Dynamical symmetry breaking under core excitation in graphite: Polarization correlation in soft X-ray recombination emission

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ABSTRACT

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 σ+ core exciton state. This indicates a large local lattice distortion around the excited carbon atom within a core hole lifetime (~10fs). Theoretical calculation based upon an ionic cluster model well reproduces the experiments. 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.

Innovations in X-ray experiments have greatly enhanced our understandings of the relaxation dynamics of core excited states in many condensed systems. Among them, spectroscopies of coherent second order processes, such as resonant Auger electron emission and resonant X-ray emission spectroscopies, once believed to be difficult to obtain have now become common and the best tool to study ultrafast relaxation dynamics of the core excited states [1].

Since the core excited atom can be regarded as an electronically equivalent atom with the valence increased by 1 (Z + 1 approximation), the sudden change of the charge balance around the excited atom may bring about many (shake-up or shake-off) satellites in the core level spectra. While electronic relaxation on core excitation has been much discussed, not much attention has been paid to the relaxation dynamics through electron-phonon coupling in the core excited states, especially in solid states. This is because many have long believed that the time scale of the phonon relaxation, which usually falls in sub picoseconds, is far longer than a core hole lifetime (less than several femtoseconds), so that core excited state immediately decays with electronic Auger decay process before heavy atoms start to move. In simple molecules and adsorbates on solid surface, however, recent experiments and theoretical analyses of resonant Auger and soft X-ray emission spectroscopies have clearly indicated a large atomic displacements in core excited states when a core electron is excited to a bound unoccupied state.

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. In the experiments, the soft X-ray recombination emission spectrum showed a long low-energy tail when the C 1s core electron is excited to a bound core excited state, indicating a large lattice distortion around an excited atom in the core exciton state. According to Z + 1 approximation C 1s core exciton can be regarded as a nitrogen impurity atom well known to form a deep level in the middle of band gap with a large off-center instability. Tanaka and Kawanuma interpreted the characteristic feature of the recombination emission spectra of diamond with a theory in which local phonon modes are strongly coupled with the quasi-degenerate core exciton states. 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. Our aim here is to experimentally reveal the lattice relaxation dynamics in the core excited state of a solid state with soft X-ray recombination emission spectrum.

In this Letter, we report the recombination emission in graphite which clearly shows low-energy tail in the emission spectrum. Considering the fact that the electronic configuration of the final state is just the same as in the initial state in the recombination emission process, the only possible mechanism responsible for this low-energy tail is the phonon relaxation in the intermediate core excited state. Thus this should be the direct evidence of the large distortion

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around the excited atom in the core exciton state in graphite. This is quite in contrast to the case of resonant Auger emission process, where the final state interaction as well plays an important role to determine the spectral feature [4], which makes the interpretation of the spectrum complicated and sometimes leaves ambiguity. In addition, we report here for the first time a strong polarization correlation of the recombination emission, which reveals the dynamical symmetry breaking by the ionic couplings in the core excited state.

Graphite has regained great attention since the discovery of carbon nanotubes that show wide unique physical properties with 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 (HOPG) was performed using a flat field soft X-ray emission spectrometer [11] newly constructed in BL27SU at SPring-8 [12]. The energy resolution of incident and emitted photons are less than 0.1eV and 0.6eV at 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 (A)'polarized' and (B)'depolarized' configurations as shown in Fig. 1. 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 σ* absorption band in Fig. 2. The valence x-ray emission band appears below 284eV [13], 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 σ* conduction states. The peak at 291.7eV has been interpreted as the transition to a localized core exciton state (σ1), which is followed by the broad absorption band attributed to the excitation to the delocalized scattering state (σ2) [14, 15, 16]. The excitation energies hΩ1 are indicated in the absorption spectrum: (a) 290.7eV, (b) 291.7eV, (c) 292.7eV, and (d) 293eV. In Fig. 2 the emission spectra in the polarized and depolarized configurations are shown by a line with open circle and a thick red line, respectively.

