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Abstract

We measured the optical reflectivity spectra under applied uniaxial strain for bulk single crystals of $BaV_{10}O_{15}$, which exhibits orbital ordering at 130 K. We found that with compressive strain, particularly along the b axis, the reflectivity spectrum at room temperature changes almost in an isotropic manner, as if it changes to that at lower temperatures. This experimental result indicates a strong coupling between the orbital degree of freedom and the strain in this compound.

Magnetic properties of a crystal are dominated by the spin degrees of freedom of electrons, which interact with each other and often become ordered at low temperatures. Such a spin degree of freedom can be coupled with a magnetic field that is its conjugate external field, and applying a magnetic field causes Zeeman splitting of the spin state and induces a change in the magnetic properties. Similarly, the orbital degrees of freedom arising from the degenerate localized d states in transition-metal ions interact with each other and sometimes become ordered at low temperatures, called orbital ordering. The external field that is conjugate to the orbital degree of freedom is anisotropic (uniaxial or biaxial) strain, which splits the energetically degenerate orbitals.

There have been several studies on the control of the physical properties of compounds through the manipulation of the orbital degree of freedom by applying anisotropic strain, but mostly on thin films. One example is the application of biaxial strain to a thin film of perovskite manganites via a lattice mismatch with a substrate or a piezoelectric effect of the substrate, thereby inducing a change in the distortion of the MnO_6 octahedra and causing a change in the magnetic state or the transition temperature [1–8]. Another example is thin films of VO_2 [9–12] and V_2O_3 [13–17], in both of which a metal-insulator transition was controlled using strain caused by a lattice mismatch with a substrate or the bending of the substrate. For VO_2, the effect of uniaxial stress on the bulk single crystal was also reported [18], although the electronic structure of the single crystal under applied uniaxial strain has barely been studied so far.

In the present study, we measured the optical reflectivity spectrum for bulk single crystals under applied uniaxial strains and demonstrated that such a measurement can detect changes in the electronic structure associated with the change in the orbital state. Since the strain $\Delta L/L$ that can be applied experimentally to bulk single crystals, which is typically the order of 10^{-3}, is relatively smaller than that to thin films, which can be larger than 10^{-2}, the effect of strain on the electronic structure must be large for that purpose. In this regard, it is preferable to use a crystal that exhibits orbital ordering at a temperature slightly lower than the measurement temperature, since a large fluctuation of the orbital can be expected under the uniaxial strain in the measurement. Such an effect is analogous to the magnetic-field effect on magnets, which is enhanced immediately above the magnetic-transition temperature because of the enhanced spin fluctuation.

Here, we chose $BaV_{10}O_{15}$, which is composed of a bilayer of quasi-triangular lattices of

V ions, as shown in Fig. 1(a). In this compound, the average valence of V is 2.8+, meaning that there are nominally four V^{3+} $(3d^2)$ ions and one V^{2+} $(3d^3)$ ion. It exhibits a structural phase transition at $T_c \sim 130$ K [19–21], which is characterized by trimerization of the V^{3+} ions over the bilayer, as illustrated in Fig. 1 (b). According to the result of resonant X-ray scattering, this structural phase transition is caused by the ordering of the triply degenerate V t_{2g} states; namely, on each side of the V trimer, either the xy, yz, or zx orbitals of the neighboring V ions form a spin-singlet bond [20]. With this orbital ordering, the electrical resistivity jumps by three orders of magnitude and a charge gap of ~ 0.3 eV opens in the optical conductivity spectrum derived from the reflectivity spectrum [19]. However, even above T_c, the spectral weight in the optical conductivity below 1 eV is gradually suppressed with decreasing T [19], probably caused by the evolution of the orbital correlation in part. For this issue, the reflectivity spectra, from which the optical conductivity was derived, at various temperatures are shown in Fig. 1 (c). Furthermore, the lattice constants exhibit a jump at T_c (the b lattice constant decreases but the a and c lattice constants increase), but even above T_c, the b lattice constant decreases more than the a and c lattice constants do with decreasing T, as exemplified by the T dependence of the strain measured by a strain gauge shown in Fig. 1 (d). This result also suggests that the orbital fluctuation evolves, particularly along the b axis, with decreasing T. These behaviors make this compound suitable for studying the effect of uniaxial strain on the optical spectrum.

