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Temperature-dependent Raman spectroscopy in $BaRuO_3$ systems

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We investigated the temperature dependence of the Raman spectra of a nine-layer $BaRuO_3$ single crystal and a four-layer $BaRuO_3$ epitaxial film, which show pseudogap formations in their metallic states. From the polarized and depolarized spectra, the observed phonon modes are assigned properly according to the predictions of group theory analysis. In both compounds, with decreasing temperature, while A_{1g} modes show a strong hardening, E_g (or E_{2g}) modes experience a softening or no significant shift. Their different temperature-dependent behaviors could be related to a direct Ru metal bonding through the face sharing of RuO_6. It is also observed that another E_{2g} mode of the oxygen participating in the face sharing becomes split at low temperatures in the four-layer $BaRuO_3$. And, the temperature dependence of the Raman continua between 250 and 600 cm^{-1} is strongly correlated to the square of the plasma frequency. Our observations imply that there should be a structural instability in the face-shared structure, which could be closely related to the pseudogap formation of $BaRuO_3$ systems.

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I. INTRODUCTION

Recently, it was reported that a pseudogap formation can occur in $4d$ transition-metal oxides, $BaRuO_3$ compounds.[1,2] Optical conductivity spectra $\sigma_1(\omega)$ of both four-layer hexagonal ($4H$) $BaRuO_3$ and nine-layer rhombohedral ($9R$) compounds show clear electrodynamic response changes resulting from the pseudogap formation. In their metallic states, concurrent developments of a gaplike feature and a coherent mode below a gaplike feature are observed due to the partial gap opening in the Fermi surface.

The pseudogap formations in the ruthenates could be closely related to their structures characterized by hexagonal close packing. As shown in Fig. 1, their layered structures include the face-sharing structure of RuO_6 octahedra along the c axis. In $4H$ and $9R$ structures, two and three adjacent RuO_6 octahedra participate in face sharing, respectively. A direct Ru-Ru metal bonding formed through such face-sharing distinguishes their physical properties from those of the perovskite ruthenates only with the Ru-O-Ru interaction through corner sharing.[3] Actually, the metal bonding has been seen to be closely related to interesting physical properties, such as a metal-insulator transition in Ti_2O_3 (Ref. 4) and non-Fermi liquid behavior in $La_4Ru_9O_{16}$.[5] In the case of $BaRuO_3$ systems, the quasi-one-dimensional (quasi-1D) Ru metal bonding along the c axis might induce a charge-density wave (CDW) instability. It was reported that a $5d$ transition-metal oxide $9R$ $BaIrO_3$, which is expected to have stronger metal-bonding character than $9R$ $BaRuO_3$ due to a more extended $5d$-orbital character, shows a static CDW instability.[6] For $BaMO_3$ ($M=$Ru, Ir) with $9R$ or $4H$ structure, it was observed that the strength of the metal bonding through the face sharing should be a parameter in determining their physical properties.[2] These strongly indicate that a CDW instability could be related to the pseudogap formation in the $BaRuO_3$ systems.

In usual 1D density wave systems, a static CDW ordering state accompanies a structural distortion with a metal-insulator transition. When Peierls-type lattice distortion occurs, in general, new phonon modes in infrared (IR) and Raman spectra can be observed due to structural symmetry breaking. This could also result in a superlattice or an additional peak in x-ray diffraction (XRD) patterns or neutron-scattering experiments. In the case of $BaRuO_3$ systems, although a 1D-like CDW instability is strongly suggested, there has been no structural report about structural distortions.[7] These might be related to a fluctuation-type instability without any static CDW ordering.

When the time scale of CDW fluctuations is long enough to induce a pseudogap formation in $\sigma_1(\omega)$, a phonon anomaly, such as the creation or splitting of a phonon, can be observed.[8–11] In the metallic state of $BaRuO_3$ compounds, the screening of free carriers makes the detailed analysis of IR-active phonons difficult. On the other hand, Raman spectroscopy is known to be less affected by free-carrier responses than IR spectroscopy. So, Raman spectroscopy could be a useful tool to address the origin of pseudogap formation of $BaRuO_3$ compounds in view of their structural properties.

