INVESTIGATION OF INELASTIC LIGHT SCATTERING IN HEAVILY ELECTRON-IRRADIATED ALKALI HALIDES

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The properties of several unusual Raman scattering peaks observed in heavily irradiated NaCl with vast amounts of colloidal sodium are investigated. A new peak (at $3580 \, cm^{-1}$) has been observed far beyond the cut-off limit of the one-phonon spectrum. This scattering phenomenon has been explained with an electron quantum confinement model where the electronic excitations are quantized as expected for wire-like structures of nano-particles of metallic sodium.

Keywords: Raman scattering; Alkali halides; Quantum confinement

Raman spectroscopy of doped, additively and electrolytically colored NaCl crystals have revealed changes in the spectra of inelastic light scattering due to the presence of small sized metallic nano-particles [1, 2]. Strong changes in the low-frequency Raman Scattering (RS) spectra and the appearance of two additional peaks higher than the maximum frequency of the one-phonon spectrum of the NaCl matrix were also discovered in heavily irradiated, doped rock salt [3]. We have concluded from our differential scanning calorimetry (DSC) experiments that these peaks (at 330 and $550 \, cm^{-1}$) are associated with ultrafine details of the small Na-particles available in our samples [4]. With the aim to learn more about the origin of inelastic light scattering in these materials, in this work, we have studied the Raman spectra of heavily damaged $NaCl:KBF_4$ and NaCl:K crystals as a function of the wavelength of the excitation light and the measuring temperature. We have measured the polarized and depolarized spectra with X(ZZ)Y and X(ZX)Y for $90°$-geometries for samples that had been irradiated under different conditions. The polarized VV and VH Raman spectra were taken for all the samples at temperatures in the range 30–250 K. The Rayleigh elastic scattering results in a strong broadening mask the Stokes intensity for all frequencies below $100 \, cm^{-1}$. To eliminate these temperature effects on the phonon spectrum close to frequency zero, we reduced the spectra by dividing the RS intensity by the factor $R_{s1}^{(1)} = (\bar{n} + 1)$, where the Bose coefficient $\bar{n}(v, T) = (e^{kv/kT} - 1)^{-1}$ and v is the phonon vibration frequency.

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The main feature of the reduced inelastic scattering spectra is the strong dependence of the VV polarized scattering spectrum on the temperature in the low-frequency region (below $100\,cm^{-1}$) and the weak temperature dependence for higher frequencies for both polarization directions (see, for example Figure 1).The different temperature behavior for the VV and VH polarization directions close to zero-frequency shows that the probe laser light interacts with both the electronic and vibrational systems of the Na-colloids giving rise to electronic and vibrational Raman scattering bands below $100\,cm^{-1}$. As in semiconductors [5] the increasing scattering cross-section with decreasing temperature for small frequency shifts can be explained by single particle plasma-like excitations of the conduction electron gas in solids.

Due to the extensive disorder in our heavily irradiated NaCl samples, as in amorphous media and highly defective crystals, with small correlation lengths the selection rules for the phonon wave-vector break down partly and as a consequence we observe the forbidden first-order Raman scattering due to the NaCl phonon modes below $300\,cm^{-1}$. In our extensively disordered samples the density of the vibrational states is obtained [6] by dividing the RS intensity by $f = R_s^{(1)}/v$. In Figure 2 we show the averaged, reduced spectra for three samples with different amounts of Na. The averages have been taken over the results obtained for all measuring temperatures.
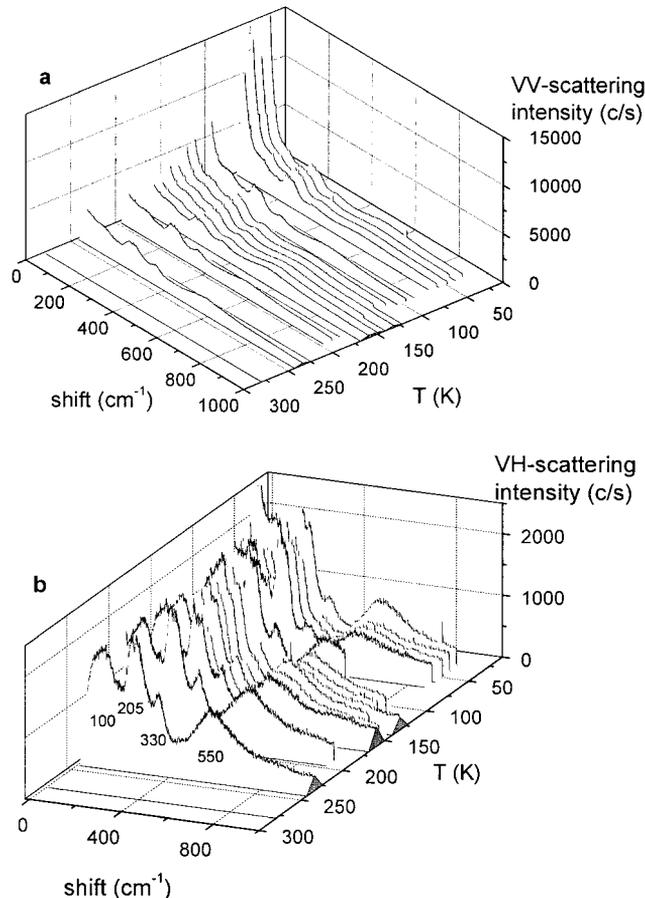

