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Nuclear wave-packet oscillations at the *F* center in KCl and RbCl

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The dynamics of nuclear wave packets at the *F* center in KCl and RbCl at 5 K is investigated by frequency up-conversion method. Oscillation frequencies of the observed nuclear wave packets are 6.0 and 3.9 THz for KCl and RbCl. The former is attributed to LO phonon modes near the center of the Brillouin zone, while the latter to LO phonon modes near zone boundaries. These results suggest that the ratio of spatial extension of the electronic wave function in the relaxed excited state to the lattice constant is smaller in RbCl than in KCl.

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I. INTRODUCTION

Ultrafast laser spectroscopies in femtosecond regime have made it possible to observe atomic motions in time domain. Since pioneering works for direct capture of the atomic motions in molecules,[1–3] vast studies of coherent atomic motions for systems in isolated and surrounded molecules have been performed.[4] Besides the investigation on the small systems, in macroscopic scale, coherent lattice motions have been investigated by coherent phonon spectroscopy for various pure crystalline materials.[5] In between the two extreme cases, as an intermediate case, local lattice motions can be also coherently excited by a pulse irradiation in the vicinity of extrinsic and intrinsic centers in solids. Examples include cage motion around a halogen molecule in rare-gas crystals,[6–8] electron bubble formation around an NO molecule embedded in rare-gas solids,[9–11] and lattice distortion associated with the formation of a self-trapped exciton in insulators.[12–17]

Coherent lattice vibrations in localized systems have attracted attentions for understanding chemical reactions,[18] defect formations,[19] and photoinduced phase transitions.[20] The localized coherent lattice vibrations are described in terms of nuclear wave packet (NWP) in a similar way to the atomic motions in molecules. An NWP is a coherent superposition of several vibrational sublevels on an adiabatic potential-energy surface (APES) along a configuration coordinate. In solids, the coordinate represents the interaction mode consisting of bulk phonon modes as well as local modes.[21] At the localized systems, vibrational properties are largely dependent on the size and symmetry of the relevant electronic wave functions. The *F* center in alkali halides is one of the model systems to study the relation between the electronic state and the lattice vibration.

The *F* center, which consists of an anion vacancy occupied by a trapped electron, is a well-known prototype of a strongly coupled localized electron-phonon system. The trapped electron is in the eigenstates similar to those of an electron in a hydrogenlike atom. The ground state is the $1s$ state and the first-excited state is composed of the $2s$ and $2p$ states. A configuration coordinate diagram is depicted in Fig. 1. The $2s$ state lies higher than the $2p$ state in the Franck-Condon state (FCS) of absorption[22] but is lower in the relaxed excited state (RES).[23] Thus, the $2s$ and $2p$ levels cross each other between the two states at the crossing point, which is indicated as the level crossing (LC) in Fig. 1. Recently, Akiyama and Muramatsu[24] performed a spectral analysis of the hot luminescence in the visible region observed by one- and two-photon excitation measurements with tens of picosecond resolution. Their results indicate that the LC has the anticrossing nature at the *F* center in KCl (dashed lines in Fig. 1). Due to the coupling to T_{1u} phonon modes, the RES consists of the $2s$ state slightly admixed with the $2p$ state and is called the $2s$-like state. The upper state of the RES is called the $2p$-like state.

In our previous works,[25–27] NWP oscillations in the excited states of the *F* center in KI and KBr were studied. Time-resolved luminescence experiments for KI *F* centers[26,27] show that the A_{1g} local mode is dominant in the NWP oscillation in the RES similar to the case of a Raman spectrum resonant with the $1s \rightarrow 2p$ transition,[28] where a pronounced narrow line mostly of the local mode appears. In contrast, the NWP oscillation in the RES of KBr *F* centers consists of LO phonon modes near the zone center (Γ point) in the Brillouin zone and LA phonon modes around singularity points along [100] and/or [110] directions,[25] although the A_{1g} local modes mainly contribute to a $1s$-$2p$ resonance Raman spectrum.[28]

In the present work, we observe NWP oscillations at the *F* center in KCl and RbCl at 5 K by using the frequency up-conversion method. It is found that LO modes near the Γ

