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Tetsuya Kodaira [a], Yasuo Nozue [a] & Takenari Goto [a]

[a] Department of Physics, Faculty of Science, Tohoku University, Aramaki Aoba, Aoba-Ku, Sendai, 980, Japan

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OPTICAL ABSORPTION SPECTRA OF SODIUM CLUSTERS INCORPORATED INTO ZEOLITE LTA

TETSUYA KODAIRA, YASUO NOZUE and TAKENARI GOTO
Department of Physics, Faculty of Science, Tohoku University,
Aramaki Aoba, Aoba-Ku, Sendai 980, Japan

Abstract Absorption spectra are reported for sodium clusters incorporated into cages of zeolite LTA crystals, where the expected cluster diameter is about 11 Å at maximum. The spectra exhibit the bands originated from the excitation of the quantum-confined electron-hole pair as well as the surface plasmon excitation.

INTRODUCTION

The optical response of small metal clusters has recently been highly active, because of the developments of the photodissociation spectroscopy of free clusters[1-5] and the theoretical calculations.[6-12] The surface plasmon-like excitation, which is the collective excitation mode of the many electron system, can be strongly observed in small metal clusters. The additional weak absorption bands are observed as the electron-hole pair-like state, where the electron and hole are quantum-confined in the cluster.[6] The interesting subjects in this field are listed as follows. (1) How does the surface plasmon state depend on the cluster shape and size? (2) What kind of the damping process is dominant in the surface plasmon state? (3) How does the electron-hole pair-like excitation dominates the absorption spectrum, as the cluster approaches the one-electron limit?

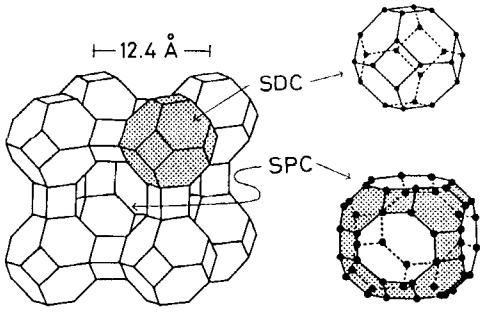

FIGURE 1 Framework of LTA. The sodalite cage (SDC) is indicated by the shadowed region in the left figure. The supercage (SPC) is located among them. Closed circles indicate Al or Si atoms.

In the present report, sodium clusters are incorporated into zeolite LTA. The zeolite method has the merits in the controllability of the maximum cluster size, that of the cluster temperature and the possibility of the structural analysis.

The framework structure of LTA is shown in Figure 1. The inner diameter of the supercage is 11.4 Å. The maximum number of Na atoms in a supercage is estimated to be 20 from the comparison with the Wigner-Seitz radius. The supercages are connected in the simple cubic structure by sharing the windows with the inner diameter of 4.2 Å.

In the present report, the electron-hole pair bands of Na-cluster are observed in the absorption spectra in addition to the surface plasmon band. The temperature dependence experiment reveals the existence of the strong electron-vibration coupling in the surface plasmon. The surface plasmon consists of two bands at 77 K. The splitting is ascribed to the O_h symmetry of the cluster.

EXPERIMENTAL PROCEDURES

Na-type LTA with the Si/Al ratio of unity was used as the container of Na clusters. This zeolite is abbreviated to Na-LTA(1), hereafter. The average powder size was about 3 μm. Zeolite powder was dehydrated at 550 ° C for 12 h, and Na was adsorbed at 150 ° C by the vapor phase successively. The absorption spectra were obtained from the Kubelka-Munk transformation of the diffuse reflection spectra.

EXPERIMENTAL RESULTS

Figure 2(a) shows the absorption spectra of Na clusters in Na-LTA(1) at room temperature. The total Na absorption time is indicated in each curve. The total amount of adsorbed Na is nearly proportional to the total adsorption time. In the most dilute sample shown by curve 10, the bands D_1 and D_2 appear. With increasing the Na density, the bands D_1 and D_2 increase and are saturated. With increasing the Na density furthermore, the bands P, S_1 and S_2 appear, and increase. There appear no absorption band between 4 and 6 eV. Figure 2(b) shows the absorption spectra at the higher Na density at room temperature. With increasing the Na density, the bands D_1 and D_2 decrease and the bands P, S_1 and S_2 increase furthermore. The broken curves mean the saturation of the diffuse reflectivity, and the Kubelka-Munk function gives no longer the correct absorption coefficient.

