

Radiation damage in NaCl. IV. Raman scattering

J. C. Groote, J. R. W. Weerkamp, J. Seinen, and H. W. den Hartog

Solid State Physics Laboratory, University Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

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Raman-scattering experiments on heavily irradiated pure and doped NaCl crystals are described. The experiments have been performed at room temperature and at approximately 25 K. The crystals had been irradiated up to a maximum dose of 95 Grad by means of electrons from a Van de Graaff accelerator. The Raman spectra show the set of phonon peaks corresponding to the NaCl modes. At low frequencies the reduced Raman intensity shows a clear power-law dependence on the frequency, $I_{\text{red}}(\omega) \propto \omega^\nu$, with an exponent $\nu \approx 1.4$, indicating that the colloids in heavily irradiated samples exhibit a fractal structure. The change in the melting peak pattern reveals that the initial form of the sodium particles is strongly affected by the performance of a Raman experiment at room temperature. At low measuring temperatures two unknown phonon peaks at 330 and 560 cm^{-1} are observed. These peaks are located well above the phonon cutoff frequency of NaCl at 260 cm^{-1} , and are associated with local modes due to the ultrafine structure of the colloids.

I. INTRODUCTION

Metallic sodium colloids are formed in irradiated NaCl crystals as a result of the aggregation of F centers. These colloids have been studied by us with different experimental techniques,¹ such as optical-absorption spectroscopy and differential scanning calorimetry (DSC) (papers I, II and III). Low-frequency Raman-scattering spectroscopy is a very appropriate experimental technique to study the colloid-NaCl interface. If the crystal containing colloids is excited in the absorption band of the colloids, the scattering is enhanced by irregularities at the surface of the colloids.^{2,3} This process is called surface-enhanced Raman scattering (SERS). For a detailed treatment we refer to the book by Chang and Furtak.⁴ The SERS spectra provide us with information on the nature and geometry of the colloids and the mismatch between the colloids and the crystal.

Rzepka and co-workers⁵⁻⁸ have studied samples containing low concentrations on defects (e.g., *F* and *V* centers, and their aggregates) in additively, electrolytically, and irradiated alkali halides. The phonon peaks found for NaCl containing colloids are located at 80, 100, 115, 134, 154, 205, and 230 cm^{-1} . These positions are consistent with the critical point phonon frequencies in NaCl obtained from neutron-scattering experiments⁵ and are within the frequency range of the phonon states in pure NaCl published by Bilz and Kress,⁹ who have calculated a phonon cutoff frequency in NaCl of $\omega_{c0} = 260 \text{ cm}^{-1}$. If defects and impurities are involved, the Raman spectrum may show additional peaks, which are due to local modes. These peaks can be located at energies higher than the phonon cutoff frequency. Rzepka and co-workers did not observe such high-frequency peaks in their crystals.

At very low frequencies ($< 100 \text{ cm}^{-1}$) a broadening of the Rayleigh line has been observed,^{3,5} instead of the usual Debye behavior at low frequencies, i.e., a quadratic relationship between the energy and the density of states.

If the interface between the colloidal particle and the host matrix is highly irregular, localized vibrational modes could contribute to the Raman intensity at low frequencies. Duval *et al.*² proposed a theory for Raman scattering on fractals to explain the extra intensity at low frequencies. If the colloid-NaCl interface can be defined in terms of fractal dimensions, this theory can be used to describe our results. In the next section a brief review of the theory of Raman scattering on fractally shaped structures will be given.