In this paper, we report the Raman spectra of $4H$ and $9R$ $BaRuO_3$ compounds. According to group theory analysis, the observed phonon modes are properly assigned. From the temperature-dependent (T-dependent) experiments, it is observed that the T-dependent behavior of phonons strongly depends on the vibrational directions, which could be related to the structural characteristics with the face sharing of RuO_6 octahedra. Interestingly, the E_{2g} mode of the face-shared oxygen in $4H$ $BaRuO_3$ becomes split with decreasing T. These observations indicate that there should be a structural instability due to the metal bonding through the face sharing of RuO_6 octahedra, which could be closely related to the pseudogap formation in these ruthenates.

II. EXPERIMENTS

$4H$ $BaRuO_3$ epitaxial film on (111) $SrTiO_3$ substrate was fabricated by a 90° off-axis sputtering technique.[12] Its thickness is about 3200 Å. XRD and transmission electron microscopy reveal that the film is composed of a high-quality single domain with a c axis structure. $9R$ $BaRuO_3$ single crystal was prepared by a flux-melting method.[13] The size of the sample is $0.5\times0.5\times0.2$ mm^3. XRD measurements showed that the c axis was pointing along the short dimension. Due to the size limitation, most Raman spectra were obtained in the a-b plane.

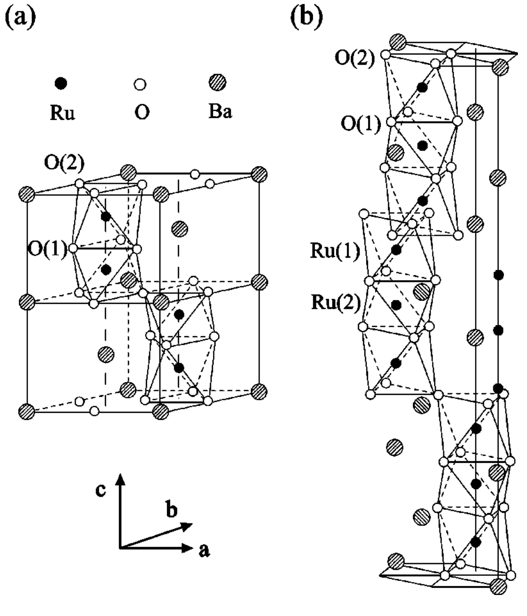

FIG. 1. Schematic diagrams of the two crystallographic forms of $BaRuO_3$; (a) $4H$ phase, (b) $9R$ phase. The arrows represent the crystallographic axes. The details are described in the text.

Raman-scattering measurements were performed in the backscattering geometry using a triple Raman spectrometer (Jobin Yvon T64000). The incident laser beam was the 514.5 nm line of an Ar-ion laser and the laser power was about 3.6 mW on the sample surface. Raman spectra were measured at various T between 5 K and 650 K. Below 300 K, a continuous flow type of cryostat was used. Above 300 K, a homemade sample heating system was used. Due to the heating effect of the focused laser, the assigned temperatures in this paper could be slightly different from the actual ones on the measured sample surface. At all T, polarized and depolarized spectra were obtained and corrected by a Bose-Einstein factor. The details are described elsewhere.[14]

III. RESULTS AND DISCUSSIONS

A. Group theory analysis and phonon assignment

The $4H$ structure has D_{6h} symmetry,[15,16] and four molecular units in the primitive cell with eight Raman-active modes $(2A_{1g}+2E_{1g}+4E_{2g})$, twelve IR-active modes $(5A_{2u}+7E_{1u})$, and eighteen silent optic modes $(A_{2g}+A_{1u}+3B_{1g}+2B_{1u}+5B_{2u}+6E_{2g})$. The Raman-active modes are composed of E_{2g} of Ba, A_{1g}, E_{1g}, and E_{2g} of Ru, and A_{1g}, E_{1g}, and $2E_{2g}$ of O. The point group for the $9R$ structure is D_{3d},[15,16] with three molecular units in the primitive cell. A factor group analysis predicts nine Raman-active modes $(4A_{1g}+5E_g)$, sixteen IR-active modes $(7A_{2u}+9E_u)$, and three silent optic modes $(2A_{1u}+A_{2g})$. The Raman-active modes are composed of A_{1g} and E_g of Ba, A_{1g} and E_g of Ru, and $2A_{1g}$ and $3E_g$ of O.