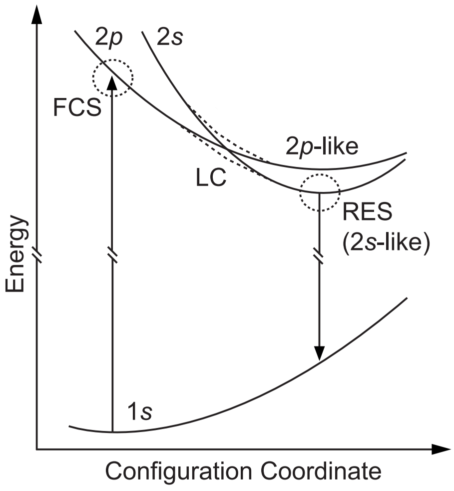

FIG. 1. Schematic of configuration coordinate diagram for the *F* center.

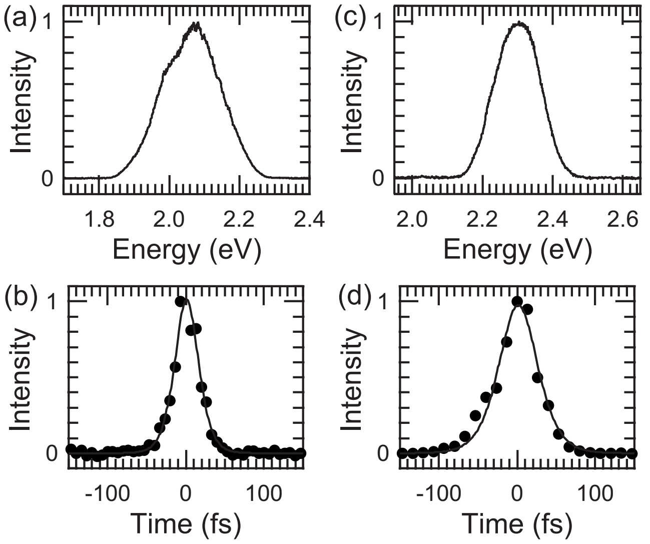

FIG. 2. Typical spectra of output pulses of the 5 kHz NOPA and cross-correlation traces of the measurement system. [(a) and (b)] Spectrum for the measurements of the *F* center in RbCl and its cross-correlation trace. The circles are measurement data. The solid line represents the sech^2 fitting with the FWHM of 35 fs. [(c) and (d)] Spectrum for the measurements of the *F* center in KCl and its cross-correlation trace. The circles are measurement data. The solid line represents the sech^2 fitting with the FWHM of 60 fs.

point are dominant in the former case, while those near zone boundaries are predominantly involved in the latter. These results indicate that the spatial extension of the electronic wave function in the RES is relatively small at the *F* center in RbCl.

II. EXPERIMENT

RbCl crystals obtained from Korth Kristalle were cleaved in size of $2\times1\times0.3$ mm^3 and colored by x-ray irradiation. The *F*-center concentration was approximately 1×10^{17} cm^{-3}. Since the absorption of x rays through the body of the irradiated crystal is not uniform, the *F*-center concentration is the average over the crystal thickness of 0.3 mm. KCl crystals obtained from Crystran were additively colored by Doorn's method[29] with an approximate number of *F* centers up to 5×10^{16} cm^{-3}. After coloration, the crystals were cleaved in pieces of size of $2\times1\times0.3$ mm^3. All samples were mounted in a He-flow cryostat operating at 5 K.

The light source was a home-built noncollinear optical parametric amplifier (NOPA) at a repetition rate of 5 kHz. The visible output of the NOPA was tuned and spectrally cut to be resonant with the absorption bands of the samples. The absorption band peaks at 2.050 (2.313) eV with the full width at half maximum (FWHM) of 0.145 (0.163) eV for the *F* center in RbCl (KCl).[30] Figures 2(a) and 2(c), respectively, show typical spectra of the output pulse centered at 2.06 eV with the FWHM of 0.20 eV for RbCl measurements and that centered at 2.30 eV with the FWHM of 0.16 eV for KCl measurements.

