RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 39, NUMBER 3 15 JANUARY 1989-II

Resonant hyper-Raman scattering due to the forbidden LO phonon in $SrTiO_3$

Kuon Inoue and Kenji Watanabe
Research Institute of Applied Electricity, Hokkaido University, Sapporo 060, Japan
(Received 11 October 1988)

The resonant behavior of the hyper-Raman scattering in a solid is reported for the first time. The scattering efficiency for the LO phonon normally forbidden in the backward geometry in $SrTiO_3$ is found to increase strikingly as twice the incident photon energy $2\hbar\omega_i$ approaches the lowest direct band gap around 3.46 eV from below. It turns out that the polarizations of incident and scattered light are not parallel to each other, which contrasts with the corresponding Raman case. An explanation in terms of the intraband Frohlich interaction is tentatively presented.

The resonant effects of Raman scattering in solids have been extensively studied in the last two decades.[1,2] It is well established that the efficiency of Raman scattering from the optic phonon increases remarkably when the energy of incident photon $\hbar\omega_i$ or scattered photon $\hbar\omega_s$ coincides with one of the main absorption energy of a solid. The mechanism of the enhancement is reasonably accounted for in terms of time-dependent perturbation theory with the adequate elementary excitations being adopted as an unperturbed system. Further, rather anomalous strong resonant effects due to the longitudinal-optic phonon have also been found to occur quite generally in the forbidden geometry in semiconductors such as CdS (Ref. 3) and GaAs,[4] and thereby are called the forbidden resonant effects. Similar effects are also observed in alkali halides such as TlBr,[5] where the optic phonon is normally forbidden irrespective of the scattering geometry adopted.

The hyper-Raman scattering is an incoherent nonlinear scattering such that two incident photons $\hbar\omega_i+\hbar\omega_i$ in energy are annihilated with one new photon (scattered) of $\hbar\omega_s$ and one phonon of $\hbar\omega_p$ both created behind. The hyper-Raman scattering is established as a spectroscopic tool for observing Raman-inactive optic phonon, complementary to Raman and infrared spectroscopies. A number of hyper-Raman studies have been done successfully to date in solids such as alkali halides[6,7] and perovskite crystals[6,8] having an inversion symmetry. However, any work concerning the resonant effect has never been reported. This may be partly because the hyper-Raman signal is generally not intense enough to enable one to make the measurement in the absorption region.

The present paper reports the first observation of the resonant phenomenon of hyper-Raman scattering in a solid. A single crystal of $SrTiO_3$ was adopted as a test sample since not only detailed information[8,9] about the hyper-Raman scattering from optic phonons was available, but also the signal in $SrTiO_3$ was relatively intense in comparison to other materials. A homemade pulsed dye laser was employed for excitation. It was pumped by the second-harmonic light generated in a potassium dihydrogen phosphate (KDP) crystal of a high-power Q-switched Nd-yttrium aluminum garnet (YAG) laser (Quanta-Ray Co., DCR-2) and had characteristics of 15-kW peak power, 5-ns pulse width, and 20 pps repetitive rate. Three kinds of dyes of pyridine-1, styryl-8, and styryl-9 were used to cover a wavelength range from 670 nm (1.85 eV) to 850 nm (1.46 eV). A rectangular parallelepiped sample of $4\times6\times8$ mm^3 in size with the surface planes perpendicular to the respective crystallographic axes was prepared. Measurement was carried out at 120 K in the cubic phase well above the structural phase-transition temperature of 105 K. The laser beam was weakly focused by a lens of $f=8$ cm onto the sample such that the focal point was 0.5 mm apart before the incident surface. This situation may allow one to approximately treat the beam as a parallel one, which simplifies the correction procedure due to absorption to raw data. Radiation scattered in the backward direction was collected by a lens with an F number of 2 onto an entrance slit of a single-grating monochromator (Ritsu Co., MC-25) of $F/4.4$ with an inverse wavelength dispersion of 29 A/mm, and was detected with a gated optical multichannel detector (Tracor Northern Co., TN-6133) cooled down to $-40\,^{\circ}$C in order to improve greatly the signal-to-noise ratio.