It is noted that only the O ions participating in the face sharing and only the Ru ions in RuO_6 octahedra participating in the corner sharing have Raman-active phonon modes. O ions in both ruthenates are positioned at two irreducible sites, i.e., a face-shared plane and an edge in RuO_6 blocks, represented by O(1) and O(2), respectively, in Fig. 1. From the group analysis, O(2) should have only the IR-active phonon modes ($A_{2u}+2E_{1u}$ for $4H$ $BaRuO_3$ and $2A_{2u}+3E_u$ for $9R$ $BaRuO_3$), while O(1) should have both IR- and Raman-active modes. Unlike $4H$ $BaRuO_3$, $9R$ $BaRuO_3$ has two irreducible Ru-ion sites, i.e., a side and a center position in the RuO_6 blocks, represented by Ru(1) and Ru(2) in Fig 1(b). Similarly to the case of O ions, Ru(2) should have the IR-active phonon modes ($A_{2u}+E_u$) only. So, it is expected that $4H$ and $9R$ $BaRuO_3$ show similar Raman-active phonon spectra in spite of the different layered structures. For convenience, we will abbreviate O(1) and Ru(1) to O and Ru, respectively.

Figure 2(a) shows the polarized and depolarized spectra of $4H$ $BaRuO_3$. Six phonon peaks are observed in the polarized spectra. In the depolarized spectra, four peaks are observed at the same frequency positions with the corresponding phonons in the polarized spectra. Note that both the A_{1g} and the E_{2g} modes in the D_{6h} symmetry contribute to the polarized signal, but only the E_{2g} modes are present in the depolarized spectra, which is an indicator for assigning the

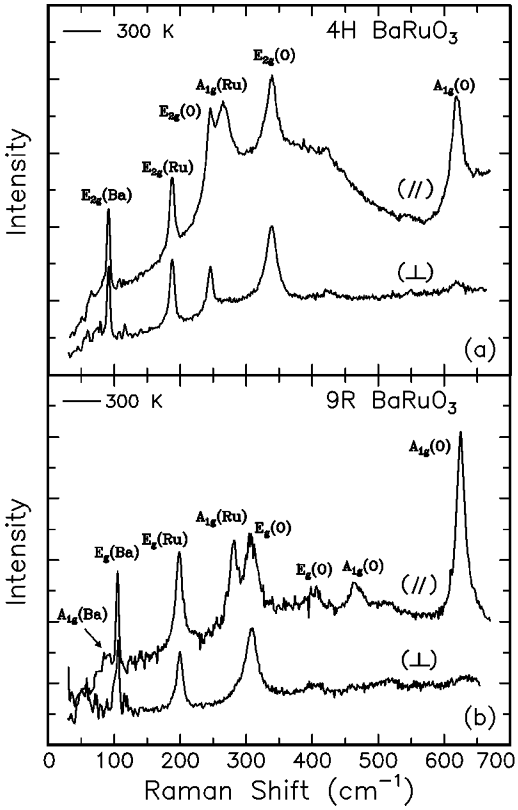

FIG. 2. Polarized (//) and depolarized (⊥) Raman spectra of (a) $4H$ and (b) $9R$ BaRuO$_3$ in the a-b plane at 300 K.

observed phonon modes.[17] So, four modes observed in depolarized spectra can be assigned as E_{2g} modes. Generally, the phonon frequencies related to the vibration of heavier ions are lower than those of lighter ions. Thus, the four modes in ascending order of their frequency are assigned as one E_{2g}(Ba), one E_{2g}(Ru), and two E_{2g}(O). The rest of the modes in the polarized spectra are assigned as A_{1g}(Ru) and A_{1g}(O) from the lowest frequency. Note that according to the predictions of group theory, two E_{1g} modes of Ru and O cannot be observed in Raman spectra from the a-b plane of the thin-film sample.

The observed phonons in $9R$ BaRuO$_3$ are assigned in a similar way. As shown in Fig. 2(b), eight phonons are observed in the polarized spectra. And, three clear modes, which are assigned as E_g(Ba), E_g(Ru), and E_g(O), are observed in the depolarized spectra. Though the mode near 403 cm^{-1} in the polarized spectra is not clearly observed in the depolarized spectra at 300 K, a distinguishable feature of this mode is detected in the depolarized spectra at low T. So, the mode is assigned as another E_g(O) mode. The rest of the modes in ascending order of their frequency in the polarized spectra are assigned as A_{1g}(Ba) near 85 cm^{-1}, A_{1g}(Ru) near 280 cm^{-1}, and two A_{1g}(O) near 463 cm^{-1} and 625 cm^{-1}. The phonon assignments of $4H$ and $9R$ BaRuO$_3$ are summarized in Table I.

