

## Differential Second-Order Raman Spectroscopy

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It is shown that measurement of the derivative of the second-order Raman spectrum with respect to wavelength of the scattered light gives information on the Van Hove critical points of the combined two-phonon energy function. The results of such a measurement on SrTiO<sub>3</sub> at 10°K are presented and discussed.

Raman spectroscopy has proved to be a very valuable tool for the investigation of elementary excitations in solids such as lattice vibrations and magnons.<sup>1</sup> First-order Raman spectroscopy furnishes information on the energies of these excitations at the center of the Brillouin zone. This information can be directly compared with theory or used as a basis for theoretical calculations. On the other hand the intensity of the continuous second-order Raman-scattered light is at any frequency an integral property over a surface in the crystal momentum space. Therefore, this spectrum cannot be compared directly with theoretical calculations of the dispersion relations, and in most cases only the sharp peaks that have been observed in this spectrum have been interpreted in terms of maxima in the combined density of states.<sup>2</sup>

The information that second-order Raman spectroscopy gives on the dispersion relations of phonons resembles, in some respects, the information that optical spectroscopy yields on the electronic band structure. The use of differential methods<sup>3</sup> (i.e., measurement of the changes in absorption or reflection coefficients caused by various external parameters) has proved to be very effective in the investigation of such band structure.

In this Letter, we describe the measurement of the differential second-order Raman spectrum and its potential use as a tool for obtaining information on excitations at critical points in the Brillouin zone. As the parameter for differentiation we have chosen the wavelength  $\lambda$  of the scattered light. The reasons for this choice are as follows.

(a) It is very easy to anticipate the general form of the spectrum of the derivative with respect to  $\lambda$  of the intensity of the Raman-scattered light,  $dI_R/d\lambda$ , as a function of the difference between the photon energy of the incident and the scattered light,  $\epsilon$ . Peaks in this spectrum appear at values of  $\epsilon$  for which the combined energy function of pairs of phonons,  $\epsilon_{ij}(\vec{K})$ , has

an ordinary critical point. [ $\epsilon_{ij}(\vec{K}) = \pm \epsilon_i(\pm \vec{K}) \pm \epsilon_j(\mp \vec{K})$ , where  $\epsilon_i(\vec{K})$  and  $\epsilon_j(\vec{K})$  are the energies of phonons with wave number  $\vec{K}$  belonging to the  $i$ th and  $j$ th branches. The upper signs refer to emitted phonons, the lower signs to absorbed phonons.] Van Hove<sup>4</sup> and Phillips<sup>5</sup> have evaluated the density-of-states function in the neighborhood of ordinary critical points. The shapes of the derivatives of the density-of-states function  $G$  with respect to the frequency  $\nu$  are shown in Fig. 1 for the different types of critical points. If the function  $\epsilon_{ij}(\vec{K})$  is degenerate at the critical point,  $dG/d\nu$  may be a superposition of these shapes. It is expected that in the neighborhood of a critical point the shape of  $dI_R/d\nu = -(\lambda^2/c)dI_R/d\lambda$  as a function of  $\epsilon$  will be similar to that of  $dG/d\nu$ .

(b) The photon energy of second-order Raman-scattered light ranges at the most over 1000 cm<sup>-1</sup> on each side of the photon energy of the incident light. Similar structure in the absorption spectrum of light caused by electronic transitions

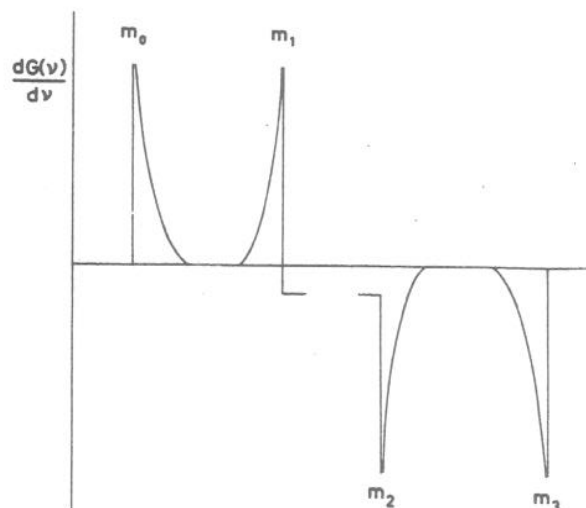


FIG. 1. Schematic shape of the derivatives of the density-of-states function with respect to frequency in the vicinity of a minimum ( $m_0$ ), a saddle point with one maximum ( $m_1$ ), a saddle point with two maxima ( $m_2$ ), and a maximum ( $m_3$ ).

will range over more than  $10^4 \text{ cm}^{-1}$ . Thus the structure in the Raman spectrum is very dense. Hence, small variations in  $\lambda$  will result in considerable depth of modulation of the second-order Raman-scattered light.

The variations in  $\lambda$  have been achieved by vibrating a slab of glass in front of the exit slit around an axis parallel to the exit slit. The shift in wavelength as a function of the angle of incidence of the light  $\theta$  is given by

$$\Delta\lambda = dr [\tan^{-1}\theta - (n^2/\sin^2\theta - 1)^{-1/2}]. \quad (1)$$

Here  $d$  is the thickness of the slab and  $r$  is the resolution of the monochromator.