II. RAMAN SCATTERING ON FRACTALS

The heavily irradiated crystals have become so defective that they can be compared with amorphous materials. Shuker and Gammon¹⁰ have derived that for amorphous materials (glasses) the intensity *I* of the Stokes scattered light in the low-frequency range can be written as

$$I(\omega) = \frac{1}{\omega} C(\omega) g(\omega) [n(\omega) + 1]. \quad (1)$$

In this equation ω is the frequency shift of the scattered light, $C(\omega)$ is the light-vibration coupling factor, $g(\omega)$ is the phonon density of states, and $n(\omega) + 1$ is the Bose factor for the Stokes part of the Raman scattering, where $n(\omega) = 1 / [\exp(\hbar\omega/k_B T) - 1]$ is the phonon occupancy. At low energies $C(\omega)$ is proportional to ω^2 (see Ref. 2).

For Debye behavior in three dimensions $g(\omega)$ is also proportional to ω^2 , such that the reduced intensity $I(\omega)\omega/[n(\omega) + 1]$ would be proportional to ω^4 . However, since we are dealing with excitations on irregularly shaped colloids in NaCl (with a short length scale) instead of Debye-type excitations, we use the relaxation theory in disordered materials of Alexander and co-workers.¹¹⁻¹⁴ These authors introduced the "fracton," a vibrational state on the fractal, that can be considered as a localized phonon. The fracton dimension (\tilde{d}) is defined by the energy dependence of the fracton localization length ($l_\omega \propto \omega^{-\tilde{d}/D}$), where *D* is the Hausdorff dimension

of the fractal on which the excitation is located. Boukenter *et al.*¹⁵ have used this theoretical treatment to describe low-frequency Raman scattering of fractal vibrational modes in silica gels. Abu Hassan, Smith, and Page¹⁶ have refined this treatment. Duval *et al.*² have used the theory of Alexander and co-workers¹¹⁻¹⁴ to describe their low-frequency Raman-scattering results of electrolytically or additively colored NaCl crystals containing Na colloids.

The results of Duval *et al.* will be presented here in some more detail. The relationship between the reduced Raman intensity and the fracton density of states $g(\omega)$ is given by

$$I_{\text{red}}(\omega) = \frac{I(\omega)\omega}{n(\omega)+1} \propto \omega^{2\tilde{d}(d_\phi/D)} g(\omega). \quad (2)$$

The exponent d_ϕ defines the exponential decay of the fracton wave function. Analogous to the phonon density of states, the fracton density of states can be expressed as¹¹

$$g(\omega) \propto \omega^{\tilde{d}-1}, \quad (3)$$

where the fracton dimension \tilde{d} is used, instead of the Euclidian dimension for phonons.

From Eqs. (2) and (3) it can be deduced, that

$$I_{\text{red}}(\omega) \propto \omega^\nu, \quad (4)$$

where

$$\nu = (\tilde{d}/D)(2d_\phi + D) - 1. \quad (5)$$

We need to know the values of \tilde{d} and d_ϕ to evaluate the Hausdorff dimension of the fractal, which will give information about the structure of the fractal. Following Boukenter, Duval, and Rosenberg,¹⁷ who have adopted the theory of Aharony *et al.*,¹⁸ the characteristic exponent d_ϕ can be written as

$$d_\phi = (2 - \tilde{d})D / \tilde{d} \quad (6)$$

with a lower bound $d_\phi > 1$.¹³

Substituting Eq. (6) into Eqs. (5) yields

$$\nu = 3 - \tilde{d}. \quad (7)$$

Hence the reduced intensity scales with the frequency as

$$I_{\text{red}}(\omega) \propto \omega^{3-\tilde{d}}. \quad (8)$$

III. EXPERIMENTS

A. Experimental setup

We have employed a standard Raman scattering setup during this investigation. A Spectra Physics model 171 Ar-ion laser was operated at 19436.35 cm^{-1} ($=514.5 \text{ nm}$). The scattered light was detected by means of a SPEX 14018 double monochromator coupled with a cooled RCA C31034 GaAs photomultiplier. The slits of the monochromator were $250 \mu\text{m}$, resulting in a resolution of 3.0 cm^{-1} . The pulses of the photomultiplier were counted by a DPC 2 pulse counter. The counts were reg-

istered on a Nucleus 2048 multichannel analyzer in an IBM-compatible personal computer.

