

## Dynamical Symmetry Breaking under Core Excitation in Graphite: Polarization Correlation in Soft X-Ray Recombination Emission

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A recombination emission spectrum is applied to study the local lattice distortion due to core excitation in graphite. The recombination emission spectrum reveals a long low-energy tail when the C 1s electron is excited to the  $\sigma^*$  core exciton state. This indicates a large local lattice distortion around the excited carbon atom within a core hole lifetime ( $\sim 10$  fs). A theoretical calculation based upon an ionic cluster model reproduces the experiments well. The strong polarization correlation between incident and emitted x rays is conclusive evidence of symmetry breaking in the core exciton state due to coupling with asymmetric vibrational modes.

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Many have long believed that the time scale of a phonon relaxation, which usually falls in subpicoseconds, is far longer than a core hole lifetime (less than several femtoseconds), so that the core excited state immediately decays with the electronic Auger decay process before heavy atoms start to move. In simple molecules and adsorbates on a solid surface, however, recent experiments and theoretical analyses of resonant Auger and soft x-ray emission spectroscopies have clearly indicated large atomic displacements in core excited states when a core electron is excited to a bound unoccupied state [1–5]. Meanwhile in solid states, there have been no reports on a large atomic displacement in a core excited state since the pioneering experiment of soft x-ray recombination emission in diamond and graphite done by Y. Ma *et al.* [6]. In their experiment, the soft x-ray recombination emission spectrum showed a long low-energy tail when the C 1s core electron is excited into a bound core excited state. Considering the fact that the initial and the final states have the same electronic configuration in the recombination emission, and the low-energy tail is strongly enhanced when the core exciton is excited, phonon relaxation in the core excited state is a possible mechanism responsible for this low-energy tail, rather than another one like simultaneous electron-hole pair creation across the Fermi energy [7].

According to  $Z + 1$  equivalent core approximation, C 1s core exciton can be regarded as a nitrogen impurity atom well known to form a deep level in the middle of a band gap with a large off-center instability [8–10]. Tanaka and Kayanuma interpreted the characteristic feature of the recombination emission spectra of diamond with a theory in which local phonon modes are strongly coupled with the quasidegenerate core exciton states [11].

They clarified that the off-center instability is induced by a cooperation of quasi-Jahn-Teller and Jahn-Teller effects in the core excited state, and predicted that the spectrum should have a distinct polarization correlation between the incident and emitted x-ray photons. This polarization correlation is decisive evidence that the local symmetry is broken by ionic coupling of a core exciton with lattice phonon systems, i.e., *dynamical symmetry breaking* in core excited states. This is quite a contrast to the case of the resonant Auger emission process, where the final state interaction as well plays an important role in determining the spectral feature [4], which makes the interpretation of the spectrum complicated and sometimes leaves ambiguity.

In this Letter, we report the strong lattice relaxation in the core excited state of graphite with the C 1s soft x-ray recombination emission spectrum, including the first observation of polarization correlation. Graphite has regained great attention since the discovery of carbon nanotubes that show wide unique physical properties with the slight change of wrapping a single graphite layer. So the study on the effect of the electron-phonon interaction in graphite is important to understand the physical properties of nanotubes.

C 1s absorption and emission of highly oriented pyrolytic graphite was performed using a flat field soft x-ray emission spectrometer [12] newly constructed in BL27SU at SPring-8 [13]. The energy resolutions of incident and emitted photons are less than 0.1 and 0.6 eV at the C 1s edge, respectively. The excitation energy was carefully calibrated using the energy position of Au 4f photoemission lines. C 1s recombination emission spectra were measured at “polarized” and “depolarized” configurations as shown in Figs. 1(a) and 1(b), respectively.

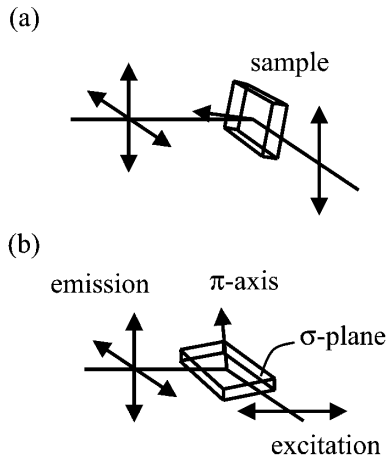


FIG. 1. Experimental geometry: (a) polarized configuration; (b) depolarized configuration. The two-headed arrow indicates the polarization vectors of incident and emitted photons.

While two independent polarizations of an emitted x ray in the polarized configuration are parallel and orthogonal to an incident x-ray polarization, they are necessarily orthogonal to that of the incident x ray in the depolarized configuration. We show the C 1s recombination emission obtained by scanning the excitation x-ray energy across the  $\sigma^*$  absorption band in Fig. 2. The valence x-ray emission band appears below 284 eV [14], which is not shown here.