The output pulse was divided into excitation and gate pulses. The excitation pulse energy was 200 nJ. Polarization of the excitation pulse was parallel to [100] crystal axis of the sample crystals. The luminescence light passed a low-pass filter (thickness: 20 μm) in order to cut the remnants of the excitation pulses. The sum frequency signal was generated by mixing the luminescence photons with the time-delayed gate pulses in a 0.3-mm-thick beta barium borate crystal (cutting angle: 35.5°). After passing through one or two high-pass filters and a double-grating monochromator, the signal light was detected by a photomultiplier tube with a photon counting system.

The time origin was defined as the center point of the cross-correlation signal between the gate pulse and the excitation pulse scattered at the surface of the sample. Typical overall time resolutions of the measurement system were 35 fs for the RbCl measurements [Fig. 2(b)] and 60 fs for the KCl measurements [Fig. 2(d)]. We believe that the former resolution is the best value ever achieved in luminescence measurements. The spectral resolution was ~0.06 eV.

For the RbCl measurements, the luminescence was detected at the photon energies of 0.95 and 1.15 eV, which is energetically equally separated from the emission peak at 1.065 eV and is involved in the stationary emission band (FWHM: 0.256 eV).[30] Similarly, for the KCl measurements, the luminescence was detected at the photon energies of 0.95 and 1.45 eV, which is energetically equally separated from the emission peak at 1.18 eV and is involved in the stationary emission band (FWHM: 0.294 eV).[30]

III. RESULTS

Figure 3(a) shows the time evolutions of luminescence intensities at 0.95 and 1.15 eV from the *F* center in RbCl at 5 K. The data at 0.95 (1.15) eV was obtained by counting for 9 s at each delay setting with a 20 (33.3) fs step size. The move time of the delay line between each step was negligibly small compared with the counting time. As the luminescence passed through a 1.5-mm-thick fused silica window of the cryostat, the time origin is shifted in this figure to compensate for the time advance to the cross-correlation signal due to the group-velocity dispersion of this window.

Periodic oscillations are seen in both wave forms. Oscillating components are extracted by subtracting smoothed traces from the original wave forms and shown in Fig. 3(b). As the smoothed traces are calculated by using a Gaussian weight function with a FWHM of 500 fs, the oscillating components with frequencies higher than 1 THz remain in the obtained wave form. An antiphase oscillation is seen between the 0.95 and 1.15 eV signals. This confirms that the observed oscillation signal is originated from a damped NWP oscillation around the potential minimum.

In order to examine the oscillation frequency, the Fourier power spectra of the oscillation signals in Fig. 3(b) are calculated and shown in Fig. 3(c). In the 1.15 and 0.95 eV spectra, a dominant structure is observed around 3.84 ± 0.05 and 3.86 ± 0.07, respectively (here and hereafter, the values with "±" mean statistical errors). These modes are identical and we call it ω_{RbCl} mode. The Fourier spectra of the wave