Figures 3(a) and 3(b) indicate the temperature dependence of the absorption bands P and S_2 at the intermediate Na-loading density. At 77 K, the band S_2 becomes sharp, and the band P shows the doublet structure as marked by bars.

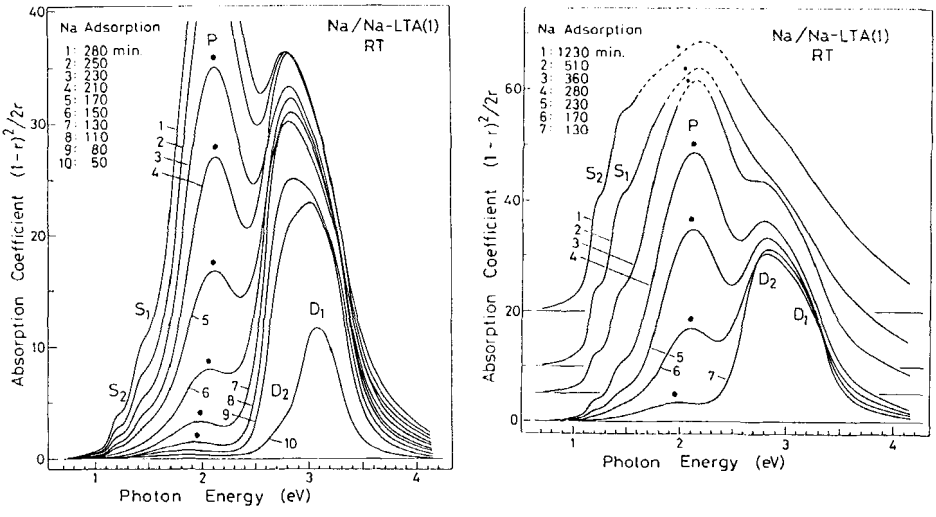

FIGURE 2 Absorption spectra of Na clusters in Na-LTA(1) at room temperature for (a) lower Na-loading densities and (b) higher ones. Total Na-adsorption times of respective curves are shown in the figure. Broken curves indicate the saturation of the diffuse reflection.

DISCUSSIONS

In Na-type zeolite, Na^+ ions are located in the space of the zeolite framework as the zeolite cations. These cations move due to the interaction with guest Na atoms, and participate in Na clusters. Hence, generated Na clusters are cationic. In Na-type FAU (faujasite) with the Si/Al ratio of 2.0, the dilutely adsorbed Na atoms generate Na_4^{3+} clusters in the sodalite cage.[13] The absorption band of the one electron transition is observed at 2.6 eV. In Na-LTA, Na_4^{3+} clusters have been anticipated from the ESR measurement.[13] In the case of the dilute Na-adsorption, an electron released from Na atom will be bound in the sodalite cage, and form Na_4^{3+} cluster, because the sodalite cage of Na-LTA(1) has the high accessibility for an electron due to the high Na^+ density. Hence, the bands D_1 and D_2 in Figure 2(a) are probably originated from Na_4^{3+} clusters located in the sodalite cage. The excitation energies are nearly the same as that in FAU. At higher Na-densities, cationic Na-clusters with many valence electrons will be generated in the supercage, because the sodalite cage has no space to be filled with Na^+.

The surface plasmon energy of the spherical metal particle, ω_s,

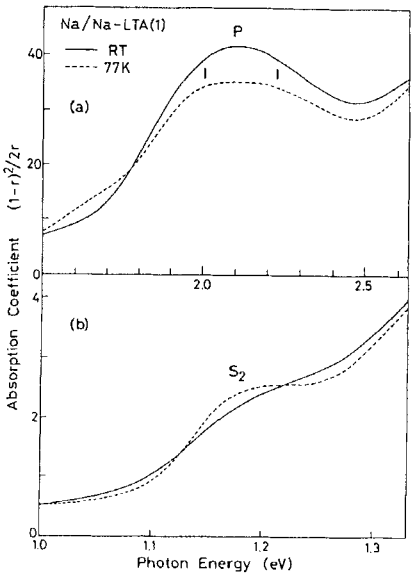

FIGURE 3 Absorption spectra of Na clusters in Na-LTA(1) at room temperature and 77 K for the spectral regions of (a) the band P and (b) the band S_2.