Optic phonons at the Γ point in $SrTiO_3$, which belongs to the point group of O_h symmetry in the cubic phase, are composed of $3F_{1u}$ polar (3TO+3LO) and 1 F_{2u} nonpolar modes, and are all hyper-Raman active but Raman inactive. Actually, those are all observed in the 90° scattering geometry by hyper-Raman spectroscopy.[6,8] According to the hyper-Raman tensor[8] for the F_{1u} polar mode, the LO phonon is, however, forbidden in the backward-scattering geometry. The present measurement was performed for this geometry in such a manner as the energy of twice the incident photon energy, $2\hbar\omega_i$, covered a range from 2.32 eV being far away from the fundamental absorption edge, to 3.45 eV close to the direct band gap. An example of the spectrum observed for excitation using a Q-switched Nd-YAG laser (Quantronix Co., 532) with $\hbar\omega_i=1.16$ eV is shown in Fig. 1(a). As can be seen there, the intensity of the LO-3 mode[8] at 798 cm^{-1} in backward scattering is very weak, as it should be, in comparison to that of the TO-1 mode[8] at 53 cm^{-1}. It is noted that, in the 90° scattering geometry, the ratio of the former against the latter is $\frac{1}{6}$.[8]

An example of the hyper-Raman spectrum observed for dye-laser excitation with $\hbar\omega_i=1.64$ eV is shown in Fig. 1(b). The LO-3 mode becomes as intense as the TO-1 mode, which is inherently allowed in the present geometry. Note, however, that for this excitation the signals

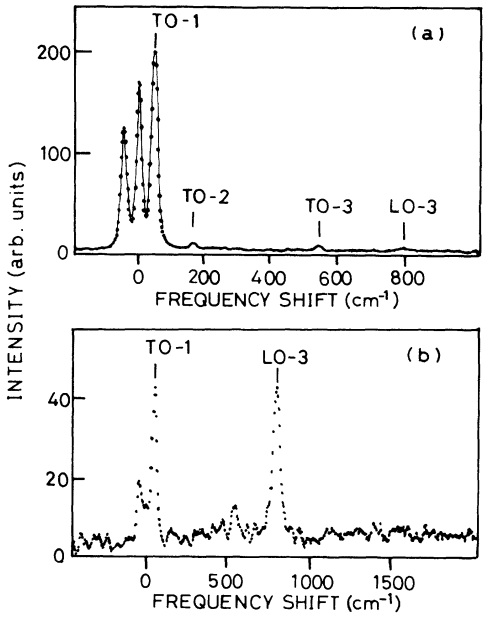

FIG. 1. Examples of the backward hyper-Raman scattering spectrum at 120 K in $SrTiO_3$, which was observed in the $z(xx, x+y)z$ configuration, i.e., the scattered radiation excited by a polarized incident laser parallel with the x axis, was detected without any analyzer inserted. Note that in the present geometry, TO mode is allowed but LO mode is forbidden. (a) A spectrum excited by a Nd-YAG laser of 1.16-eV photon energy. The solid curve is a guide to the eye. One LO mode weakly detected at 798 cm^{-1} was confirmed to arise mainly from a leak signal due to slight misalignment of optical system in this case. (b) A spectrum excited by a dye laser of 1.64-eV photon energy.