In the present study, we measured the optical reflectivity spectrum for $BaV_{10}O_{15}$ at room temperature with various polarization directions when uniaxial strain is applied along various crystal axes. The single crystals of $BaV_{10}O_{15}$ used in this study were grown by the floating zone method [19]. The crystalline axes of the grown crystal were determined by the Laue method, and the ab plane and the bc plane were cut and polished with alumina powder. The temperature dependence of the optical spectra on a polished surface [19] is quantitatively different from that on a cleaved surface [22], but such a difference does not affect the result below. To investigate the change in the reflectivity of the crystal with applied uniaxial strain, we used an apparatus with three piezoelectric actuators [23]. A sample is mounted on two metal blocks in such a way that the polished surface is attached to the plane of the metal blocks, and the distance between the two metal blocks was changed by adjusting the piezoelectric actuators. The magnitude of the strain was measured with a strain gauge, and in the following we show the data measured with the strain of $|\Delta L/L| = 3.0 \times 10^{-3}$. The
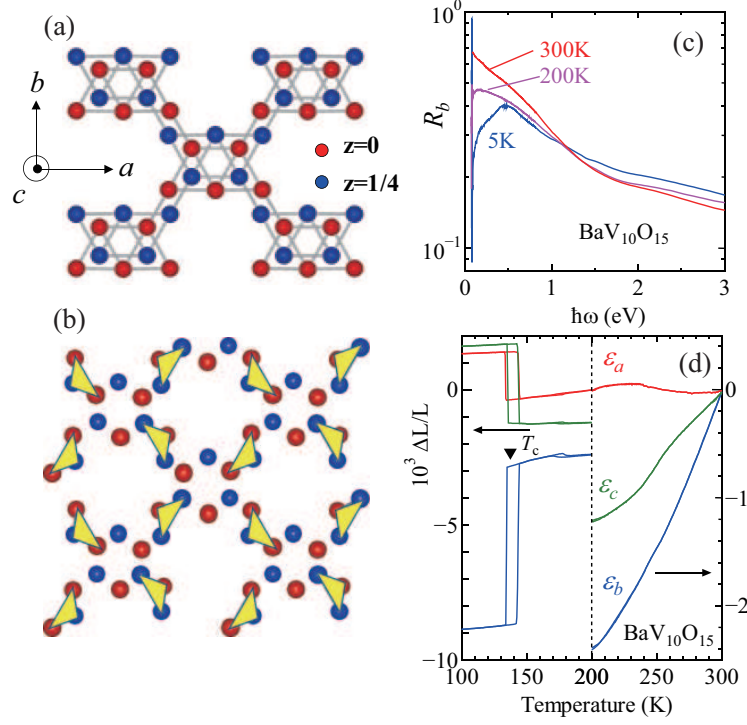
FIG. 1. (a) Arrangement of the V ions in $BaV_{10}O_{15}$ at room temperature. (b) Schematic of the V trimers below T_c. (c) Reflectivity spectra at various temperatures, (d) Temperature dependence of the strain (the shrinkage of the crystal measured by a strain gauge) along the a, b, and c axes for $BaV_{10}O_{15}$.

optical reflectivity measurement was performed at room temperature with a halogen lamp as the light source, which was monochromated with a grating spectrometer between 0.8 eV and 3.0 eV and focused onto the sample surface between the two metal blocks. Details of the measurement method are described in the supplementary information [24].

Figures 2 (a) and (b) show the change in the reflectivity spectrum on the bc plane of the sample with b polarization [$(\Delta R/R)_b$ spectra] and the c polarization [$(\Delta R/R)_c$ spectra] when a tensile ($\Delta L > 0$) or compressive ($\Delta L < 0$) strain is applied along the b axis (ΔL_b). With a compressive strain $\Delta L_b < 0$, the $(\Delta R/R)_b$ spectrum is positive and increases with increasing $\hbar\omega$ above 1 eV, whereas it is negative and decreases with increasing $\hbar\omega$ with a tensile strain $\Delta L_b > 0$. It is noteworthy that the $|(\Delta R/R)_b|$ spectra are almost the same and only the signs of $(\Delta R/R)_b$ are different between compressive and tensile strain. Furthermore, the $(\Delta R/R)_c$ spectra behave in a similar manner to the $(\Delta R/R)_b$ spectra with a compressive or tensile strain along the b axis; they are positive with a compressive strain and negative

