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RAMAN SCATTERING INDUCED BY DIELECTRIC-METALLIC COLLOID INTERFACES

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Résumé — Nous montrons que l'élargissement de la raie Rayleigh observé sur les spectres de diffusion Raman induits par des colloïdes métalliques dans un diélectrique, peut être dû au caractère plan de l'interface colloid-matrice hôte. La très faible durée de vie des états électroniques excités des colloïdes métalliques peut expliquer la très faible intensité de la diffusion Raman multi-phonons. Les deux modes localisés à l'interface (111) colloïde de potassium-KI, calculés à l'aide d'un modèle élémentaire, situés à 83 cm\(^{-1}\) et à 118 cm\(^{-1}\), sont en bon accord avec les résultats expérimentaux (84 cm\(^{-1}\) et 120 cm\(^{-1}\)).

Abstract — We show that the broadening of the Rayleigh line observed on the Raman scattering spectra induced by metallic colloids in dielectric can come from the plane character of the colloid-matrix interface. The very short lifetime of metallic colloid excited electronic states can explain the very weak intensities of the multiphonon Raman scattering. Using a simple model, we have calculated two localized modes at the (111) potassium colloids-KI interface, peaked at 83 cm\(^{-1}\) and 118 cm\(^{-1}\), in good agreement with the experimental results (84 cm\(^{-1}\) and 120 cm\(^{-1}\)).

The first-order Raman scattering spectra induced by metallic colloids (Na, Ag) in dielectrics (NaI, NaCl, NaBr) have already been described previously /1/. The main results of this study are recalled:

i) The very strong intensity of scattering when the exciting laser line is in resonance with the absorption bands of the surface plasmons shows that the latter are involved in the scattering process.

ii) When the colloid metal is the same as the host crystal metal, the observed modes have lower frequencies than the phonon cut-off value (\(\omega_L\)) in the pure crystal. On the contrary, silver colloids in NaI, NaBr and NaCl induce localized modes at higher frequencies than \(\omega_L\).

iii) The above results show that the Raman scattering occurs at the dielectric-colloid interface.

However, two effects still require interpretation:

i) The broadening of the Rayleigh line as a function of the temperature.

ii) The absence of overtones. This important result is to be compared with the enhanced Raman scattering of molecules adsorbed on metallic surfaces (SERS) /2/. Recently it has been observed a two-phonon Raman scattering of molecules (\(\text{O}_2\) and \(\text{CO}\)) adsorbed on a Pt (111) surface /3/, but the intensity is much weaker than that of one-phonon lines.

The aim of this paper is to show with the help of an example—the potassium colloids in KI—what might be the origin of these effects and which parameters are involved.

In order to calculate the frequencies of localized modes at the colloid-dielectric interface a simple theory applied to the case of potassium colloids in KI was used.

EXPERIMENTAL RESULTS

Raman scattering by potassium colloids in KI obtained by aggregation of \(F\) centers /4/ have been studied. Thus in the same sample, \(F\) centers and colloids are present simultaneously. So, the optical absorption spectrum contains the \(F\) band due to \(F\) centers and

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Fig. 1 - Experimental absorption and Raman spectra of KI containing F centers and K colloids.
(a) absorption spectrum at 78 K; 
\( \lambda_L = 676.4 \) nm.
(b) Raman spectrum at \( T = 10 \) K; 
\( \lambda_L = 676.4 \) nm.
(c) Raman spectrum at \( T = 10 \) K; 
\( \lambda_L = 752.5 \) nm.
(d) Raman spectrum at \( T = 78 \) K; 
\( \lambda_L = 752.5 \) nm.

the \( C_1 \) and \( C_2 \) bands due to colloids (fig. 1a). The colloids do not have the body-centered cubic structure of the alkali metal but retain the face-centered cubic structure of the original cation sites /5/. Furthermore it was shown that the relaxation of the atoms in the colloid from their original position in the host lattice is weak /5/.

The observed Raman spectra in such a sample depends heavily on the laser line wavelength used. Figures 1b and 1c show the spectra obtained with two Krypton laser lines: one at 676.4 nm in resonance in the \( F \) band and the other at 752.5 nm in resonance in the \( C_1 \) band. The spectrum in fig. 1b is characteristic of the F centers in KI /6/ and differs basically from that in fig. 1c which can be attributed to the colloid-matrix interface, except the line at 96.5 cm\(^{-1}\) still due to the F centers. The reason for this attribution is that one can observe a pronounced resonance effect when the laser line falls in the \( C_1 \) and \( C_2 \) absorption bands themselves attributed to surface plasmons /1/.

Thus, the study of potassium colloids in KI allows us to compare Raman scattering by a point defect (the F center) and Raman scattering by an interface (metallic colloid-insulating crystalline matrix).

We have in this way brought to light two main differences:

i) The background is almost zero at the base of the Rayleigh line on the F center spectrum (fig. 1b) while it is intense on the colloid spectrum (fig. 1c) and increases strongly with the temperature (fig. 1d) as does the width of the Rayleigh line.

ii) The phonon cut-off value \( \omega_R \) in pure KI is shown on the spectra. In fig. 1c the Raman scattering cancels above this frequency (only a weak background remains) so that one can deduce that the lines observed on this spectrum correspond to a one-phonon scattering. On the contrary, in fig. 1b the spectrum spreads out far above \( \omega_R \) with a non-negligible intensity. It has been shown /7/ /8/ that the lines observed in this range are due to a multi-phonon scattering.