The light reflected from the slab presents some experimental difficulty. The intensity of the transmitted light is expressed by the equation

$$I_T = I_0(\lambda)[1 - R(\theta)], \quad (2)$$

and thus the intensity varies not only because of the variation in  $\lambda$  but also because of the variation of the reflectivity  $R$  with  $\theta$ . However,  $R$  is an even function of  $\theta$ . Thus, if the vibration of the slab at frequency  $\omega$  is tuned to be symmetric around  $\theta=0$ ,  $R(\theta)$  will vary with a frequency of  $2\omega$  which can be easily separated by phase-sensitive detection from the variation of  $I_0(\lambda)$ , which varies with a frequency of  $\omega$ . In our measurement the component of  $R$  with frequency  $\omega$  has been reduced to less than  $10^{-4}$  of the total intensity of the scattered light, which is negligible compared to that of the detected signals. The detection system itself will be described elsewhere.

The measurement of  $dI_R/d\lambda$  has been carried out on a single crystal of  $\text{SrTiO}_3$ . The crystal was polished into the shape of a platelet of thickness  $100 \mu\text{m}$ . The incident light from an argon laser entered the crystal through its thin edge and the scattered light emanating from one of its faces was focused on the entrance slit of a double monochromator. The measurement was carried out with nonpolarized light in order to obtain a better signal-to-noise ratio. The results obtained at  $10^\circ\text{K}$  are shown in Fig. 2.

The interpretation of these results is based mainly on the comparison between energies of structures in the spectra obtained in our measurement (see Fig. 2) and energies of phonons in the center of the zone and at the point  $X$  in the zone, obtained from Raman,<sup>6</sup> infrared,<sup>7</sup> and neutron-diffraction<sup>8</sup> measurements.

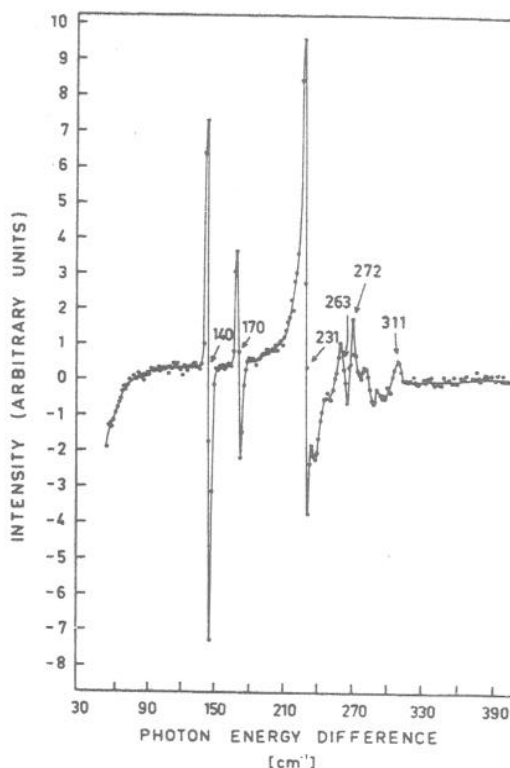


FIG. 2. The spectrum of  $dI_R/d\nu$  of  $\text{SrTiO}_3$  at  $10^\circ\text{K}$ .

The first two structures appearing at  $144$  and  $170 \text{ cm}^{-1}$  refer to first-order Raman peaks. The structure at  $231 \text{ cm}^{-1}$  corresponds to the following combinations: (1) first-order Raman line involving phonons from the corner of the Brillouin zone of the perovskite structure (because of the distortion of the crystal from perovskite structure, the corner of the Brillouin zone is folded into the center of the zone<sup>9</sup>) and (2) second-order Raman scattering involving phonons at the edge of the zone at point  $X$ . The possible combinations are  $2TA$  and  $2TO_1$ . The structure at  $263 \text{ cm}^{-1}$  agrees in shape and in energy with the silent mode. The positive peak at  $272 \text{ cm}^{-1}$  can possibly be associated with emission of the pairs  $TO_1 + TO_3$  and  $TO_1 + LO_2$  at the point  $\Gamma$ . At this point the combined energy of each pair of branches has a minimum. This agrees with the positive peak observed. The energy of the pairs  $TA + LA$  and  $TO_1 + LA$  at point  $X$  is equivalent to  $271 \text{ cm}^{-1}$  and can therefore also contribute to the peak observed at  $272 \text{ cm}^{-1}$ . Group theory shows, however, that only one of the pairs will contribute to Raman scattering. If model I of Cowley is correct,  $TO_1 + LA$  may contribute. If model III is correct only  $TA + LA$  may contribute. Notice that if any one of these

pairs does contribute significantly, it should have a saddle point with one maximum and two minima. The peak at  $311\text{ cm}^{-1}$  can be interpreted to arise from the emission of 2LA phonons at point X. In that case the branch should have a saddle point with one maximum and two minima.

The rest of the structure observed cannot be interpreted in terms of phonon energies measured by other methods. Further measurements must be carried out using polarized incident and scattered light properly oriented with respect to crystallographic orientations in order to obtain a more complete identification of this additional structure.

In conclusion, the usefulness of differential measurements of second-order Raman spectra has been demonstrated. It is shown that considerable new information may be obtained using such a method.

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