TABLE I. Summaries of the Raman-active phonon modes in $4H$ and $9R$ BaRuO$_3$ at 300 K.

$4H$ BaRuO$_3$			$9R$ BaRuO$_3$		
Mode	Frequency (cm^{-1})	Assignment	Mode	Frequency (cm^{-1})	Assignment
			A_{1g}	85	Ba
E_{2g}	91	Ba	E_g	105	Ba
E_{2g}	187	Ru	E_g	199	Ru
E_{2g}	245	O			
A_{1g}	264	Ru	$A_{1g}(E_g)$	282	Ru(O)
E_{2g}	339	O	E_g	307	O
			E_g	403	O
			A_{1g}	463	O
A_{1g}	619	O	A_{1g}	625	O

On the other hand, Quilty *et al.*,[18] from the c-axis measurement of $9R$ BaRuO$_3$, assigned the A_{1g}(Ru) mode at 280 cm^{-1} as another O(E_g) mode. We note, as we will discuss later, that T dependence of this mode and its frequency are quite similar to those of the A_{1g}(Ru) mode in $4H$ BaRuO$_3$. So, it is very likely that the mode at 280 cm^{-1} is assigned as a A_{1g}(Ru) mode. It might be possible that a weak E_g(O) and a strong A_{1g}(Ru) mode are at nearly the same frequency.

B. T-dependent phonon spectra

Figures 3(a) and 3(b) show the T dependent polarized spectra of $4H$ and $9R$ BaRuO$_3$, respectively. The spectra are

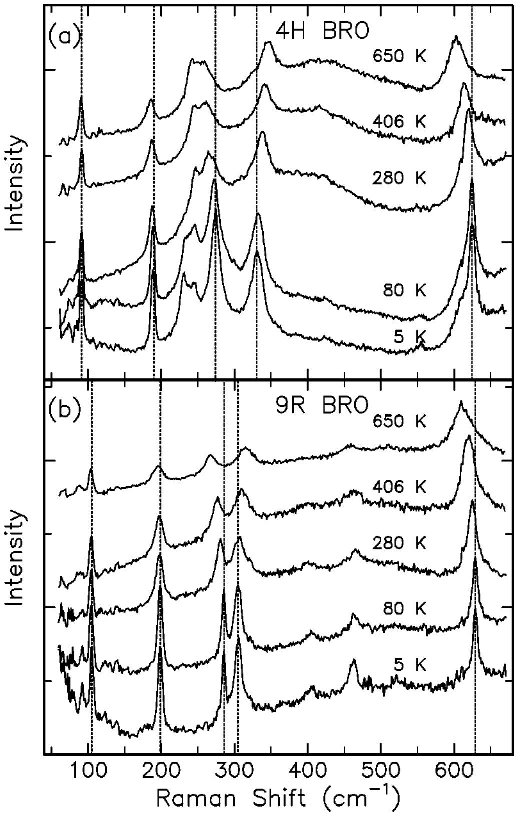

FIG. 3. Temperature-dependent polarized spectra of (a) $4H$ and (b) $9R$ BaRuO$_3$ in the a-b plane. The spectra are shifted up for clear presentation. The dotted lines are for guidance.

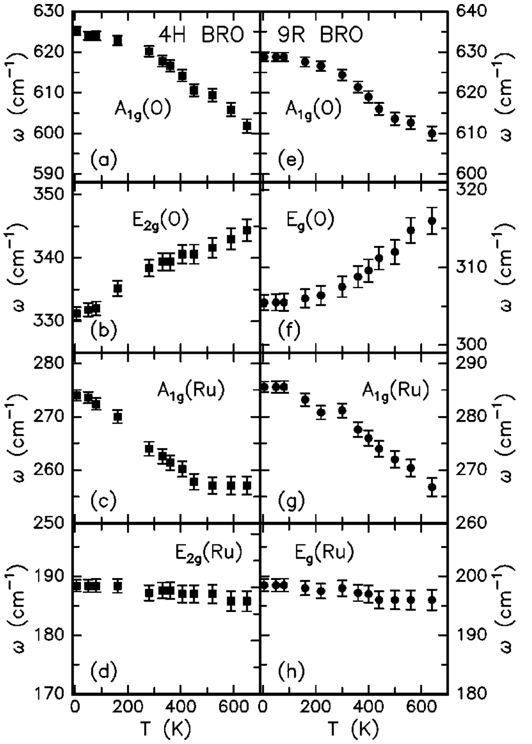

FIG. 4. The temperature-dependence of the phonon frequencies of (a) A_{1g}(O), (b) E_{2g}(O), (c) A_{1g}(Ru), and (d) E_{2g}(Ru) in 4*H* $BaRuO_3$, (e) A_{1g}(O), (f) E_g(O), (g) A_{1g}(Ru), and (h) E_g(Ru) in 9*R* $BaRuO_3$.