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with a tensile strain. If uniaxial strain simply induces anisotropy in the electronic structure, the behavior of the $(\Delta R/R)_c$ spectrum as a function of ΔL_b will be different from that of the $(\Delta R/R)_b$ spectra and most likely, the sign of $(\Delta R/R)_c$ will be opposite that of $(\Delta R/R)_b$ for the same sign of ΔL_b. Thus, the present experimental result that $(\Delta R/R)_b$ and $(\Delta R/R)_c$ behave similarly as a function of ΔL_b means that a nearly *isotropic* change in the electric state is induced by a uniaxial strain applied along the b axis in $BaV_{10}O_{15}$.

To understand what kind of change occurs in the electronic structure with an applied uniaxial strain along the b axis, the difference in the reflectivity spectra between 300 K and 200 K is plotted in Figs. 2(c) for R_b and (d) for R_c [19]. In these figures, the spectrum for $R(200K)/R(300K) - 1$, which is dominated by a reduction in the spectral weight in the optical conductivity spectrum below 1 eV, and the spectrum for $-\{R(200K)/R(300K) - 1\}$ are both plotted. For both polarizations, the change in the reflectivity spectrum when a compressive strain is applied along the b axis is similar to the spectrum of $R(200K)/R(300K) - 1$, whereas the change when a tensile strain is applied is similar to the spectrum of $-\{R(200K)/R(200K) - 1\}$. This comparison indicates that, for $BaV_{10}O_{15}$, a compressive strain induces a change in the electronic state to that at a lower temperature, where the b lattice constant decreases and the orbital correlation is enhanced, whereas a tensile strain induces the opposite change.

Figure 3 shows the changes in the reflectivity spectra when a uniaxial strain is applied along the a axis (L_a) or along the c axis (L_c). Similarly to the case when the strain is applied along the b axis (L_b) shown in Figs. 2(a) and (b), the $|\Delta R/R|$ spectra are almost the same for the compressive ($L < 0$) and tensile ($L > 0$) strain and only the signs of $(\Delta R/R)$ are different between $L < 0$ and $L > 0$ with strain along the a axis and the c axis. Furthermore, the change in the reflectivity with applied uniaxial strain is nearly isotropic in terms of the polarization direction, similarly to the case of L_b; namely, the signs of $\Delta R/R$ with different polarization directions are the same for the same sign of ΔL_a or ΔL_c. The only difference is that the absolute value $|(\Delta R/R)|$ under the c-axis strain (L_c) is smaller than that under the b-axis strain (L_b), and even the sign of $(\Delta R/R)$ is opposite under the a-axis strain (L_a). Namely, both the $(\Delta R/R)_b$ and $(\Delta R/R)_c$ spectra are negative with the compressive strain $\Delta L_a < 0$ and vice versa, oppositely to the case of ΔL_b and ΔL_c.

Figure 4 (a) shows the $(\Delta R/R)_b$ spectrum when a strain is applied along the b axis (L_b) on the ab plane. Even though both the directions of strain and polarization for these
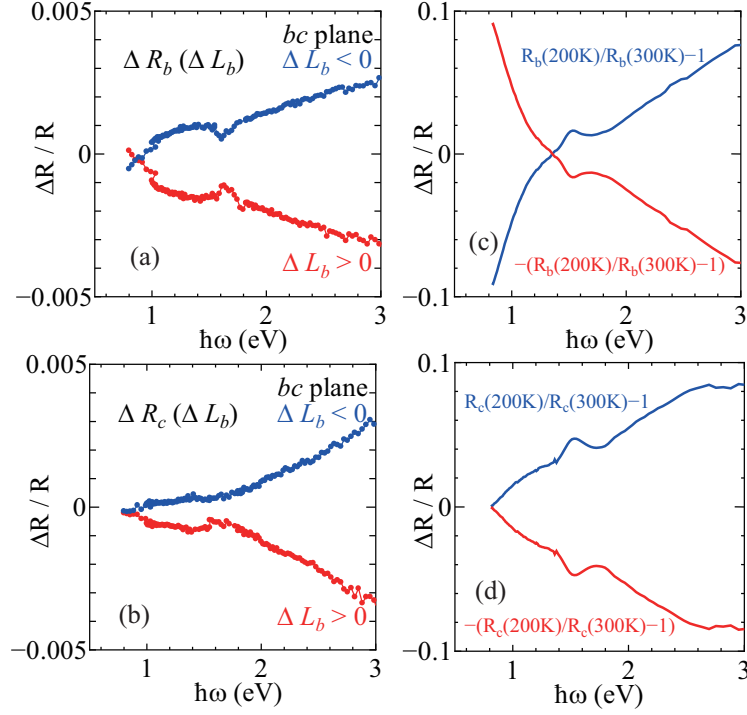
FIG. 2. (a)(b) Change in reflectivity spectra when compressive ($\Delta L < 0$) or tensile ($\Delta > 0$) strain is applied along the b axis (a) with b polarization and (b) with c polarization. (c)(d) Change in reflectivity spectra with temperature, $R(200\mathrm{K})/R(300\mathrm{K}) - 1$ and $-\{R(200\mathrm{K})/R(200\mathrm{K}) - 1\}$, (c) with b polarization and (d) with c polarization.