INTERPRETATION

The interpretation of these results requires a theoretical model in order to compare Raman scattering of F centers to that of colloids. The theory of Raman scattering by F centers has been extensively developed /9/ and we merely recall the relevant results. To treat a colloid we consider that it constitutes a two-dimensional defect following crystallographic planes, that is to say, infinite in two directions and having a certain thickness in the direction perpendicular to the plane so defined. As shown by experimental results, we suppose that Raman scattering processes occur in the neighbourhood of colloid-host crystal interface.
A.- BACKGROUND AND BROADENING OF RAYLEIGH LINE

For a point defect the differential Stokes Raman scattering cross section relative to vibrations of \( \Gamma \) type is proportional to \( \theta/ \):

\[
\frac{d^2 \sigma (\Gamma)}{d\Omega d\omega} \propto B^{(\Gamma)}_{\eta \eta'} (E_L) \times \sum_{\Sigma S} C^{(\Sigma)}_{\Gamma} C^{(S)}_{\Gamma} \frac{n(\omega)+1}{\omega} \rho_{RS} (\Gamma, \omega)
\]

where \( B^{(\Gamma)}_{\eta \eta'} (E_L) \) depends on the wavelength of the incident energy, \( E_L \) and polarization directions of the incident light \( \eta \) and of the scattered light \( \eta' \). The \( C^{(\Sigma)}_{\Gamma} \) coefficients represent the coupling of the point defect with the neighboring ions. The quantities \( \rho_{RS} (\Gamma, \omega) \) are the perturbed normalized projected densities of one-phonon states, and \( n(\omega) = (\exp(\hbar \omega/k_B T) - 1) \) is the Bose factor.

**Fig. 2** — Histogram of the unperturbed projected densities of one-phonon states.
(a) projection on the \( \Gamma^1 \) vibrations of the first ionic shell surrounding the F center in KI.
(b) projection on the transverse vibrations of the cationic (111) plane in KI at \( k_{||} = 0 \).

**Fig. 3** — Calculated unperturbed first-order Stokes Raman spectra.
(---) : \( T = 10K \), (---) : \( T = 78 k \), (----) : \( T = 293 k \).
(a) for a point defect.
(b) for a plane defect.

In the case of a two-dimensional defect, the translation symmetry is destroyed in the direction perpendicular to the interface, but remains in the other two. The wave vector in the defect plane \( k_{||} \) remains a good quantum number and during a Raman scattering process the light can only interact with phonons at \( k_{||} \approx 0 \). For these defects, in equation (1), we must replace the perturbed projected state densities \( \rho_{RS} (\Gamma, \omega) \) by those of the interface related to \( k_{||} = 0 \), i.e.: \( \rho_{RS} (k_{||} = 0, \Gamma, \omega) \).

The perturbed projected state densities of the interface are calculated from the perturbation and densities of unperturbed projected state densities: \( \rho_{RS}^{\circ} (k_{||} = 0, \Gamma, \omega) \) at low frequencies they behave similarly to the latter. We show (fig. 2b) the unperturbed state density at \( k_{||} = 0 \) of transverse phonons projected on the cations of an (111) interface in KI: \( \rho_{RS} (k_{||} = 0, \Gamma, \omega) \).

Note that (fig. 2b), when the frequency goes to zero, the projected state densities tend to a non-zero constant, which gives:

\[
\frac{n(\omega)+1}{\omega} \rho_{RS}^{\circ} (k_{||} = 0, \Gamma, \omega) \propto \frac{n(\omega)+1}{\omega}
\]

Therefore, following (2), \( \frac{n(\omega)+1}{\omega} \rho_{CC}^{\circ} (k_{||} = 0, \Gamma, \omega) \) tends to an infinite value when \( \omega \) goes to zero (fig. 3b), producing a background at low frequencies as well as a broadening of the
Rayleigh line. These effects, from the term \( n(\omega) \), depend heavily on temperature (fig. 3b). In this figure we have normalized the three curves so that the optic line at 100 cm\(^{-1}\) has the same intensity. These results are consistent with the experiment (figs. 1c and 1d). In figs. 2a and 3a we show, for comparison, the calculations for the \( \mathbb{F} \) center in KI.

