Chapter 4

Analysis of FTIR Spectra of Nanoparticles of AgI, Ag$_2$Hgl$_4$ and Cul
4.1 Introduction

Generally, the vibrational spectrum of small particles is expected to differ from the spectrum of bulk material. The reduction in the size of the particles will lead to the breakdown of the law of conservation of momentum and ultimately vibrational modes corresponding to \( k \neq 0 \), where \( k \) is the wave vector of the phonons, will no longer be forbidden. Nanoparticles characteristically have a high value for surface-to-volume ratio. Most of the unusual properties of nanoparticles are due to the fact that a nanoparticle is mostly a surface. The vibrational spectra of nanoparticles could be influenced by the surfaces because of the change of the atomic arrangement on the surfaces as compared to the packing in the bulk of the crystal.

Infrared absorption in small crystals has been studied in detail by many authors. In the harmonic approximation, a large (that is, size of the crystal large compared to the wavelength of the light in the surrounding medium) ionic crystal absorbs light only at \( \omega_r \), the frequency of long wavelength transverse optical mode. If the crystal size is small compared to the wavelength of light in the medium surrounding it, the frequency of the peak absorption is increased to \( \omega_F \) by the polarization charge at the crystal surface. Frohlich showed that the mode of vibration with uniform polarization in a small ionic sphere has the frequency

\[ \omega_F^2 = \omega_r^2 \frac{(\varepsilon_0 + 2\varepsilon_m)}{(\varepsilon_\infty + 2\varepsilon_m)} \]

where \( \omega_F \) is the frequency of the mode, called Frohlich mode, \( \varepsilon_\infty \) and \( \varepsilon_0 \) are the high and low frequency dielectric constants of the sphere. \( \varepsilon_m \) is the dielectric constant of the
surrounding medium. Even though this mode is not localized at the surface, it is often called a surface mode since its origin lies in the finite size of the sample. The scattering and absorption by ionic spheres of arbitrary size was calculated independently by Fuchs and Kliever, and Englman and Ruppin. According to these calculations, the existence of a series of surface modes with frequencies between $\omega_S$ and $\omega_T$ were predicted, where $\omega_S$ is defined as the frequency at which the real part of the dielectric constant equals minus $\varepsilon_m$. The Frohlich mode belongs to the series as the lowest frequency mode. Infrared measurements have been used by many authors to study the surface modes in small crystals. Infrared transmission spectra of ZnO, CdS and BeO particles much smaller than the wavelength of incident light were analysed by Hayashi et al. and they observed features specific to surface modes. The observed features of the spectra were explained by taking into account both the optical anisotropy and the actual shape of the particles. Experimental observation of surface phonon modes in the IR spectra has also been made in small crystals of various materials like MgO, ZnO, NiO, etc.

Many interesting results have been reported from infrared studies of small crystals. In the case of sodium chloride small crystals, a broad absorption band was observed and the frequency of this band was found to be different from the reststrahl frequency of the bulk crystal. The reason behind this difference in frequency was attributed to the restoring force created by the surface polarization charge. In the case of nanocrystals, dipolar interactions, interfacial effects, surface amorphousness, high internal stress, etc. are reported to be the reasons for the observed changes in the vibrational modes. A general conclusion has been obtained from these studies that optical absorption and scattering in the fundamental lattice absorption region are size dependent. In the present chapter, the changes observed in the far-IR transmission spectra of nanoparticles of AgI, Ag$_2$HgI$_4$ and CuI compared to the respective bulk spectra are qualitatively discussed.
4.2 Experimental

Nanoparticles of AgI, Ag$_2$HgI$_4$ and CuI were prepared through chemical routes as described in the section 3.2.1 of this thesis. XRD patterns of the particles were recorded using a Bruker AXS D5005 X-ray diffractometer. The particle sizes were estimated from the line broadening of the diffraction lines using Scherrer’s equation$^{19}$ and were found to be 17, 20 and 22nm respectively for AgI, Ag$_2$HgI$_4$ and CuI nanoparticles. FTIR spectra of all the three samples were recorded in the region 50-200 cm$^{-1}$ using a BOMEM DA-8 FTIR spectrometer with polyethylene as the dielectric medium surrounding the particles.

4.3 Results

4.3.1 AgI Nanoparticles

X-ray diffraction pattern of the nanoparticles of AgI is shown in Fig. 3.1 of chapter 3. The three diffraction peaks between 20 angles 22 and 26° are useful in determining the hexagonal (β) and cubic (γ) phases of AgI.$^{20}$ All three peaks will be present in hexagonal phase while only the central peak will be in cubic phase. An estimation of the relative percentage of β and γ phases$^{21}$ as discussed in chapter 3 of this thesis shows that the present sample of the AgI nanoparticles contains 55% of hexagonal phase and 45% of cubic phase. However, the transmission spectrum recorded in the 50-150 cm$^{-1}$ range can be considered as the far-infrared spectrum of β-AgI nanoparticles since the frequencies of the phonon modes of γ phase are greater than 150 cm$^{-1}$.$^{22}$ The far-infrared spectrum of nanoparticles of silver iodide is shown in Fig. 4.1. A typical far-IR spectrum of single crystals of β-AgI at room temperature has been reported to contain a broad main residual absorption near 110 cm$^{-1}$ corresponding to the TO modes of symmetry A1 and E1 in the transmission mode.$^{23}$ In the present study, the spectrum of nanoparticles of AgI was found to consist of two clearly resolved bands at 87 cm$^{-1}$ and 109 cm$^{-1}$. The intensity of these bands was found to be less than that of the bands in the reported bulk spectrum. A new feature was observed near 140 cm$^{-1}$ in the spectrum of nanoparticles. The interesting observation of the present study was the clear resolution of a peak at 87 cm$^{-1}$, which is not resolved in the transmission spectrum of bulk sample.$^{23}$
Fig. 4.1. FTIR spectrum of nanoparticles of AgI