We have employed unpolarized light in a 90° scattering geometry. At room temperature (300 K) no light scattering could be detected from the sample holder. For the measurements at low temperatures (approximately 25 K) the samples were glued onto a copper sample holder of a cryostat. The cryostat contained quartz windows. Extra light scattering has been detected from this sample holder for unirradiated samples, because of the scattering at the copper holder. For the irradiated samples no extra scattering has been observed.

The NaCl crystals have been irradiated by 1.35-MeV electrons, with typical doses between 5 and 95 Grad. In earlier papers we have described the irradiation facility,¹⁹ in which numerous crystals have been irradiated. The irradiated crystals were cleaned thoroughly before the Raman-scattering measurements. Immediately after polishing with polishing paper (grit size $4 \mu\text{m}$), the samples were measured. During room-temperature measurements no effect on the surface of the samples in the open air could be observed. In the vacuum of the cryostat no surface effects have been observed either.

B. Room-temperature experiments

We have measured the Raman intensity for several doped samples irradiated at doses higher than 5 Grad. Background scattering has been taken into account. The spectra of all irradiated samples, which have been investigated at room temperature, show the same features. The phonon peaks are located at approximately the same positions as mentioned in the literature (80, 100, 115, 134, 154, 205, and 230 cm^{-1}), where the ones at 80, 134, and 154 cm^{-1} are difficult to observe. Minor variations of 10 cm^{-1} in the peak positions have been observed in different samples. Above the cutoff frequency of NaCl no peak intensities have been observed as reported in the literature.

The resulting spectra after reduction according to Eq. (2) can be presented in linear form which is convenient for the examination of the peaks in the spectrum. On the other hand, the logarithmic form is convenient if the frequency dependence of the scattered light intensity has to be calculated in the low-frequency part of the spectrum. The logarithmic plot in Fig. 1 shows that the Raman intensity depends on the frequency in the low-frequency region according to a power law, as predicted by Eq. (4). The exponent ν differs only slightly for the different samples, varying from 1.35 to 1.54 for irradiation temperatures between 80 and 140°C . For the samples irradiated at low temperatures (25°C), the exponent ν varies between 1.65 and 1.97. No relation has been found with the concentration or type of dopant.

We have also measured by means of differential scanning calorimetry the latent heat associated with the melting transition of the sodium colloids in irradiated crystals. The melting transition consists of three different melting peaks (see Fig. 2). The first two peaks are located at 83 and 92°C (denoted as peaks 1 and 2, see paper III), and the third one is positioned at temperatures higher

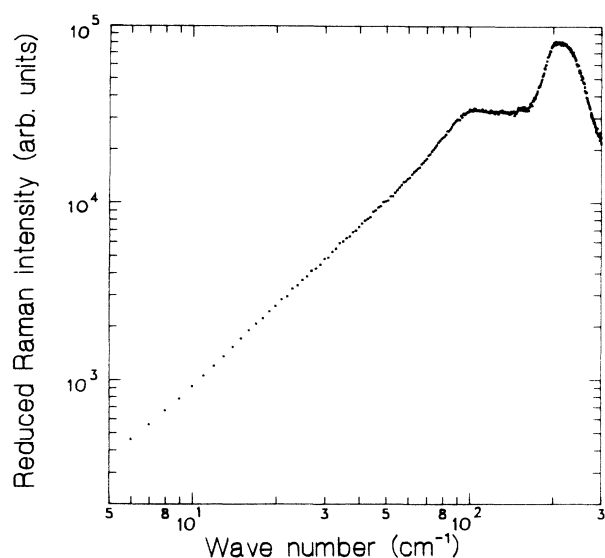


FIG. 1. Logarithmic plot of the Raman spectrum measured at room temperature (300 ppm KBF_4 -doped NaCl crystal; 250 Mrad/h, 80 Grad; $T_{\text{irr}} = 130^\circ\text{C}$).

than the bulk melting temperature of sodium (97.8°C), in this case at about 111°C (denoted as peak 3). This melting peak at relatively high temperatures is attributed to very small sodium particles.²⁰ The peak is observed only in high dose (higher than 20 Grad) irradiated samples. In the Raman spectra, however, no difference has been observed between samples containing the high-temperature melting peak and those without the high-temperature melting peak.