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 hΩ1 is tuned with σ1 core exciton peak (Fig. 2b)). This low energy tail almost disappears when hΩ1 is 1.0eV off-resonant below the σ1 resonance (Fig. 2a)). Similarly when hΩ1 is increased, the low energy tail is shortened (Fig. 2c)), and at the σ2 excitation, we cannot see any asymmetry in the spectral shape (Fig. 2d)). 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. 2a)), the whole recombination emission process from the initial to
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 disappearance of the low-energy tail \[1\]. In addition, we have found out a small hump around 285eV 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 \[17, 18\]. These structures are hardly seen in the resonant Raman scattering spectrum in 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 structure. Since it is these hot luminescence spectral features that well reflect the very early stage of the relaxation process \[17, 18\], the soft X-ray recombination emission is 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 \(\sigma^*\) 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 \(\sigma^*\) 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 $\sigma^*$ 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 a three antibonding $sp^2$ hybridized orbitals as an electronic basis set 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

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

with

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

where $H_0$ is unperturbed Hamiltonian for the vibrational systems; $b_i$ ($b_i^\dagger$) is 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 $s (p = x, y)$ mode. The energies of the $s$ and $p$ states at $Q = 0$ 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. The unit of the horizontal axis is then evaluated to be $\sqrt{\hbar/M\omega_{s,p}}$, where $M$ denotes the mass of carbon atom. 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 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

![FIG. 3: The calculated adiabatic potential surface in the core excited state along a bond direction.](image-url)
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 line and dashed line, respectively. The intensity of the depolarized spectra is multiplied by 2. The X-ray absorption spectrum is shown in the inset.

is shifted about 0.2Å away from the origin with about 1.27eV 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 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 [10]. 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 unit 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 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 BCl$_3$ molecule with a same point symmetry, $D_{3h}$, where the coupling with symmetric stretching mode plays an important role. 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 (Fig. 4(c) and (d)), asymmetry in the recombination emission disappears consistently with the experiments, for the reason mentioned above. In reality, when $h\Omega_1$ 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\[19\], letting the emission peak 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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[1] F. Gel’mukhanov and H. Ågren, Phys. Rep. 312, 87 (1999).
[2] J. -E. Rubbenson, J. Electron Spectrosc. Relat. Phenom., 110-111, 135 (2000).
[3] A. Kotani and S. Shin, Rev. Mod. Phys. 73, 203 (2001).
[4] P. A. Brühwiler et al., Rev. Mod. Phys. 74, 703 (2002).
[5] K. Ueda et al., Phys. Rev. Lett. 85, 3129 (2000).
[6] Y. Ma et al., Phys. Rev. Lett. 71, 3725 (1993).
[7] K. Jackson et al., Phys. Rev. B 41, 12641 (1990)
[8] A. Mainwood and A. M. Stoneham, J. Phys.:Condens. Matter 6, 4917 (1994).
[9] F. Mauri and R. Car, Phys. Rev. Lett. 75, 3166 (1995).
[10] S. Tanaka and Y. Kayanuma, Solid State Commun. 100, 77 (1996).
[11] T.Tokushima et al., Surf. Rev. Lett. 9, 503 (2002).
[12] H.Ohashi et al., Nucl. Instrum. Methods A 467-468, 529 (2001).
[13] C.P.Franck et al., Phys. Rev. B31, 5366 (1985); P.Skytt et al., Phys. Rev. B50, 10457 (1994); J.A.Carlisle et al., Phys. Rev. Lett.74, 1234 (1995); M.vanVeenendaal and P.Carra, Phys Rev. Lett. 78, 2839 (1997).
[14] P. E. Batson, Phys. Rev. B 48, 2608 (1993).
[15] P. A. Brühwiler et al., Phys. Rev. Lett. 74, 614 (1995).
[16] D. C. McCulloch and R. Brydson, J. Phys.:Condens. Matter 8, 3835 (1996).
[17] G. D. Mahan, Phys. Rev. B 15, 4587 (1977).
[18] Y. Kayanuma, J. Phys. Soc. Jpn. 57, 292 (1988).
[19] Y. Toyozawa, Optical Processes in Solids(Cambridge, 2003), Chap. 10, p192.