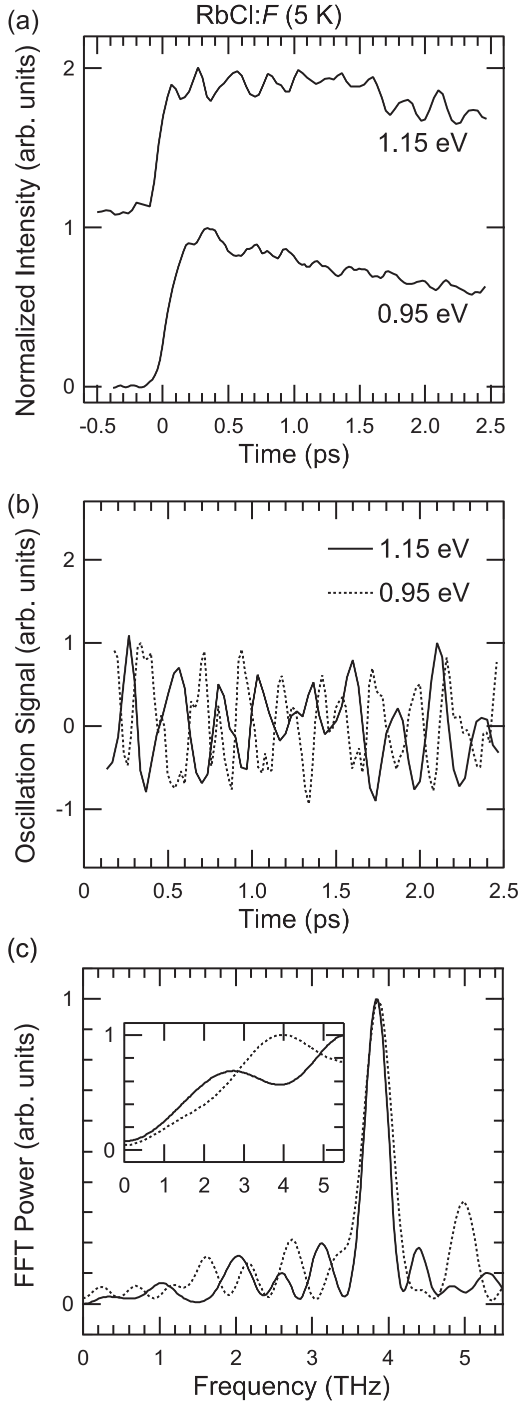

FIG. 3. (a) Time evolutions of luminescence intensities at 0.95 and 1.15 eV from the *F* center in RbCl. (b) Oscillation components obtained by subtracting smoothed traces from the wave forms in (a). The solid and dotted lines represent the 1.15 and 0.95 eV signals, respectively. (c) Fourier power spectra of the oscillation components in (b). The solid and dotted lines represent the 1.15 and 0.95 eV spectra, respectively. The inset shows the Fourier power spectra of the 1.15 and 0.95 eV signals before $t=0$.

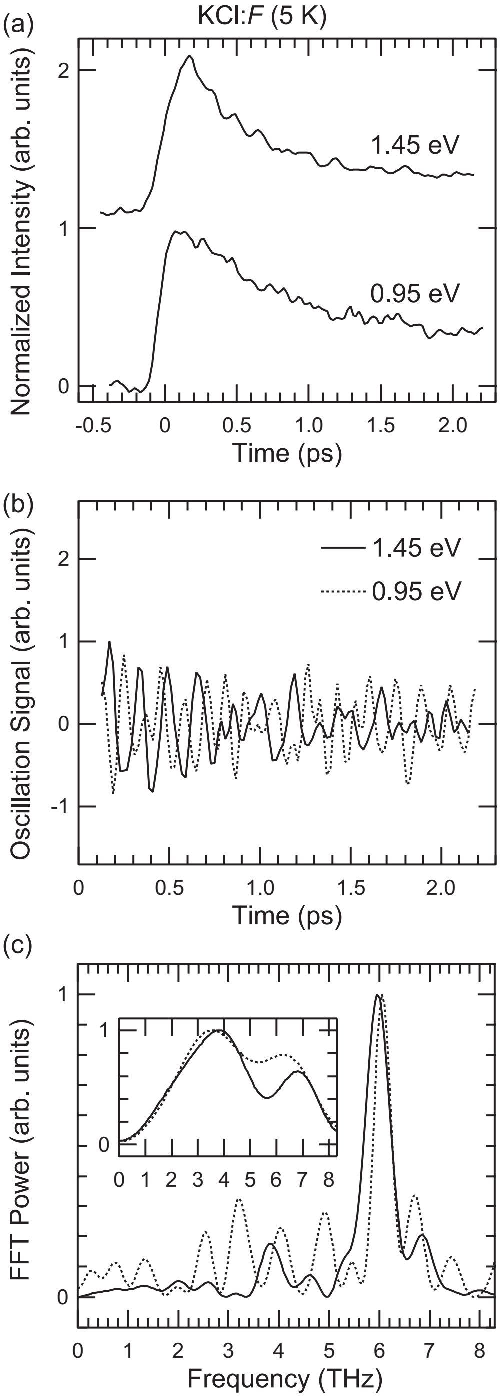

FIG. 4. (a) Time evolutions of luminescence intensities at 0.95 and 1.45 eV from the *F* center in KCl. (b) Oscillation components obtained by subtracting smoothed traces from the wave forms in (a). The solid and dotted lines represent the 1.45 and 0.95 eV signals, respectively. (c) Fourier power spectra of the oscillation components in (b). The solid and dotted lines represent the 1.45 and 0.95 eV spectra, respectively. The inset shows the Fourier power spectra of the 1.45 and 0.95 eV signals before $t=0$.

forms before $t=0$ shown in the inset of Fig. 3(c) have no identifiable structures. In addition to this, the different step size of the 0.95 and 1.15 eV scans confirms that the ω_{RbCl} mode structure does not arise from low-frequency noises due to fluctuations of the laser source and the system environment.