From Fig. 2 it is clear that the latent heat peaks measured after the Raman-scattering measurements (carried out at room temperature) differ significantly from the ones measured before the Raman-scattering measurements. The change of the latent heat peak pattern is probably caused by the high-intensity laser light. Obviously, photostimulated diffusion affects the characteristic features of the colloids drastically at room temperature. At low temperatures this photostimulated diffusion does not occur, as will be shown in the next section.

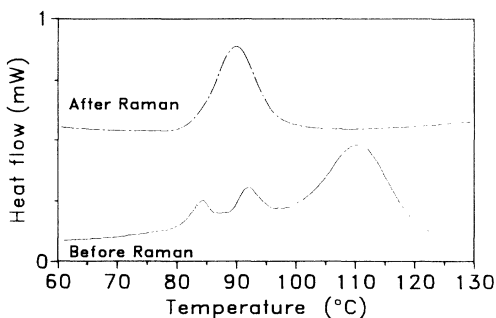


FIG. 2. The results of latent heat experiments on the sample as in Fig. 1, before and after the Raman measurements at room temperature.

C. Low-temperature experiments

Raman-scattering experiments have been performed on high-dose-irradiated samples. The samples have been selected on the appearance of the high-temperature latent heat peaks (peak 3), indicating the existence of small sodium particles.²⁰ The Raman-scattering experiments have been performed at low temperatures (approximately 25 K) in order to avoid the change in characteristic features of the investigated samples. Due to the incident laser light the temperature of the sample increases. Especially the surface layer will have an increased temperature, because of the large optical-absorption coefficient of the samples. The temperature of the surface layer where the Raman scattering occurs, has been estimated to increase from 25 to 50 K during illuminations. This has been checked by comparing the resulting spectra measured at different intensities of the incident laser light. The reduced spectra for the same sample at different light intensities were comparable if the temperature used for the reduction was estimated to be 50 K.

Figure 3 shows the linear plot of the Raman spectrum of a sample for which we observed only one large melting peak at 108°C . The latent heat peak patterns did not differ before and after the Raman experiment. We have observed only minor changes caused by the heat treatment of the latent heat experiment itself. Even after prolonged exposure at higher temperatures (80 and 110 K) during the Raman-scattering experiments no changes could be observed.

In Fig. 3 we observe peaks at 103, 210, and 233 cm^{-1} , which correspond very well within measuring errors with the NaCl phonon peaks at 100/115, 205, and 230 cm^{-1} . The NaCl phonon peaks at 80, 134, and 154 cm^{-1} have not been observed, probably because they were too weak. In contrast with the spectra measured at room temperature, two extra peaks are observed at 330 and 561 cm^{-1} .