FIGURE 1   Reduced (a) VV and (b) VH spectra for NaCl:KBF$_4$ (12.4%Na) at measuring temperatures: 1–30 K, 2–40 K, 3–50 K, 4–60 K, 5–100 K, 6–11-(120 K, 130 K, 140 K, 150 K, 160 K, 170 K), 12–13 (200 K, 250 K).
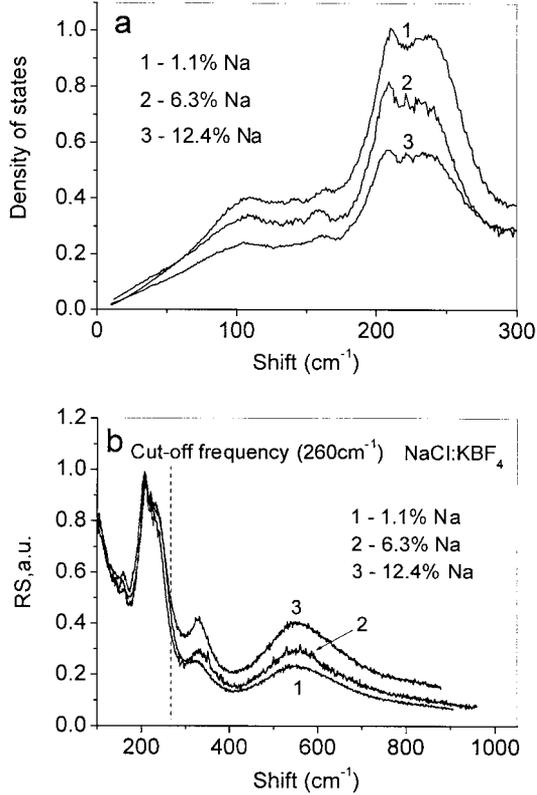
FIGURE 2 Density of vibrational states for NaCl:KBF$_4$ and intensity of scattering higher than $300 \, \text{cm}^{-1}$ at different concentrations of Na nano-particles: $1 - 1.1\%$Na, $2 - 6.3\%$Na, $3 - 12.4\%$Na.

Comparing the plots in Figure 2a we see that the DOS decreases with increasing damage. This observation can be explained by the increasing optical density of the sample and the small penetration depth of the excitation light. Taking into account this change of the penetration depth we have fitted the spectra and observed an increase of the intensities of the 330 and 550 peaks (Figure 2b) with increasing volume fraction of Na-colloids. As an alternative to local phonon modes, we have explained elsewhere [7] the appearance of these peaks beyond the limits of the one-phonon spectrum of NaCl in terms of electron quantum confinement in nano-wires consisting of Na-colloids with a mean size of about 6 nm.

Now we have succeeded in observing a new inelastic scattering line (at $3580 \, \text{cm}^{-1}$, Figure 3) very far beyond the one-phonon cut-off frequency. In fact, inelastic scattering of these high frequencies can hardly be assigned to some sort of local phonon excitations. The concept of quantum confinement in inelastic scattering allows us to find the upward energy shift of the peaks associated with electrons, which are confined to a narrow potential well. In the case of one-dimensional colloids (quantum wires along the z direction) the behavior of the confined electrons can be described by a rectangular cylindrical potential well. The spectrum of energy eigenvalues for such a quantum well looks like [7]

$$E_{n,l,p_z} = \frac{\hbar^2 j_{n,l}^2}{2m^* \rho_0^2} + \frac{\rho_z^2}{2m^*}, \tag{1}$$

where $j_{n,l}$ is *n*th root of the Bessel function of *l*th order and $n = 1, 2, 3 \ldots$