is given by $\omega_p/\sqrt{3}$ in the classical electro-magnetic theory, where ω_p is the plasmon energy in the bulk crystal. The value of ω_s is calculated to be 3.4 eV in Na. In free Na_8 cluster, the surface plasmon energy has been observed at 2.5 eV.[1,2] The red shift of the surface plasmon energy has been discussed in detail in the literatures. Main origin is ascribed to the spillout of the valence electrons.[1]

In cationic clusters, the potential depth is deeper than that of the neutral cluster, and valence electrons are tightly bound inside the cluster. Therefore, electrons of Na clusters are expected to be confined inside the cage without the strong interaction with the framework. In free Na clusters, the energy of the surface plasmon of the cationic cluster is calculated to be slightly higher than that of the neutral cluster.[12]

The bands P, S_1 and S_2 in Figures 2(a) and 2(b) grow together with the loading density and have the same relative intensities, indicating that these bands are originated from the same Na clusters. The band P shows a strong oscillator strength which is characteristic of the surface plasmon, while the bands S_1 and S_2 are very weak compared with the band P. Therefore, the band P is ascribed to the surface plasmon-like excitation, and the bands S_1 and S_2 the electron-hole-like ones.

The peak energy of the band P is 2.1 eV at room temperature. In spite of the cationic cluster, this energy is remarkably lower than the surface plasmon energy of Na_8 free cluster, 2.55 eV.[2] In the zeolite, Na atoms are adsorbed to the inner surface of the supercage, and its center may be empty of Na^+. Valence electrons, however, can be partly distributed at the center, because the potential height for electrons is finite there. It leads to the decrease in the average electron density, and finally the surface plasmon energy shifts to the lower energy. The dielectric contribution of the zeolite framework may play a supplemental role in the red shift of the band P.

In the case of the intermediate Na density, various sizes of Na clusters are expected inside the supercage. However, the absorption spectra of the bands P, S_1 and S_2 at the intermediate Na-density are scarcely different from those at high Na-densities. Therefore, Na atoms are not dispersed uniformly, but may gather with each other as giving nearly the same size of Na cluster. The number of valence electrons is roughly estimated to be about 10 from the spectra at the maximum loading density (the spectra are not shown here).

Usually, the spectral width of the absorption band depends on the temperature according to the strength of the electron-vibration interaction. The temperature dependence of the absorption spectra in Figure 3 indicates some degree of the electron-vibration interaction. The bands P and S_2 show the spectral narrowing at 77 K. The doublet structure of the band P is obvious at 77 K.

Generally, the surface plasmon energy depends on the shape of metal particles. In the spheroidal shape, for example, the surface plasmon energy splits into two levels. In the cluster region, this process provides the strong interaction between the surface plasmon and the vibration.[6] The zero-point oscillation of the cluster shape leads to the finite spectral width of the surface plasmon even at 0 K. The large spectral width and the temperature dependence of the band P are mainly ascribed to the surface plasmon-vibration coupling. That in the band S_2 is ascribed to the usual electron-vibration coupling in the localized electronic state. Besides the surface plasmon-vibration coupling, it is expected that the surface plasmon energy is broadened by the Landau damping, if the electron-hole excitations are located at the same energy.[14] This damping is remarkable in small metal particles, and independent of the temperature. In the present case, the existence of the electron-hole excitations can not be excluded around the band P, and the Landau damping may be one of the origin of the finite width of the band P.

The calculation of the long-range interaction by the transition dipole moment in the small dielectric cube reveals the splitting of the dipole active mode which is degenerated in the spherical shape.[15] Two of them have the strong oscillator strength and others the weak ones. The supercage of LTA has the O_h symmetry with disregard of the difference between Al and Si atoms, and the Na clusters are expected to have the O_h symmetry. The mode splitting is expected to be nearly the same as that in the small dielectric cube. Hence, the doublet structure of the band P is ascribed to the splitting of the surface plasmon mode of the Na cluster with the O_h symmetry.

CONCLUSION

Na clusters are formed in Na-LTA(1). The spectra exhibit the band P and the bands S_1 and S_2 originated from the surface plasmon-like and the electron-hole pair-like excitations, respectively. Some degree of the surface plasmon-vibration coupling is observed. The band P is consisted of the two components ascribed to the splitting of the surface plasmon due to the expected shape of the Na clusters.

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