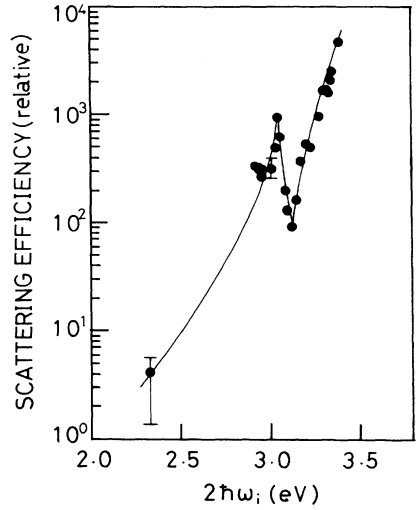

FIG. 2. Variation of the hyper-Raman efficiency of the forbidden LO mode in $SrTiO_3$ as a function of twice the incident photon energy $2\hbar\omega_i$ which clearly indicates a strong enhancement when $2\hbar\omega_i$ approaches the lowest direct band gap around 3.46 eV. The line is a guide to eye.

suffer the intrinsic absorption as is seen from the Stokes–anti-Stokes intensity ratio of the TO-1 mode, and that the situation concerning the magnitude of raw spectrum is in favor of the LO-3 mode against the TO-1 mode. Similar spectra were observed with the energy of the incident photon alone varying from 1.46 to 1.74 eV. Otherwise, measurements were performed under the same experimental conditions as shown in Fig. 1(b), keeping the incident power constant at 10 kW. From those spectra, the relative scattering efficiency η can be estimated as a function of incident photon energy. In doing so, various required corrections such as those caused by variations of the refractive indices at $\hbar\omega_i$ and $\hbar\omega_s$, as well as absorption at $\hbar\omega_s$, and by wavelength dependences of the optical tools employed were made in a way similar to those in the Raman scattering case.[2,10] Available data at 121 K in the literature[11] were utilized for the absorption coefficient. A correction due to the ω_s^4 dependence of the magnitude of signal was also taken into account. The result is plotted in Fig. 2. There, the point at 2.32 eV which alone is obtained from the data for Nd-YAG laser excitation is plotted relative to others in the following manner. The relative intensities of the TO-1 mode in $SrTiO_3$ between excitations at 1.16 and 1.51 eV are normalized on the basis of those of the TO mode in a reference crystal of KI, for which the frequency dispersion of the efficiency can be considered to be small enough. Thus, the point at $2\hbar\omega_i = 2\times 1.16$ eV is obtained relative to that at 3.01 eV from the respective intensity ratio of the LO-3 against the TO-1 mode in $SrTiO_3$. The ratio at 2.32 eV was carefully estimated to be about 1.2×10^{-2} or less from a direct measurement on the signal intensities.

Next, Fig. 3 indicates that the LO-3 spectral line does not exhibit any appreciable polarization dependence. It should be noted that this fact contrasts remarkably to that of the forbidden Raman case,[1,2] where the polarizations of incident and scattered lights are parallel to each other.

The result shown in Fig. 2 clearly indicates that the scattering efficiency increases strikingly as the value of

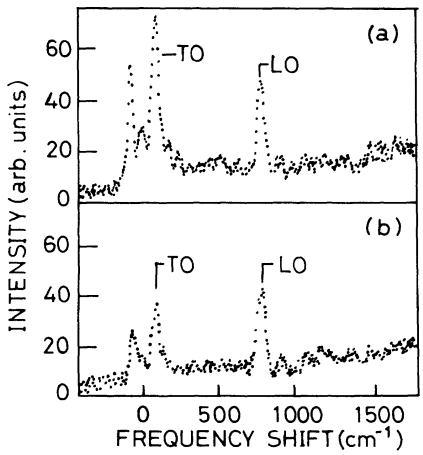

FIG. 3. Examples showing polarization dependence of the backward hyper-Raman spectrum at 297 K in $SrTiO_3$, which was excited by a dye laser of 1.5-eV photon energy: (a) $z(xx,x)z$ and (b) $z(xx,y)z$. Notice that the scattered light from the forbidden LO mode was not substantially polarized.

$2\hbar\omega_i$ approaches from below the direct band gap[11,12] around 3.46 eV and further, another resonant behavior is superposed around 3.05 eV on the curve of the efficiency η vs $2\hbar\omega_i$.