spectra are the same as those shown in Fig. 2 (a), which are also plotted in Fig. 4 (a) by solid lines, the $(\Delta R/R)_b$ spectra are discernibly different, particularly above 2 eV. This difference is likely caused by the difference in the strain perpendicular to the direction of the strain applied via piezoelectric actuators. When a compressive uniaxial strain is applied to a freestanding crystal, the crystal is elongated along the other two axes, and the magnitude of the elongation is determined by Poisson's ratio. In the present experiment, however, one surface of the crystal is attached to the metal blocks and as a result, when a compressive uniaxial strain is applied to the crystal using piezoelectric actuators along the first axis of the sample surface, the strain along the second axis of the sample surface is approximately zero, and the crystal is elongated only along the third axis perpendicular to the sample surface [Fig. 4 (c)]. Assuming that the change in volume is invariant whether the crystal is freestanding or attached to a plane, the magnitude of the strain along the third axis when a compressive strain is applied along one axis of the sample surface attached to a plane can
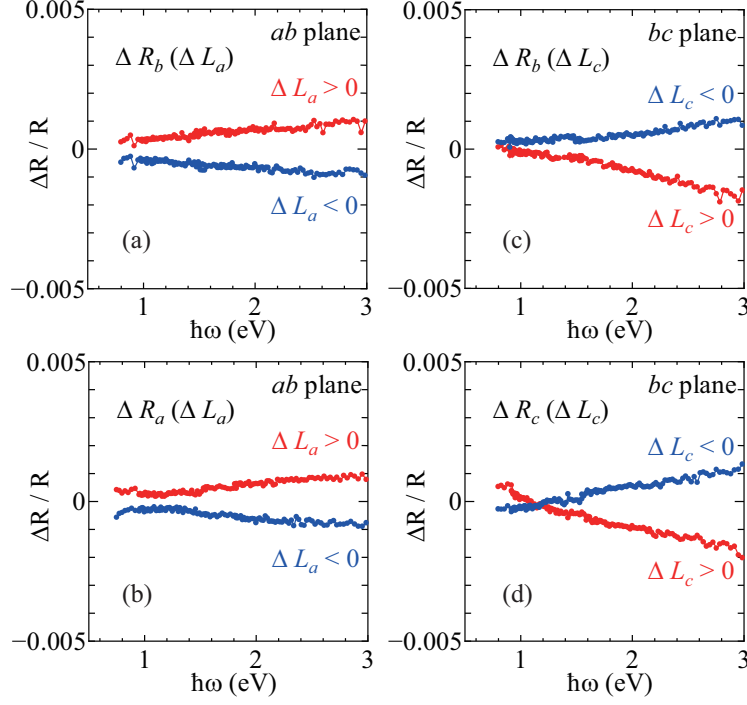
FIG. 3. (a)(b) Change in reflectivity spectra when compressive ($\Delta L < 0$) or tensile ($\Delta > 0$) strain is applied along the a axis (a) with b polarization and (b) with a polarization. (c)(d) Change in reflectivity spectrum when strain is applied along the c axis (c) with b polarization and (d) with c polarization.

be determined from

$$1 + \Delta V/V = (1 + a)(1 - \nu a)^2 = (1 + a)(1 - \nu' a), \tag{1}$$

where V is the volume of the crystal, ΔV is the change in the volume of the crystal, ν is Poisson's ratio, and ν' is the ratio of the tensile strain along the third direction to the compressive strain along the first axis with zero strain along the second axis. This assumption gives $\nu' = 2\nu$.