shifted up for clarity. It is observed that both compounds show similar phonon spectra. Except for the E_{2g}(O) mode near 245 cm^{-1} in 4*H* $BaRuO_3$, five distinct phonon modes are observed at similar frequencies in both compounds. The A_{1g} and E_{2g} modes of 4*H* $BaRuO_3$ correspond to the A_{1g} and E_g modes of 9*R* $BaRuO_3$, respectively. It is noted that the corresponding phonon modes in both ruthenates show similar *T*-dependent behavior.

The A_{1g} modes show different *T*-dependent behavior from the $E_{2g}(E_g)$ modes in both compounds. First, the A_{1g}(Ru) mode near 620 cm^{-1} and the A_{1g}(O) mode near 270 cm^{-1} strongly shift to higher frequencies with decreasing *T*. [The A_{1g}(Ba) mode in 9*R* $BaRuO_3$ shows a relatively weak hardening.] On the contrary, the E_{2g}(O) mode in 4*H* $BaRuO_3$ near 340 cm^{-1} and the E_g(O) mode in 9*R* $BaRuO_3$ near 300 cm^{-1} show a strong softening at lower *T*. These softenings are quite unusual in that the general *T*-dependent behavior of phonons is to show a hardening at lower *T* due to an anharmonicity of lattice vibrations. Even in a quite wide *T* variation by ~650 K, the E_{2g} (Ba, Ru) mode in 4*H* $BaRuO_3$ and E_g(Ba, Ru) mode in 9*R* $BaRuO_3$ show a very small change. On the other hand, as shown in Fig. 3(b), another E_{2g}(O) mode near 245 cm^{-1}, which is present only in the 4*H* $BaRuO_3$, shows an anomalous *T* dependence. This mode splits into two modes at low *T*. (The details will be discussed in the following section.)

Figure 4 shows the detailed *T* dependence of the phonons. The left panels, Figs. 4 (a), 4(b), 4(c), and 4(d) show the *T* dependencies of the A_{1g}(O), E_{2g}(O), A_{1g}(Ru), and E_{2g}(Ru) modes, respectively, of 4*H* $BaRuO_3$. The right panels, Figs. 4(e), 4(f), 4(g), and 4(h) show the *T* dependence of the phonons of 9*R* $BaRuO_3$ corresponding to those of 4*H* $BaRuO_3$, in sequence. While A_{1g}(O) modes show strong hardenings, E_{2g}(O) (or E_g) modes show softenings with decreasing *T*. Similarly, A_{1g}(Ru) modes show strong hardenings, but no significant change of E_{2g}(Ru) (or E_g) modes is observed. It is clear that A_{1g} modes show different *T*-dependent behavior from E_{2g} (E_g) modes.[19]

It is noted that the *T*-dependent behavior of the phonon modes closely depends on the direction of lattice vibrations. As a tentative description, E_g (or E_{2g}) and A_{1g} modes are related to the vibrations in the *a*-*b* plane and along the *c* axis, respectively. The different *T* dependence of the A_{1g} and E_{2g} (or E_g) modes could originate from their anisotropic structural properties with the face sharing of RuO_6 octahedra along the *c* axis, through which a strong anisotropic interaction, i.e., a direct Ru metal bonding, occurs.