The upward frequency shift in the Raman spectra associated with transitions between the lowest neighboring energy states (*i.e.*, the Fermi level and the 1s-state with $n = 1$, $l = 0$) is

$$v_{1s}(\text{cm}^{-1}) = 1.21 \times 10^3 \cdot \frac{j_{1,0}^2}{qd^2}, \tag{2}$$

and using the value of the root $j_{1,0} = 3.83$ we obtain

$$d(\text{nm}) = \frac{133}{\sqrt{qv_{1s}(\text{cm}^{-1})}}, \tag{3}$$

where *q* is the ratio of the effective and free electron mass and the diameter of the wire *d* is expressed in nanometers. For sodium $q = 1.24$ and using the shift $3580 \, \text{cm}^{-1}$ we evaluate for the size of the Na colloid $d = 2 \, \text{nm}$. Because in our case the observed energy shift (0.44 eV) is much larger than maximum value of *kT* (at room temperature *kT* is about
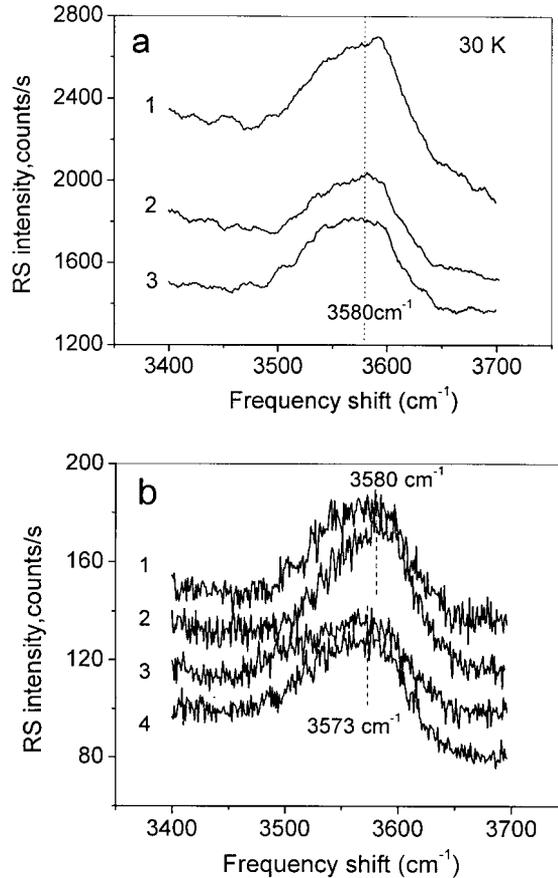

FIGURE 3 High-frequency inelastic scattering of NaCl doped with KCl or KBF$_4$, for a wide range of Na-concentrations, observed at measuring temperatures of 30 and 250 K and with excitation wavelengths of 488 and 514 nm. a: 1-NaCl:K (6.4%Na, 514 nm), 2-NaCl:KBF$_4$ (12.4%Na, 488 nm), 3-NaCl:KBF$_4$ (7.8%Na, 488 nm), all at 30 K b: NaCl:KBF$_4$ (7.8%Na, 488 nm), at 30 K (1 – before, 2 – after annealing at 200 °C for 2 min), at 250 K (3 – before, 4 – after annealing).

0.03 eV) there is practically no dependence of the 3580 cm^{-1}-peak intensity on the measuring temperature (Figure 3b). Slight annealing of the samples (2 min at 200 °C) results in a small decrease (a few cm^{-1}) of the mean frequency of the scattering peak, which might be caused by a small increase of the average colloid sizes due to rearrangements and a transition from the fcc- to the bcc-structure. We have observed a phase transformation of Na-colloids under the above mentioned annealing conditions by means of differential scanning calorimetry (for the sample with 7.7%Na). Prior to annealing the melting temperature of metallic Na was 107 °C and it was 92.5 °C after annealing. Thus the 3580 cm^{-1} peak can be explained by inelastic scattering caused by very small sodium particles with mean sizes of about 2 nm. We propose that the peak is caused by quantum confined electronic excitations. This conclusion is supported by recent observations of quantum well luminescence from Na-monolayers [8].

Acknowledgements

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