First, let us discuss the origin of the major resonant behavior, aside from an anomaly at 3.05 eV, on the basis of the band structure calculated by Mattheiss.[13] The result may be explained in terms of two-band models illustrated in Fig. 4. Based on time-dependent perturbation theory, the dominant terms in the hyper-Raman tensor, the square of which the scattering efficiency is proportional to, may be described by those including a successive product of the matrix elements for three electron-radiation interaction H_{er} and one electron-lattice interaction H_{el}. Here, H_{el} is considered to be the q-dependent Frohlich interaction[1,2,14] (intraband one), as is the case for the forbidden resonant Raman scattering. In the process shown in Fig. 4, the second one among the three H_{er} should be of the quadrupolar interaction type. This is because $SrTiO_3$ has an inversion symmetry and, as a consequence, the states at the high-symmetry points in the Brillouin zone which should make dominant contribution as intermediate states to the efficiency have their own definite parity. It is well known that the lowest direct optical transitions are governed by those from the highest valence band ($\Gamma_{15}-X_5'$, odd) to the lowest conduction band ($\Gamma_{25}'-X_3$, even) in the Δ direction, and that both bands have very small dispersion,[13] thereby showing the nature of quasi-two-dimensional character.[15] The value of the lowest direct band gap is thought to be around 3.46 eV.[11,12] Owing to one quadrupolar interaction involved, the proposed process can explain well the result of polarization dependence, which differs from that of the forbidden Raman scattering. The reason why, despite the higher-order process, the intensity of the forbidden LO mode is comparable to that of the allowed TO phonon may be twofold. One is that an important role may be played by the double resonance terms,[1,15] similar to the forbidden Raman case, in the denominator such as $[(E^{a'}-\hbar\omega_s)(E^{a}-2\hbar\omega_i)]^{-1}$ in the equation describing hyper-Raman tensor, where $E^{a,a'}$ represents the energy of the electron-hole pair states due to the excitation between two bands. These terms should make a large contribution to the efficiency because of its quasi-two-dimensional character.[15] The second, is that the deformation potential involved in the allowed TO scattering should be of the interband rather than of the intraband type and it would be considerably small in the present case because the lowest conduction (highest valence) band of odd (even) parity is located[13] far from that of even (odd) parity. For the above reason, the present mechanism seems to be the most likely one. It is remarked, however, that the partial contribution from another mechanism described below should not be necessarily excluded. The $SrTiO_3$ crystals, particularly Verneuil-grown ones, are known[16] to be somewhat "disordered" and include impurity levels having relatively high densities of states which are widely distributed[17,18] below

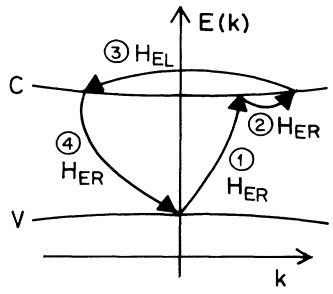

FIG. 4. Schematic diagram of the virtual electronic transitions in the two-band hyper-Raman process (v, valence band; c, conduction band) which should play a dominant role in the forbidden resonant case for centrosymmetric crystal where H_{er} and H_{el} represent the electron-radiation and electron-lattice (q-dependent Fröhlich) interactions, respectively. The numbers indicate the order of the transitions.

the lowest conduction band. Many of those states should lose their definite parity, thereby allowing dipole-dipole virtual transitions through those levels between the two bands under investigation instead of one dipole transition followed by an intraband quadrupolar one.

Next, as to the resonant behavior at 3.05 eV, it is at present less clear to us. Impurity levels[17,18] of dominantly odd parity are presumably present around 3.05 eV, though there is no direct evidence from the two-photon absorption experiment, and those may cause the observed behavior due to the single resonance term with the transition through H_{el} being the ordinary interband interaction between these levels and the lowest conduction band. If this is the case, the observed shape of η vs $2\hbar\omega_i$ around 3.05 eV can be shown to be reproduced at least qualitatively.