The C 1s x-ray absorption spectrum (C 1s XAS) shown in the inset is attributed to the transition of a C 1s core electron to the antibonding  $\sigma^*$  conduction states. The peak at 291.7 eV has been interpreted as the transition to a localized core exciton state ( $\sigma_1^*$ ), which is followed by the broad absorption band attributed to the excitation to the delocalized scattering state ( $\sigma_2^*$ ) [15–17].

The recombination emission spectra strongly depend on the excitation energy. The spectrum has a long tail starting from the elastic line (Rayleigh line) towards the low-energy side when  $\hbar\Omega_1$  is tuned with  $\sigma_1^*$  core exciton peak [Fig. 2(b)]. This low-energy tail almost disappears when  $\hbar\Omega_1$  is 1.0 eV off-resonant below the  $\sigma_1^*$  resonance [Fig. 2(a)]. Similarly when  $\hbar\Omega_1$  is increased, the low-energy tail is shortened [Fig. 2(c)], and at the  $\sigma_2^*$  excitation, we cannot see any asymmetry in the spectral shape [Fig. 2(d)]. The appearance of this low-energy tail is interpreted as a *hot luminescence*, the photon emission taking place as the phonon relaxation proceeds [11]: The emitted soft x-ray photon energy is gradually lowered as a part of electronic excitation energy being transferred to the vibrational subsystems. When the excitation becomes off-resonant [Fig. 2(a)], the whole recombination emission process from the initial to the final states becomes coherent and the intermediate core exciton state is virtually passed through. The effective time during which the core excited state can be effectively coupled with phonon systems becomes shortened, resulting in the

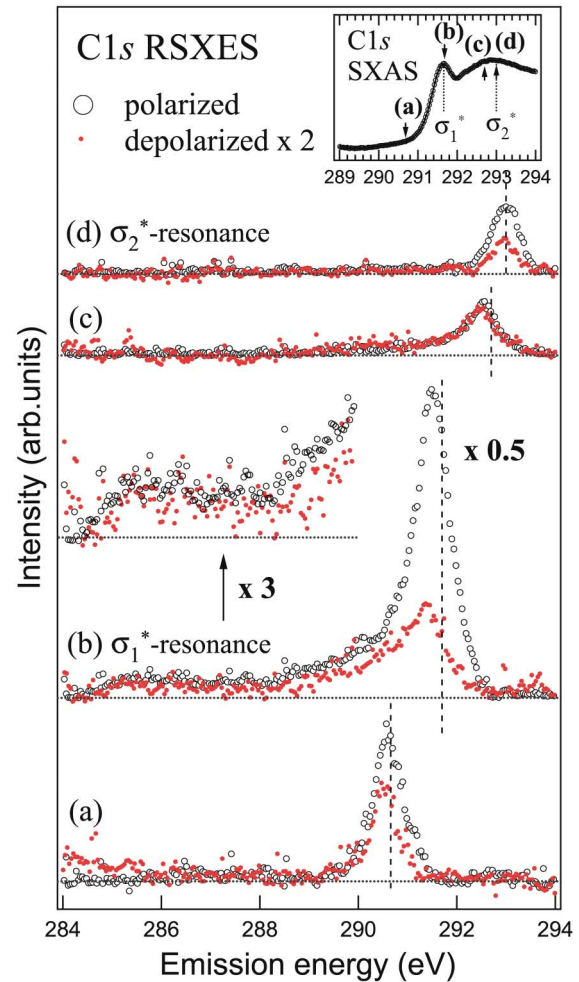


FIG. 2 (color). C 1s resonant soft x-ray emission spectra of graphite. The excitation energies are shown in the absorption spectrum in the inset; they are tuned at (a)  $\hbar\Omega_1 = 290.7$  eV, (b)  $\hbar\Omega_1 = 291.7$  eV, (c)  $\hbar\Omega_1 = 292.7$  eV, and (d)  $\hbar\Omega_1 = 293$  eV. Dashed vertical lines indicate the position of the excitation energy. Polarized and depolarized spectra are drawn with open circles and red dots, respectively.

disappearance of the low-energy tail [1]. In addition, we have found out a small hump around 285 eV in Fig. 2(b). This is attributed to the recombination emission when an induced coherent vibrational wave packet turns back at a turning point on an adiabatic potential surface of the core exciton state [18,19]. These structures are hardly seen in the resonant Raman scattering spectrum in the optical region because the lifetime of the excited state is usually so long that the ordinary luminescence from the relaxed excited state dominates over these faint structures. Since it is these hot luminescence spectral features that reflect well the very early stage of the relaxation process [18,19], the soft x-ray recombination emission is a powerful tool to study the ultrafast relaxation dynamics of the core excited state.