### B. - TWO-PHONON RAMAN SCATTERING

It has been shown in the case of \( \mathbb{F} \) centers that multiphonon Raman scattering is strong /7,8/. It depends on the wavelength of the exciting light and has its highest value when the laser line is tuned in the \( \mathbb{F} \) band maximum /8/. By a calculation similar to that of ref. 8, in which the spin-orbit coupling is neglected, the total Raman cross section by \( m \) identical phonons \( \sigma_m \) of \( \Gamma_1^+ \) symmetry is given by /11/:

\[
\frac{d\sigma_m}{d\Omega} = \alpha \left( \frac{\sigma_1(\Gamma_1^+)}{\sigma(\Gamma_1^+)} \right)^m |\phi_m(Z)|^2
\]

where

\[
\phi_m(Z) = (2/m!2^m)^{1/2} \left( \frac{d}{dZ} \right)^m \left\{ \frac{\pi}{2} - i \int_0^Z e^{x^2} dx \right\} e^{-z^2}
\]

and

\[
Z = \{ E_L - E_F - \frac{\gamma}{2} \} / \sqrt{2} B_1
\]

\( E_F \) is the energy of the \( \mathbb{F} \) band maximum, \( E_L \) the energy of the incident light and \( \gamma \) is the inverse of the lifetime of the excited electronic level which gives rise to the \( \mathbb{F} \) band. \( B_1^2 \) is the contribution of the \( \Gamma_1^+ \) modes to the second moment of the \( \mathbb{F} \) band. The factor \( \left( \frac{\sigma_1(\Gamma_1^+)}{\sigma(\Gamma_1^+)} \right) \) represents the relative scattering cross section for mode \( \Gamma_1^+ \). From (3) and (4) the ratio of the intensity \( I_2 \) of the Raman scattering by two phonons \( \sigma_m \) over the intensity \( I_1 \) of the Raman scattering by one phonon \( \sigma_1 \) is obtained. At the resonance (\( E_L = E_F \)) this ratio is shown in fig. 4.

In the case of \( \mathbb{F} \) centers, since the lifetime of the first excited state is about \( 10^{-7}-10^{-6} \) s /12/, and the coefficient \( B_1 \) is of the order of several hundred cm\(^{-1}\) (NaI: 625 cm\(^{-1}\); KI: 366 cm\(^{-1}\))/8/, the ratio \( \gamma/B_1 \) is lower than \( 10^{-7} \) which corresponds to a virtually zero value (fig. 4).

In this case we have:

\[
\frac{I_2}{I_1} = \frac{\pi}{4} \left( \frac{\sigma_1(\Gamma_1^+)}{\sigma(\Gamma_1^+)} \right)
\]

Relation (5) shows that if the scattering system contains an intense resonant mode \( R \), the ratio \( \left( \frac{\sigma_1(\Gamma_1^+)}{\sigma(\Gamma_1^+)} \right) \) is large for this mode. Then the second order Raman spectrum is intense compared to the first order spectrum and is structured. This is the case of \( \mathbb{F} \) centers in NaBr /13/, KI /7/ and NaI /8/. On the contrary, in the absence of an intense resonant mode, the second order Raman spectrum is weak and gives rise to a more or less structured background. This occurs for \( \mathbb{F} \) centers in NaCl /14/, KCl /13/ and RbCl /15/.

In the case of Raman scattering by potassium colloids in KI, the \( B_1 \) parameter can be supposed to have the same order of magnitude as for \( \mathbb{F} \) centers in KI. On the contrary, the lifetimes of the excited states, because of their coupling with the metallic colloid electronic states, can reasonably be supposed to be much weaker. The lifetimes of excited electronic levels for molecules adsorbed on a silver surface have been determined /16/. The obtained values are from \( 10^{-12} \) to \( 10^{-13} \) s, giving rise to a damping factor of the order from 50 to 5000 cm\(^{-1}\). When \( \gamma \) is about 5000 cm\(^{-1}\), \( \gamma/B_1 \) is of the order of 10. Thus, fig. 4 shows that the ratio of the second-over the first-order is, at the maximum resonance, about 0.06 and this without taking into account the \( \sigma_1(\Gamma_1^+)/\sigma(\Gamma_1^+) \) factor. From fig. 1c, this ratio is weak whatever the considered phonon, resulting in a very weak second-order Raman spectrum.
Variation of the second-order Raman scattering with respect to first-order as a function of the damping factor. \( \sigma_1(\Gamma^{+1})/\sigma(\Gamma^{+1}) = 1 \).

C. - CALCULATION OF LOCALIZED MODE FREQUENCIES

We have tried to account for frequencies of the strong 84 and 120 cm\(^{-1}\) modes. A calculation based on a softening of interionic force constants was done in the case of an (111) interface, when anions are replaced by vacancies so as to constitute the colloids. It was shown that a 40% softening of the longitudinal interionic force constant between first neighbours induces two localized vibrational modes at the interface: one at 83 cm\(^{-1}\) in the interface plane and the other at 118 cm\(^{-1}\) perpendicular to the interface, in agreement with experimental results.

DISCUSSION

The theory of two-phonon Raman scattering developed in this paper, is valid for un point defect, but cannot be applied in the case of colloids. However, it does allow us to determine the influence of some parameters on first and second-order Raman scattering by colloids. Moreover it is not sure that the colloids are large enough to be treated as two-dimensional defect. It has been shown in the case of silver colloids in NaI, that the size of the colloids modifies to a slight extent the Raman spectra, in particular the broadening of the Rayleigh line. This presumably shows that other effect could also be at the origin of this broadening. For example, it has been suggested that it comes from single-particle excitation of the electron gas of the quasi metallic particles.

REFERENCES