So far, a tentative explanation of the result has been presented. For confirmation, however, of the mechanism on the basis of a quantitative argument, more information which includes the impurity levels as well as the data of the efficiency beyond 3.5 eV is needed. Some measurements are now in progress.

Finally, resonant hyper-Raman scattering spectroscopy will be promising for studying electronic states in solids in the ultraviolet region, much as the resonant Raman one has been useful in the visible region, since intense near-ultraviolet lasers are readily available. In this connection, it is noted that very recently the observation[19] of the resonant hyper-Raman spectra in gas, i.e., ammonia in such a manner that $2\hbar\omega_i$ is just resonant with vibrational levels of the electronic excited states has been made.

We wish to thank Professor F. Minami and Dr. A. Yamanaka for valuable discussion. This work was supported by Grant-in-Aid for Scientific Research from Ministry of Education, Science and Culture, and also by the Yamada Foundation for Basic Scientific Research Aid.

[1]A. Pinczuk and E. Burstein, in *Light Scattering in Solids I,* edited by M. Cardona (Springer-Verlag, Berlin, 1983), Chap. 2; R. M. Martin and L. M. Falicov, *ibid.*, Chap. 3.

[2]M. Cardona, in *Light Scattering in Solid II,* edited by M. Cardona and G. Guntherodt (Springer-Verlag, Berlin, 1982), Chap. 2.

[3]P. J. Colwell and M. V. Klein, Solid State Commun. **8**, 2095 (1970); R. M. Martin and T. C. Damen, Phys. Rev. Lett. **26**, 86 (1971).

[4]R. Trommer and M. Cardona, Phys. Rev. B **17**, 1865 (1978).

[5]H. Takenaka, K. Kobayashi, K. Takiyama, J. Nakahara, and T. Fujita, J. Phys. Soc. Jpn. **52**, 4377 (1983).

[6]H. Vogt and G. Neumann, Phys. Status Solidi (b) **92**, 57 (1979).

[7]H. Vogt and H. Presting, Phys. Rev. B **31**, 6731 (1985).

[8]K. Inoue, N. Asai, and T. Sameshima, J. Phys. Soc. Jpn. **50**, 1291 (1981).

[9]K. Inoue, Jpn. J. Appl. Phys. **24**, Suppl. 24-2, 107 (1985).

[10]R. Loudon, J. Phys. (Paris) **26**, 677 (1965).

[11]M. Capizzi and A. Frova, Phys. Rev. Lett. **25**, 1298 (1970).

[12]D. Goldschmidt and H. L. Tuller, Phys. Rev. B **35**, 4360 (1987).

[13]L. F. Mattheiss, Phys. Rev. B **6**, 4718 (1972).

[14]R. M. Martin, Phys. Rev. B **4**, 3676 (1971); R. Zeyher, C. S. Ting, and J. L. Birman, *ibid.* **10**, 1725 (1974).

[15]T. Wolfram, Phys. Rev. Lett. **29**, 1383 (1972).

[16]H. J. Scheel, J. G. Bednorz, and P. Dill, Ferroelectrics **13**, 507 (1976); J. G. Bednorz and H. J. Scheel, J. Cryst. Growth **41**, 5 (1977).

[17]L. Grabner, Phys. Rev. **177**, 1315 (1969).

[18]G. Blasse, Mater. Res. Bull. **18**, 525 (1983); H. Ihrig, J. H. T. Hengst, and M. Klerk, Z. Phys. B **40**, 301 (1981).

[19]L. D. Ziegler and J. L. Roebber, Chem. Phys. Lett. **136**, 377 (1987); L. D. Ziegler, Y. C. Chung, and Y. P. Zhang, J. Chem. Phys. **87**, 4498 (1987).