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RAMAN SCATTERING IN FERROELECTRICS

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Résumé. — Dans cet article, nous passons en revue l’effet Raman dans les ferroélectriques et les matériaux voisins.

Abstract. — This paper gives a review on Raman effect in ferroelectrics and related materials.

Raman scattering experiments have become a powerful tool during recent years for the study of phase transitions in solids, particularly in ferroelectrics. This is partly due to the fact that Raman scattering is complementary in nature to infrared absorption, and partly that it can be applied to much smaller single crystals than inelastic neutron scattering. In this review, an outline of the general theoretical concepts is given which are involved in light scattering by optical phonons, starting with the expansion of the polarizability in terms of normal coordinates of lattice vibrations. Selection rules are imposed on the system by the crystal symmetry. It is shown how they are used to determine the symmetry of a particular Raman line and the atomic motions involved in it.

For the case of soft phonon modes, it is seen that damping, resulting from anharmonic interactions with other modes, influences the shape of the observed Raman lines considerably, leading to different line shapes, with the two limiting cases of underdamped modes (sharp lines) and of overdamped modes (broad lines centered about zero frequency).

A description of the modern techniques is given, which are used for a careful study of Raman scattering near phase transitions in transparent and opaque crystals. The problem of resolving weak lines near the laser line and of detecting low light levels are discussed in detail.

A review of the experimental results on ferroelectrics, antiferroelectrics and related materials is presented with special emphasis on the phenomena involved in the phase transitions. Typical examples are discussed for the different classes of soft mode materials:

1. Soft ferroelectric modes (soft infrared active modes, occurring at $k = 0$ in the Brillouin zone). — A well behaved, underdamped mode of this type is found in the almost-ferroelectric SrTiO$_3$ (and also in KTaO$_3$). The observed frequency of the soft mode stays finite at all temperatures and agrees well with the static dielectric constant using the Lyddane-Sachs-Teller relation. The results compare well with inelastic neutron scattering data. Of special interest is the technique of electric field induced Raman scattering employed in SrTiO$_3$. The applied electric field reduces the crystal symmetry and produces Raman activity of an otherwise Raman inactive ferroelectric mode. As an example of an opaque material, the most simple, diatomic ferroelectric GeTe is discussed in which no spontaneous polarization can develop because of the high number of conduction electrons, but in which Raman measurements permit the determination of the soft modes. Tetragonal BaTiO$_3$ is a material where the soft ferroelectric mode appears as broad line centered about zero frequency. The analysis shows that this is caused by the fact that the soft mode damping constant is larger than its frequency. The interesting results found recently by inelastic neutron scattering show that further optical measurements are highly desirable for BaTiO$_3$. The predominant example for Raman scattering in order-disorder type ferroelectrics is KH$_2$PO$_4$ where a strongly overdamped mode (a mixture between a tunnelling and a phonon mode) is observed, of which the frequency and damping constant are determined. Correlating these data with most recent results of Raman, Brillouin and inelastic neutron scattering on KD$_2$PO$_4$, KH$_2$AsO$_4$ and CsH$_2$AsO$_4$ one is left with many open questions. Further work in this field is required to answer them. One suggestion which might bring a solution is that in addition to the overdamped soft mode, scattering intensity near the phase transition can also be produced by collective phonon excitations (phonon density fluctuations). Such effects are observed in SrTiO$_3$ and SbSI where a diffusive mode is reported in addition to a soft mode, which in these cases is underdamped. This is in accordance with recent microscopic theories. Whenever the soft mode is overdamped, the situation is of course not as simple, but the same effect of collective phonon excitations is proposed to be pertinent also for KH$_2$AsO$_4$ and CsH$_2$AsO$_4$.

2. Infrared inactive zone center modes. — This type is observed in the modes determining the $\alpha$-$\beta$ transition in quartz and AlPO$_4$. 

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3. **Soft zone boundary modes.** — This occurs at the structural transitions in some perovskites and is often called antiferroelectric transition, because it causes a doubling of the unit cell. As a well-known example of this type, the 105 °K cubic to tetragonal transition of SrTiO₃ is discussed. In the tetragonal phase the soft modes of titanate octahedra rotation are Raman active. They can be used to determine the critical behaviour, which for this material was thoroughly studied by E. P. R. and ultrasonic measurements.

The fact that soft modes change their frequency with temperatures (or electric field) offers the interesting possibility of observing mode interaction, whenever a soft mode crosses a temperature (or field) independent mode. Such a case is discussed for SbSI, where an analysis in terms of two coupled quasiharmonic oscillators produces excellent agreement with the experimental findings. The interaction is found to be purely nondissipative in this case. Other examples are given by the electric field induced interaction in SrTiO₃, the coupling of soft optic with the acoustic mode in BaTiO₃, and others. All these cases can well be described within the framework of the two coupled oscillator model. Often, however, the interaction can be dissipative in nature. A microscopic understanding of this is still required.

The topics which are likely to be of interest for Raman scattering in the future are the following:

1) The study of linewidths and lineshapes of the soft modes, in order to get information on the mechanism of anharmonic interaction.

2) A more thorough microscopic investigation of the occurrence of lineshape anomalies in the coupled mode problem.

3) More accurate measurements of frequency and linewidth in the critical regime, where the fluctuations of the order parameter are large compared to the mean value.

4) The use of the Raman technique for determining light scattering by critical fluctuations (critical Rayleigh scattering). Of particular interest will be the detailed analysis in terms of single mode and collective excitations for cases where an overdamped soft mode is present.

The last two points in connection with the study of other critical quantities, are of importance for obtaining further insight into the static and dynamic critical behaviour. Light scattering will thus be able to make important contributions to the study of critical phenomena in ferroelectrics.