Figure 4 shows the results of the KCl measurements in a display similar to Fig. 3. The data at 0.95 (1.45) eV was

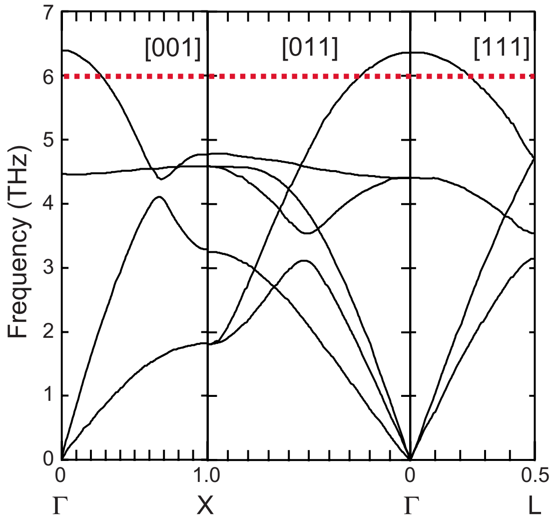

FIG. 5. (Color online) Schematic of phonon-dispersion curves in a pure KCl crystal at 80 K. The curves are drawn by referring to Ref. 32. The dotted horizontal line indicates 6.0 THz.

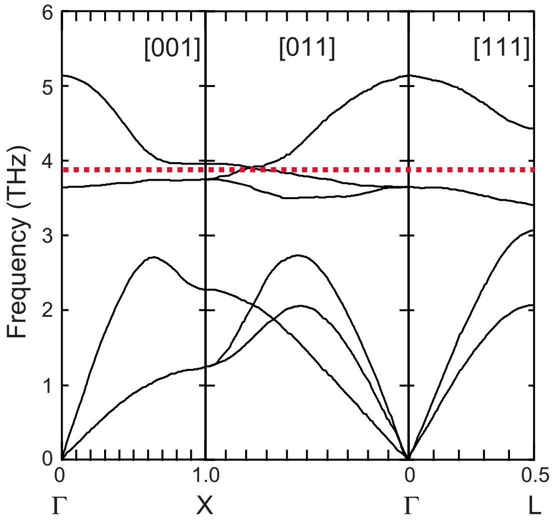

FIG. 6. (Color online) Schematic of phonon-dispersion curves in a pure RbCl crystal at 80 K. The curves are drawn by referring to Ref. 32. The dotted horizontal line indicates 3.9 THz.

obtained by counting for 4 (9) s at each delay setting with a 20 fs step size. Oscillating components are extracted in the same manner as the case of the RbCl results and are displayed in Fig. 4(b). An antiphase oscillation is seen between the 0.95 and 1.45 eV signals. Figure 4(c) shows the Fourier power spectra of these oscillation signals. A dominant structure is observed around 5.96 ± 0.19 and 6.05 ± 0.33 in the 1.45 and 0.95 eV spectra, respectively. These modes agree within the errors and are recognized as identical; we call it ω_{KCl} mode. As shown in the case of RbCl, the Fourier spectra of the wave forms before $t=0$ [shown in the inset of Fig. 4(c)] have no identifiable structures. In addition, the different counting time of the 0.95 and 1.45 eV scans confirms that the ω_{KCl} mode structure is not an artifact due to the low-frequency fluctuations.

IV. DISCUSSION

Resonance Raman spectra of the *F* center in KCl and RbCl have been reported in Ref. 28, exhibiting broad features corresponding to bulk phonon modes. The frequencies of the peaks are largely dependent on the excitation wavelength and no indication of local modes is shown. We try to make assignments of the observed dominant modes using the bulk phonon dispersions of pure KCl and RbCl crystals.