The strong hardenings of A_{1g} modes indicate that the bonding stiffness along the *c* axis becomes larger. This also implies that the interaction along the *c* axis, i.e., a direct Ru metal bonding, becomes stronger. It is noted that strong hardenings of A_{1g} modes cannot be simply explained by the variation of the *c* axis lattice constant **c**. The A_{1g} modes vibrating along the *c* axis are expected to have a close relation with **c**. However, while synchrotron XRD experiments with 4*H* $BaRuO_3$ report that its **c** is changed just by ~0.005 Å with *T* varying between 30 K and 310 K,[20] the phonon frequency ω_{ph} of the A_{1g} modes is changed by ~10 cm^{-1} in the corresponding *T* range. These changes of the $\omega_{ph}(A_{1g})$ are much larger than those of the cuprates, where the stretching modes in Cu-O planes are quite sensitive to Cu-O bonding distances; while the lattice constant in the *a*-*b* plane is reduced by about 0.1 Å , the ω_{ph} increases higher by 100 cm^{-1}.[21] The relatively large change of the $\omega_{ph}(A_{1g})$ in $BaRuO_3$ systems means that there must be another electronic contribution to the strong hardening of the A_{1g} modes in addition to those of the lattice effect.[22] It is noted that similar hardening of the phonon modes in some manganites are observed due to charge ordering fluctuation.[23] On the other hand, in the infinite 1D chain cuprates, i.e., $Ca_{2-x}Sr_xCuO_3$, Drechsler *et al.* suggested the possible existence of a dynamic Peierl-type distortion and predicted phonon anomalies such as a hardening or a splitting.[24] The strong hardenings of the A_{1g} modes in the 1D-like ruthenates might be related to the CDW fluctuation by the metal bonding.

Unlike the A_{1g} modes, E_{2g} (or E_g) modes vibrating normally to the metal bonding direction show softenings or no significant change. Especially, strong softenings of the E_{2g}(O) (or E_g) modes are quite unusual. It is noted that only the oxygens participating in the face sharing have Raman-active modes. So, the softenings of the E_{2g}(O) (or E_g) modes indicate that the bonding stiffness among the face-shared oxygens reduces and that there should be a kind of structural instability in the face-shared O structure. This also implies that the Ru-O-Ru interaction weakens as a Ru-Ru interaction strengthens, which could induce the stronger 1D

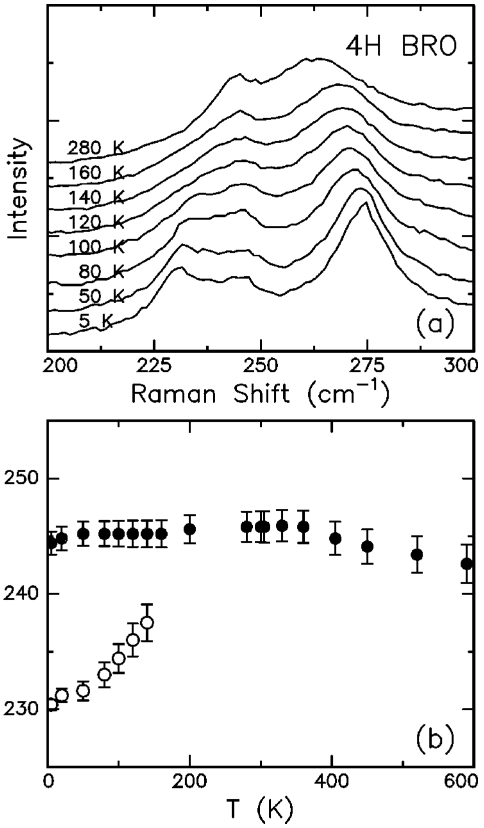

FIG. 5. (a) Temperature-dependent behavior of E_{2g}(O) mode in $4H$ $BaRuO_3$. (b) Phonon frequency vs temperature. The solid and open circle symbols represent the E_{2g}(O) mode and a new phonon mode, respectively.

character. These differences in T dependence between A_{1g} and E_g (E_{2g}) modes in $BaRuO_3$ could be a unique feature reflecting a structural instability due to the increase of the metal-bonding strength.[25]

C. Splitting of E_{2g}(O) mode in $4H$ $BaRuO_3$

Another important observation is that the E_{2g}(O) mode near 245 cm^{-1} in $4H$ $BaRuO_3$ shows a clear splitting. It is noted that this E_{2g}(O) mode is not permitted in $9R$ $BaRuO_3$ from group theory analysis. As shown in Fig. 5(a), as T decreases, the E_{2g}(O) mode becomes suppressed and a new mode at lower frequency develops. Together with the softenings of other E_{2g}(O) modes, this splitting clearly indicates the existence of a structural instability in the face-shared structure. While the onset temperature of the phonon splitting is not clear, as shown in Fig. 5(b), some anomaly is observed at ~360 K, where the T dependence of the E_{2g}(O) mode is changed. This appears consistent with the optical observation that the pseudogap feature is still observed at 300 K.[2] It is very likely that this structural instability is closely related to the origin of the pseudogap formation in the ruthenates, i.e., the CDW instability.