The most intriguing features are the polarization correlation in Fig. 2. The following two points should be

stressed here: (i) The low-energy tail in recombination emission has been observed both in depolarized as well as polarized configurations. (ii) The intensity of the low-energy tail relative to the integrated intensity of the recombination emission on the  $\sigma_1^*$  core excitation is more pronounced in depolarized configuration than in polarized configuration. These suggest that the local symmetry around the excited atom is broken under the  $\sigma_1^*$  core excitation. Considering a minimal cluster consisting of four C atoms—at the center is the excited atom surrounded by three nearest neighbor atoms—we have three stretching vibrational modes as major coupling vibrations with the core exciton state: one symmetric and two asymmetric stretching vibrational modes. Since the depolarization process requires at least one symmetry breaking phonon emission, the asymmetric vibrations must be induced under the  $\sigma^*$  core excitation through the ionic coupling, while the coupling with the symmetric vibration does not change the structural symmetry. A theoretical analysis of these spectral shapes enables us to evaluate the coupling strengths of the core exciton with these vibrational modes.

Based on the cluster model, we consider three anti-bonding  $sp^2$  hybridized orbitals as an electronic basis set,

$$H_e = \begin{bmatrix} \epsilon_s - (\alpha/\sqrt{3})Q_s & & -(\beta/\sqrt{3})Q_x & & -(\beta/\sqrt{3})Q_y \\ -(\beta/\sqrt{3})Q_x & \epsilon_p - (\alpha/\sqrt{3})Q_s - (\beta/\sqrt{6})Q_y & & & -(\beta/\sqrt{6})Q_x \\ -(\beta/\sqrt{3})Q_y & & -(\beta/\sqrt{6})Q_x & & \\ & & & \epsilon_p - (\alpha/\sqrt{3})Q_s + (\beta/\sqrt{6})Q_y & \\ & & & & \end{bmatrix} + H_0, \quad (1)$$

with

$$H_0 = \hbar\omega_s b_s^\dagger b_s + \sum_{i=x,y} \hbar\omega_p b_i^\dagger b_i, \quad (2)$$

where  $H_0$  is the unperturbed Hamiltonian for the vibrational systems;  $b_i$  ( $b_i^\dagger$ ) is the boson annihilation (creation) operator for each mode:  $Q_i = 1/\sqrt{2}(b_i + b_i^\dagger)$  ( $i = s, x, y$ );  $\hbar\omega_s$  ( $\hbar\omega_p$ ) is the energy of the vibrational system in the  $s$  ( $p = x, y$ ) mode. The energies of the  $s$  and  $p$  states at  $\mathbf{Q} = \mathbf{0}$  are denoted by  $\epsilon_s$  and  $\epsilon_p$ , respectively, and  $\alpha$  ( $\beta$ ) is the coupling strength with the symmetric (asymmetric) modes. Because of the lack of inversion symmetry, the coupling with asymmetric modes  $Q_x$  and  $Q_y$  brings about simultaneously the Jahn-Teller coupling within  $p$  symmetry core exciton states and the quasi-Jahn-Teller coupling between the  $s$  and  $p$  symmetry core exciton states.

In Fig. 3, we depicted an aspect of adiabatic potential surfaces in the core excited state for a set of parameters shown below. The horizontal axis represents the atomic displacement of the excited atom along a bond direction. Doubly degenerated  $p$  symmetry core exciton states at  $Q = 0$  is split into  $A_1$  and  $B_1$  states by Jahn-Teller coupling, and the lowest branch for the  $s$  symmetry core exciton state is greatly lowered by the quasi-Jahn-Teller coupling with the upper branch. For symmetry reasons, one of the upper branches can couple with the lowest

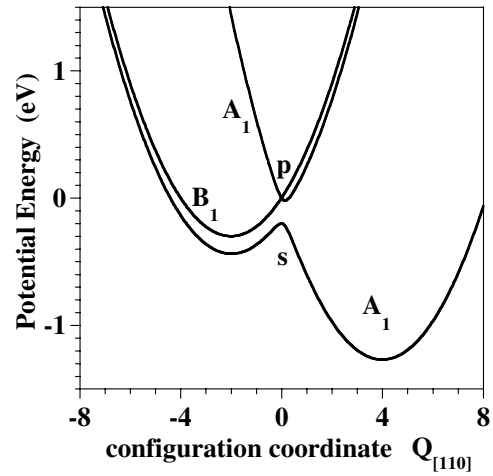


FIG. 3. The calculated adiabatic potential surface in the core excited state along a bond direction. The unit of the horizontal axis is evaluated to be  $\sqrt{(\hbar/M\omega_{s,p})}$ , where  $M$  denotes the mass of the carbon atom.