First, the KCl results are discussed. According to the phonon-dispersion curves in Refs. 31 and 32, in a KCl crystal at 80 K, the upper limit frequency of TO phonon branches is 4.76 THz (TO[011] phonon), and phonons at higher frequency belong to LO phonons, whose upper limit frequency is 6.39 THz [LO(Γ) phonon]. The phonon-dispersion curves are schematically depicted in Fig. 5. The ω_{KCl} mode corresponds to $\mathrm{LO}[00\zeta_1]$, $\mathrm{LO}[0\zeta_2\zeta_2]$, and $\mathrm{LO}[\zeta_3\zeta_3\zeta_3]$, where $\zeta_1=0.27$, $\zeta_2=0.24$, and $\zeta_3=0.24$. Thus, the mode is attributed to the LO phonon modes near the Γ point, i.e., long-wavelength LO modes.

In the Raman spectra,[28] enhancement of the LO modes around 6.0 THz is observed under excitation resonant with the higher-excited states ($3p$ or higher states) rather than the first-excited state ($2p$ state). This result suggests that the LO modes couple strongly to the electron, which has a spatially spread wave function.[33,34] In the present experiment, we observe an NWP oscillation around the potential minimum of the $2s$-like APES, which corresponds to the equilibrium position of lattice in the excited state. Here, the surrounding ions shift outward, and the wave function of the trapped electron in the RES expands larger than in the $2p$ FCS. An electron-nuclear double-resonance (ENDOR) measurement[35] revealed that the probability amplitude of the wave function in the RES approaches a maximum at 3ρ, where ρ is the nearest cation-anion distance, and decreases very gradually; the amplitude has one-tenth of the maximum value even at 7ρ. Thus, the long-wavelength LO modes are predominantly observed in our experiment, which is sensitive to the transition from around the RES. It is further suggested by the present result that the spatial size of the electronic wave function in the RES will approach equivalent to that of the higher state ($3p, 4p, \ldots$) in the FCS, where the lattice is unrelaxed.

Then, we follow with the discussion of the RbCl results. In a Raman spectrum resonant with the $1s \rightarrow np$ ($n \geq 3$) transition, enhancement of LO modes around 5.1 THz with a cutoff at ~5.14 THz of the LO mode at the zone center is observed.[28] The coupling to the phonons with large wavelengths indicates that the extension of the electron wave function is large in the higher state of the FCS, as suggested in the case of KCl. Considering an analogy to the KCl case, we might expect that the large-wavelength LO phonons should be also predominantly involved in an NWP oscillation in the RES at the *F* center in RbCl. However, the frequency of the observed ω_{RbCl} mode is far below 5.1 THz, so that the large-wavelength LO modes do not mainly contribute to the NWP oscillation.

Findings from the phonon-dispersion curves in Ref. 32, which are schematically drawn in Fig. 6, show that the ω_{RbCl} mode is attributed to LO phonon modes around zone boundaries, i.e., short-wavelength LO modes, which have relatively high densities of states. The coupling of the electron with the short-wavelength LO modes will be ascribed to the smaller spatial extension of the wave function of the RES compared with that of the *np* ($n \geq 3$) state in the FCS. This suggestion will be verified by an ENDOR measurement.

V. CONCLUSION

In summary, we built a measurement system of transmissive up-conversion spectroscopy with the highest time resolution of 35 fs based on a 5 kHz NOPA. By employing this system, NWP oscillations at the *F* center in KCl and RbCl at 5 K were observed. At the *F* center in KCl, the oscillation of the NWP consists mainly of 6.0 THz mode. The mode is attributed to LO phonons near the center of the Brillouin zone. This result suggests that the spatial size of the electronic wave function in the RES will approach equivalent to that of the higher state in the FCS. At the *F* center of RbCl, the frequency of a dominant mode in the NWP oscillation is 3.9 THz. The mode is ascribed to LO phonons near zone boundaries. This result has not been expected by Raman spectroscopy and suggests that the ratio of spatial extension of the electronic wave function in the RES to the lattice constant is smaller in RbCl than in KCl.

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