It is noted that the phonon splitting happens in the E_{2g}(O) mode vibrating normally to the metal-bonding direction. The splitting of an IR-active phonon mode in the a-b plane was also observed for a static CDW $9R$ $BaIrO_3$.[6] This implies that the charge modulation along the c axis might be closely related to the structural instability in the a-b plane. On the other hand, it is interesting that only the E_{2g}(O) mode near 245 cm^{-1} shows the splitting. This means that the local structural distortion related to this mode occurs, maintaining the total crystallographic symmetry of the $4H$ compound. More theoretical and experimental studies are needed to understand the unusual CDW instability and its detailed relation to the pseudogap formation.

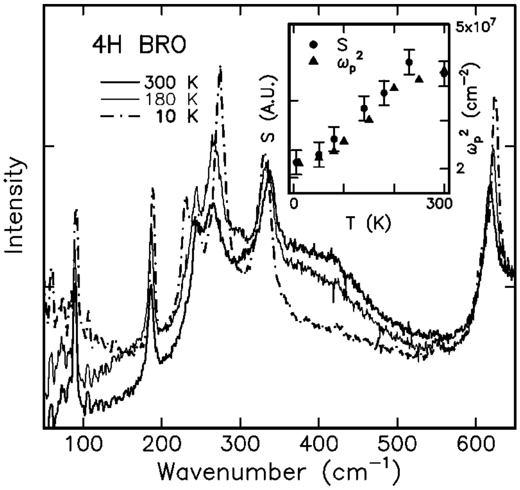

FIG. 6. Temperature-dependent Raman spectra of the $4H$ $BaRuO_3$ in the polarized direction. Inset, the solid circle and the solid triangle symbols represent the integrated Raman backgrounds S and the square of the plasma frequency ω_p^2 (quoted from Ref. 21).

D. Electronic Raman continua

Electronic Raman continua give important information about the electronic excitation. Figure 6 shows T dependent polarized spectra of $4H$ $BaRuO_3$. As T decreases, Raman continua below 200 cm^{-1} increase. This behavior is commonly observed in polarized and depolarized spectra in both ruthenates. The increase of Raman continua in low-frequency region could be due to the reduction of the screening of free carriers on elastic scatterings, such as Rayleigh responses. This is consistent with optical observations that a reduction of carrier density n occurs with pseudogap formation.[1,2] Similar behavior was observed in some perovskite manganites with the metal-insulator transition.[26]

Another important point is that a broad Raman continuum near 400 cm^{-1} in $4H$ $BaRuO_3$ is observed with a significant T dependence.[27] As shown in Fig. 6, this broad continuum becomes suppressed with decreasing T. Because the maximum of the continuum is at a relatively high frequency, it cannot be an electronic Raman scattering by charge fluctuations arising from electron-hole excitations near the Fermi energy.[28] And, its position is different from that of the pseudogap position, ~650 cm^{-1}.[2] To get qualitative physical insights, we integrated the Raman backgrounds in the frequency region of 250–600 cm^{-1}, where the T dependence is dominant.[29] Interestingly, as shown in the inset of Fig. 6, the integrated area S is strongly correlated with the square of the plasma frequency ω_p^2, obtained by optical measurement.[2] The reduction in ω_p^2 originates mainly from a reduction in n caused by a partial gap opening on the Fermi surface. The strong correlation between S and ω_p^2 indicates that the suppression of the distinct Raman excitation near 400 cm^{-1} might be closely related to the pseudogap formation.

IV. SUMMARY

Raman spectra in 4H and 9R BaRuO$_3$ show interesting features related to the metal bonding formed through the face sharing of RuO$_6$ octahedra. The temperature dependence of the observed phonons strongly depend on the vibration direction with respect to the metal bonding. For 4H BaRuO$_3$, another E_{2g} mode of the oxygen participating in the face sharing is split clearly. The temperature dependence of the broad electronic Raman continua near 400 cm^{-1} suggests a partial gap opening on the Fermi surface. These observations indicate that there occurs a kind of structural instability due to the metal bonding, which could be closely related to the pseudogap formation in the BaRuO$_3$ systems.

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