which are coupled with the three stretching vibrations [5]. In a representation of a symmetrized basis set, the Hamiltonian for the core exciton states is represented by

branch. It is clearly seen that as a result of the quasi-Jahn-Teller coupling the on-center position becomes unstable and the equilibrium position is shifted about 0.2 Å away from the origin with about 1.27 eV relaxation energy. The C 1s core electron is excited to the dipole allowed  $p$  symmetry core exciton states, at  $Q = 0$  of the upper branch, and a nonadiabatic coupling causes it to decay into the lowest branch. The low-energy tail in the recombination emission is attributed to the relaxation process going along the lowest branch toward the equilibrium, and the hump structure is due to the hot luminescence at the turning point. As the lattice relaxation proceeds along with the potential surface of the asymmetric modes, the local symmetry around the excited atom is broken down, which causes the observed prominent low-energy tail structure in the depolarized configuration.

We show the calculations of the recombination emission in Fig. 4, which is calculated fully quantum mechanically by the formula for a second order optical process [11]. We have determined the parameter values so that the experiments can be well reproduced:  $\hbar\omega_s = \hbar\omega_p = 0.15$  eV,  $\epsilon_p - \epsilon_s = 0.4$  eV,  $\alpha = 0$ ,  $\beta = 4.9$  in units of  $\hbar\omega_p$ , and  $\Gamma_{1s} = 45$  meV. In our model, the damping of phonon oscillation is neglected for simplicity. This approximation is justified because the core excited state decays before reaching the thermal equilibrium, and

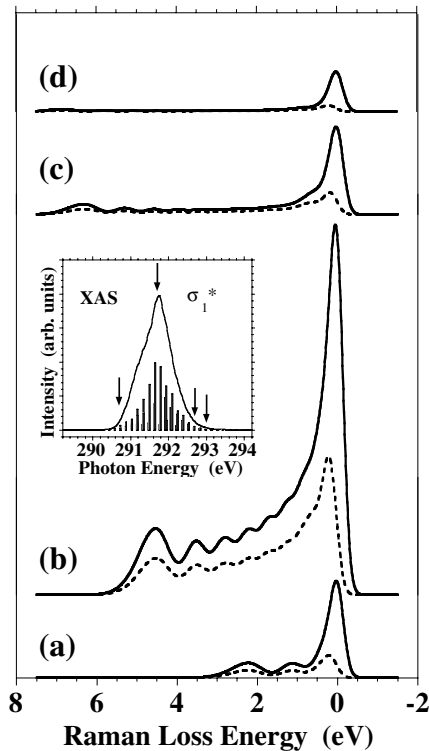


FIG. 4. The calculated results of resonant soft x-ray emission spectra across the  $\sigma^*$  absorption peak. Polarized and depolarized spectra are drawn with the solid line and dashed line, respectively. The x-ray absorption spectrum is shown in the inset.

the x-ray emission takes place only within that short lifetime of the core hole. The recombination emissions are plotted for the same excitation energies in the experiments. The calculated absorption spectrum is also shown in the inset, and the excitation energies are indicated by arrows. The calculations satisfactorily explain the experiments. The low-energy tail is prominent when the excitation energy is tuned with the  $\sigma_1^*$  peak both in the polarized and the depolarized configurations. The relative intensity of the low-energy tail is more pronounced in the depolarized configuration than in the polarized configuration because the strong Rayleigh component is forbidden in the depolarized configuration. The couplings with the asymmetric modes are essential to reproduce the experiments; in fact, the coupling with the symmetric mode has been neglected here. This is quite in contrast to the case of a  $\text{BCl}_3$  molecule with a same point symmetry,  $D_{3h}$ , where the coupling with a symmetric stretching mode plays an important role [5]. This may reflect a qualitative difference of the vibrational coupling effects between molecules and crystals; In graphite the expansion of the cluster may be greatly suppressed by the existence of surrounding atoms.

Under the higher excitation [Figs. 4(c) and 4(d)], asymmetry in the recombination emission disappears consis-

tently with the experiments, for the reason mentioned above [1]. In reality, when the  $\hbar\Omega_1$  is well into high energy continuum, we should take into account itinerancy of the excited electron over the entire crystal. The delocalization of the excited electron makes the exciton-phonon coupling suppressed [20], letting the emission peak be symmetric.

In conclusion, our experiments of the recombination emission confirm a large local lattice distortion around an excited atom in the core exciton state in graphite. A remarkable polarization correlation between incident and emitted x rays has been observed for the first time, leading to the conclusion that the dynamical symmetry breaking in the core exciton state is mainly due to the coupling of the core exciton states with asymmetric vibrational modes.

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