Using this parameter $\nu' = 2\nu$, the change in the reflectivity spectrum experimentally obtained with the b polarization direction when uniaxial strain was applied along various directions on various surfaces can be given as follows:

$$\begin{pmatrix} \Delta R_b(\Delta L_a)_{ba} \\ \Delta R_b(\Delta L_b)_{ba} \\ \Delta R_b(\Delta L_b)_{bc} \\ \Delta R_b(\Delta L_c)_{bc} \end{pmatrix} = \begin{pmatrix} 1 & 0 & -2\nu \\ 0 & 1 & -2\nu \\ -2\nu & 1 & 0 \\ -2\nu & 0 & 1 \end{pmatrix} \begin{pmatrix} \Delta R_{ba} \\ \Delta R_{bb} \\ \Delta R_{bc} \end{pmatrix}, \tag{2}$$

where $\Delta R_b (\Delta L_i)_{bj}$ ($i = a, b, c, j = a, c$) corresponds to the change in the reflectivity spectrum experimentally obtained with b polarization for the sample attached on the bj plane when a strain is applied along the i axis via piezoelectric actuators. ΔR_{bi} ($i = a, b, c$) corresponds to the hypothetical change in the reflectivity with the b polarization direction when a uniaxial strain is applied only along the i axis while there is no strain along the other two axes. Based on Eq. 2, we can calculate three components of ΔR_{bi} ($i = a, b, c$) from the two sets of data, for example, $\Delta R_b (\Delta L_a)_{ba}$, $\Delta R_b (\Delta L_b)_{ba}$, $\Delta R_b (\Delta L_c)_{bc}$ (set 1), and $\Delta R_b (\Delta L_a)_{ba}$, $\Delta R_b (\Delta L_b)_{bc}$, $\Delta R_b (\Delta L_c)_{bc}$ (set 2), and thus, a cross-check of the data is possible. Here, since Poisson's ratio of the present compound is unknown, we used Poisson's ratio of V_2O_3 ($\nu = 0.32$) instead.

Figure 4 (b) shows the spectra of $(\Delta R/R)_{bi}$ ($i = a, b, c$). Note that for $(\Delta R/R)_{ba}$ and $(\Delta R/R)_{bc}$, the calculated values from the two data sets are analytically identical, and only the $(\Delta R/R)_{bb}$ spectra calculated using the two data sets are subject to a cross check. As can be seen, the $(\Delta R/R)_{bb}$ spectra calculated from set 1 and set 2 are reasonably similar, and the experimental results are such that the change in the reflectivity with the b polarization direction is largest when a strain is applied along the b axis, and the magnitude of the change is smaller when it is applied along the c axis and is almost zero when it is applied along the a axis [24].

Such a dependence of the change in reflectivity on the direction of the strain seems to be correlated with the change in the lattice constants with temperature shown in Fig. 1 (d). Namely, when the temperature decreases from room temperature, both the b and c lattice constants decrease but the b lattice constant decreases more than the c lattice constant, whereas the a lattice constant is almost independent of temperature. This is similar to the dependence of the reflectivity change with the strain on the direction of the strain.

