic oxides, such as BiFeO$_3$.

As is evident from the inset of Fig. 7, the Bose–Einstein model satisfactorily reproduced the overall temperature-dependent band gap in CuFeO$_2$. Notably, the band gap deviated from the theoretical predictions of the Bose–Einstein model below 11 K. The band gap exhibited a softening of 2 meV. A similar discontinuous shift behavior has been observed in other oxide materials, such as SrTiO$_3$ and PbTiO$_3$. In the monoclinic phase, the first-principles calculation predicted the band gap value is 0.05 eV.

The inset of Fig. 7 illustrates an energy level diagram for the electronic states of Fe$^{3+}$ ions. In the high temperature rhombohedral phase, non-distorted FeO$_6$ octahedral units led to the splitting of Fe$^{3+}$ d$^5$ electronic orbitals to lower $t_2g$ energy levels and higher $e_g$ energy levels because of the crystal field effect of octahedral structure. The Fe 3d $t_2g$, O 2p, and Cu 3d orbitals comprised the highest valence band states. The Fe 3d $e_g$ and Cu 4s orbitals comprised the lowest conduction band states.

For the high spin state ($S = 5/2$) of Fe$^{3+}$ ions, all electrons occupied the Fe 3d orbital evenly. The red arrow in the inset of Fig. 7 indicates that the band gap is the electronic excitation from the Fe 3d $t_{2g}$ to Fe 3d $e_g$ levels. In the low temperature monoclinic phase, the compression of the c-axis lattice constant and the elongation of the $ab$-plane due to the structural phase transition resulted in the distortions of the FeO$_6$ octahedral unit. From the rhombohedral to monoclinic phase, the bond length of Fe–O in the FeO$_6$ octahedral unit was split into two values. The in-plane bond length of Fe–O increased. By contrast, the out-of-plane bond length of Fe–O decreased. This Jahn–Teller distortion of FeO$_6$ octahedral unit occurred in other iron oxides as well. The compression of the FeO$_6$ octahedral unit led to the $t_{2g}$ energy level splitting to a lower $d_{xy}$ energy level and a higher $d_{xz}/d_{yz}$ energy level. The elongation of the $ab$-plane led to $e_g$ energy splitting to a lower $d_{x^2-y^2}$ energy level and a higher $d_{xy}$ energy level. The blue arrow in the inset of Fig. 7 indicates that the band gap is the electronic excitation from the Fe $d_{x^2-y^2}$ to Fe $d_{xy}$ levels. Under the Jahn–Teller distortion, the band gap decreased, which was in good agreement with the observed band gap redshift below 11 K.

To gain further insight into the electronic structure of CuFeO$_3$, we plotted the temperature-dependent peak position, linewidth, and normalized intensity of the optical transitions at 1.76 and 4.33 eV in Fig. 8. We also used the Bose–Einstein model to describe the temperature-dependent optical absorption peak energy and linewidth:

$$E = a - b \left[ 1 + \frac{2}{e^{\theta_T/T} - 1} \right]$$  \hspace{1cm} (6)

and

$$\Gamma = \Gamma_0 \left[ 1 + \frac{2}{e^{\theta_T/T} - 1} \right] + \Gamma_1$$  \hspace{1cm} (7)

where $\Gamma_1$ and $a$ are the linewidth and transition energy at 0 K, respectively, $b$ and $\Gamma_0$ represent the strength of the electron–phonon interactions, and $\theta_T$ is the average phonon temperature. By analyzing the d–d electronic excitation at 1.76 eV, we...
determined the values of \( a (\approx 1.77 \text{ eV}), b (\approx 30 \text{ meV}), G_1 (\approx 0.38 \text{ eV}), G_o (\approx 0.12 \text{ eV}), \text{ and } \Theta (\approx 441 \text{ K}) \). By analyzing the charge transfer excitation at 4.33 eV, we determined the values of \( a (\approx 4.33 \text{ eV}), b (\approx 5 \text{ meV}), G_1 (\approx 0.77 \text{ eV}), G_o (\approx 0.14 \text{ eV}), \text{ and } \Theta (\approx 450 \text{ K}) \). Theoretical predictions based on eqn (6) and (7) are represented by the solid lines in Fig. 8(a) and (b). The peak position and linewidth of 1.76 eV optical transition followed the predictions of the Bose–Einstein model with no anomalies across the structural phase transition temperature, indicating that the charge-lattice coupling was too weak to be observed for this electronic excitation. Notably, the peak position of 4.33 eV optical transition differed slightly from the Bose–Einstein model below 11 K as a result of the structural phase transition.

![Fig. 8 Temperature-dependent peak energy, linewidth, and normalized intensity of (a) 1.76 and (b) 4.33 eV optical transitions. The fitting results of the Bose–Einstein model are represented in the solid lines. The vertical dashed lines denote the phase transition temperatures at 11 and 16 K.](image)

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

### Author contributions
H. L. L. and G. J. S. conceived the research and was responsible for the experimental design. H. W. C. conducted the experiments. C. Y. H. and G. J. S. were responsible for the sample preparation. H. W. C. and H. L. L. drafted the paper. All contributing authors have discussed the results and provided their comments regarding the manuscript.

### Conflicts of interest
The authors declare no competing interests.

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