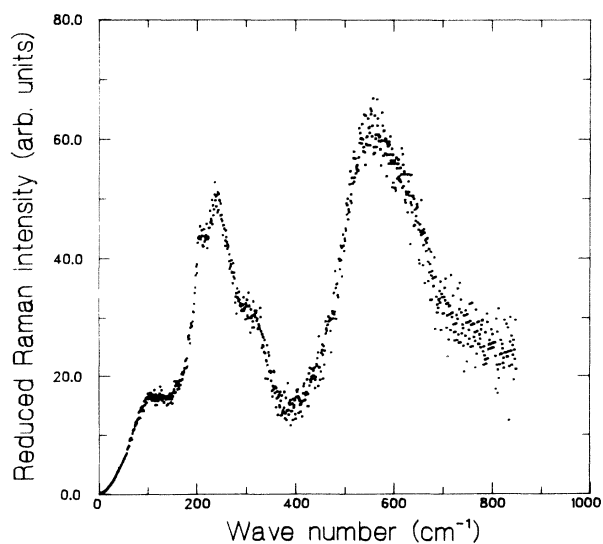


FIG. 3. The spectrum of a Raman-scattering experiment at a low temperature for a high-dose-irradiated sample (300 ppm KBF_4 -doped NaCl crystal; 250 Mrad/h, 95 Grad; $T_{\text{irr}} = 130^\circ\text{C}$).

Since these peaks are located at extraordinary positions, at higher frequencies than the cutoff frequency of NaCl (260 cm^{-1}), we conclude that localized excitations are involved.

From the low-frequency part of the spectrum we have deduced that also at low temperatures the Raman intensity depends on the frequency according to a power law. The exponent for the low-temperature measurements, is slightly lower than for the room-temperature measurements. For the low-temperature experiments we have calculated a value of 1.32 ± 0.05 for the exponent ν , for the room-temperature measurements we have calculated 1.45 ± 0.05 . The difference may be caused by the difficulties of the temperature measurement at low temperatures. The reduction of the measured spectrum is very sensitive to the measuring temperature. An error in temperature of 5 K has a relatively large influence on the Bose factor for measurements at low temperature.

IV. CONCLUSIONS

The phonon frequencies of the NaCl modes have been observed for both the room-temperature as well as the low-temperature measurements. At low measuring temperatures ($\approx 25 \text{ K}$), two extra Raman-scattering peaks have been observed that are located far beyond the cutoff frequency of the phonon spectrum of NaCl. These peaks have not been observed in low dose (less than 5 Grad) irradiated crystals. We conclude that these high-energy peaks are associated with ultrafine details of the small particles that are present in high-dose-irradiated samples, as shown by DSC experiments (paper III of this series).²⁰ The melting peak patterns of the sodium colloids changes drastically, if the Raman-scattering experiment is performed at room temperature. This implies that the initial form of the sodium colloids is affected by the laser light. It explains the lack of observation of the high-frequency peaks at room temperature, since the ultrafine details will disappear as a result of rearrangements due to photo-stimulated diffusion.

At low frequencies the usual Debye behavior of the phonon spectrum is not observed. The power-law dependence of the Raman intensity indicates that the interface between the NaCl host matrix and the Na metallic particles exhibits a fractal geometry. From the low-temperature experiments we obtained a slope $\nu=1.4$, such that according to Eq. (7) the fracton dimension becomes $\bar{d}=1.6$. Aharony *et al.*¹⁸ have derived, that for percolating systems in all (Euclidean) dimensions, \bar{d} should be equal to $\frac{4}{3}$. The exponent reported here is not too far from this value. The exact dimension of the fractally shaped interface is not known. We assume that the Hausdorff dimension (D) of the surface is close to the generally accepted value for percolating systems, which is approximately 2.5. If we use Eq. (6) the geometrical exponent becomes $d_\phi=0.625$. This value is lower than the lower bound mentioned in the literature ($d_\phi > 1$),¹³ which implies that the fracton wave function is less localized than suggested in the literature.

An explanation for a fractal shape of the colloids is based on the surface energy of the metal. Mariotto *et al.*²¹ have stated that silver particles in the NaCl host possess a smooth surface. The surface energy of sodium ($\approx 0.200 \text{ J/m}^2$) is much lower than the surface energy of silver ($\approx 0.920 \text{ J/m}^2$).²² Since the surface energy of sodium is low, the need for rearrangements in order to minimize the surface is relatively low. Therefore, it is not unlikely, that the growth of dendritic sodium structures is kinetically favorable. A fractal geometry will be formed, which determines the extra Raman intensity at low frequencies.

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