Let us discuss the possible microscopic mechanism of the coupling. The orbital-orbital coupling that induces the orbital ordering can be written as $J_{ij}^{\alpha\beta} n_i^\alpha n_j^\beta$, where n_i^α is the number operator of the α orbital ($\alpha = 1, 2, 3$ corresponding to the three degenerate t_{2g} states) at the i site [25, 26]. If there is no orbital ordering, $\langle n_i^\alpha \rangle$ is the same for any α and i ($= 2/3$ if the number of d electrons is two), but deviates from the value in the orbital-ordered state. Here, there are two ways of coupling between the strain u^k ($k = x, y, z$) and the orbital n_i^α: bilinear coupling, $\Gamma^{k\alpha} u^k n_i^\alpha$, which induces Jahn-Teller splitting of the orbital, and quadratic coupling in terms of the orbital, $\Gamma_{ij}^{k\alpha\beta} u^k n_i^\alpha n_j^\beta$, caused by the change in the transfer integral between
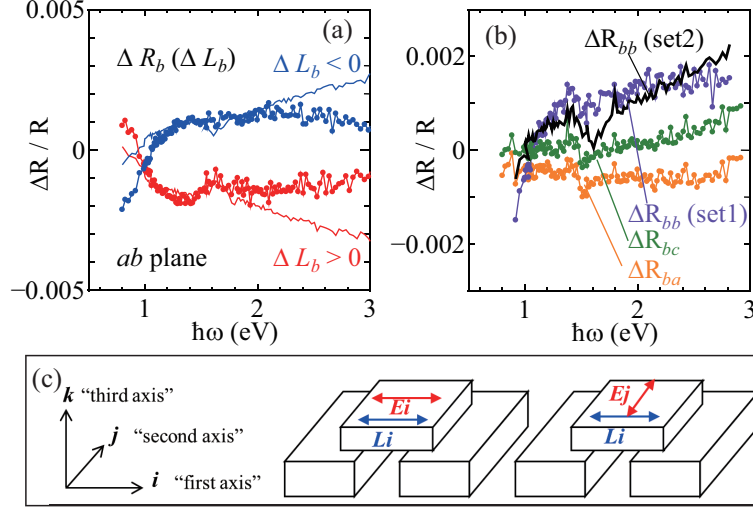
FIG. 4. (a) Change in reflectivity spectrum with b polarization when compressive ($L < 0$) or tensile ($L > 0$) strain is applied along the b axis on the ab plane. The solid lines are the results with the same polarization and strain directions but on the bc plane [shown in Fig. 1 (a)]. (b) Hypothetical change in reflectivity spectra with b polarization when compressive strain is applied only along the a, b, or c axis while no strain is applied along the other two axes. The two lines for R_{bb} were calculated using the two different data sets to demonstrate the consistency (see the text). (c) Schematic of the measurement with the directions of strain and polarization.

the d orbitals of the i and j sites with strain u^k. Since the change in the lattice constant with T above T_c is dominated by the latter coupling, we only consider the term $\Gamma_{ij}^{k\alpha\beta} u^k n_i^\alpha n_j^\beta$. Here, $\langle n_i^\alpha n_j^\beta \rangle$ exhibits a T dependence even above T_c because of the fluctuation of the orbital. Furthermore, we assume that $\langle n_i^\alpha n_j^\beta \rangle$ dominates the optical conductivity spectrum discussed in the present study, since the optical spectrum at $1 - 3$ eV corresponds to the excitation of a d electron from a V ion to a neighboring V ion. On the basis of this coupling and the assumption, the change in $\langle u_k \rangle$ caused by the applied strain naturally induces a change in $\langle n_i^\alpha n_j^\beta \rangle$ and changes the optical conductivity spectrum. The coupling constant $\Gamma_{ij}^{k\alpha\beta}$ can have anisotropy in terms of the direction k, and this leads to the different magnitudes of the change in $\langle n_i^\alpha n_j^\beta \rangle$ and the change in the optical spectrum depending on the direction k of the strain $\langle u_k \rangle$. This anisotropy in $\Gamma_{ij}^{k\alpha\beta}$ also dominates the anisotropy in the T dependence of the lattice constant since, upon the variation in the orbital correlation $\langle n_i^\alpha n_j^\beta \rangle$ with T, $\langle u_k \rangle$ also changes through this quadratic coupling, with the change in $\langle u_k \rangle$ becoming larger for k with a larger coupling constant $\Gamma_{ij}^{k\alpha\beta}$. In BaV$_{10}O_{15}$, since V trimers align along the b

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axis below T_c [Fig. 2 (b)], we speculate that the coupling between the orbital and the strain is largest when the strain is along the b axis.

In summary, we measured the change in the optical reflectivity spectra under applied strain at room temperature for $BaV_{10}O_{15}$, which exhibits orbital ordering at 130 K. We found that a uniaxial strain induces a nearly isotropic change in the electronic structure in this compound in such a way that a compressive strain induces a spectral change similar to that observed with decreasing temperature. The magnitude of such a spectral change strongly depends on the direction of the strain and is largest when the strain is applied along the b axis. The correlation between these experimental results and the T dependence of the lattice constants, which is the largest for the b lattice constant, can be explained by the quadratic coupling between the orbital and the strain with anisotropy.

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