Fig. 4.2. FTIR spectrum of nanoparticles of CuI
4.3.2 Ag$_2$HgI$_4$ Nanoparticles

The X-ray diffraction peaks of the nanoparticles of Ag$_2$HgI$_4$ revealed the presence of cubic (α) phase in addition to the tetragonal (β) phase at room temperature (section 3.4.3 of chapter 3). In polycrystalline Ag$_2$HgI$_4$, the cubic phase exists only in the high temperature disordered (α) phase. The far-IR transmission spectrum of polycrystalline Ag$_2$HgI$_4$ has been reported to consist of bands at 105, 120 and 160 cm$^{-1}$. It is also reported that the bands in the 80-140 cm$^{-1}$ region are due to the stretching modes of AgI and (Hgl)$_2$. The far-infrared transmission spectrum of nanoparticles of Ag$_2$HgI$_4$ in the present investigation is shown in the Fig. 4.2. The band corresponding to 105 cm$^{-1}$ of the polycrystalline sample is found to have shifted to the lower energy side to around 103 cm$^{-1}$ while the band at 120 cm$^{-1}$ is found to be shifted to 118 cm$^{-1}$ in the nanocrystal spectrum. The intensity of these bands are nearly equal to the intensity of the bulk bands.
4.3.3 CuI Nanoparticles

Copper (I) Iodide at normal temperature and pressure exhibits a zinc blende structure. The far-IR transmission spectrum of CuI nanoparticles in the frequency range 50-200 cm\(^{-1}\) is shown in Fig. 4.3. The far-infrared spectrum of the CuI thin film was reported to contain a sharp band at 124 cm\(^{-1}\).\(^{26}\) In the present study, the infrared spectrum of nanoparticles of CuI showed two bands at 125 cm\(^{-1}\) and ~131 cm\(^{-1}\) with nearly equal intensities.

4.4 Discussion

Infrared study of small particles of NaCl and KBr\(^{16}\) has shown that the mode corresponding to the maximum absorption has undergone a frequency shift to the higher values. In small alkali halide crystals,\(^{16}\) as the crystal size decreases, the intensity of the bulk mode decreases and after a particular size of the crystal, this bulk band vanishes. A surface band is observed in the forbidden region, between the bulk TO and LO phonon frequencies, and this band shifts to higher frequencies as the crystal size is further decreased. The peaks obtained in larger NaCl particles (~10 \(\mu\)m) are mainly due to scattering and partly due to the absorption by the first surface mode.\(^{16}\) When the size is reduced, this mode shifts to the higher frequencies and absorption prevails over scattering. The observed frequency shift to the higher frequency side in LiF and NaCl small particles has been accounted for on the basis of the additional restoring force created by the surface polarization charge\(^{9}\) and the observation of the broad band was explained on the basis of the surface phonons, characteristic of small particles. Broad bands were observed in nano alumina powder also\(^{17}\) and these bands were explained based on the 'interfacial effect'\(^{17}\) of the nano solid. Reduced density and modified coordination numbers in the boundary regions in nanocrystalline materials affects the electronic wave function of a solid and hence the interatomic bonds in the boundary regions will be different from the ones of an infinite crystal.\(^{27}\) Hence the vibrational spectra of nanocrystalline materials may be expected to be different from the coarser grained material.
In the present study, the modes in AgI and CuI nanoparticles have been observed to be shifted to higher frequencies. This may be attributed to the increased polarization charge at the surface of the nanoparticles. Theoretical calculations on the infrared transmission studies of bulk AgI predicted a peak at a frequency of 84 cm\(^{-1}\) at 145K. The far-IR reflectivity spectrum of the bulk sample was reported to contain a clearly resolved structure at 80 cm\(^{-1}\) in addition to a band around 110 cm\(^{-1}\). A structure near 85 cm\(^{-1}\) was observed in Raman spectrum also. But no band near 80 cm\(^{-1}\) was observed in the transmission spectrum of bulk \(\beta\)-silver iodide. In the present study of nanoparticles of AgI, in addition to a peak around 109 cm\(^{-1}\), a clearly resolved peak was obtained around 87 cm\(^{-1}\) in the transmission spectra itself. The observed peak at 87 cm\(^{-1}\) is identified as the peak corresponding to the 80 cm\(^{-1}\) structure of bulk AgI.

The appearance of additional structure in the far-IR reflection spectra and the Raman spectra of bulk AgI near 80 cm\(^{-1}\) was explained by Bruesh et al. using two mechanisms based on: 1) a two phonon process and 2) defects. The two phonon process was based on a perfectly ordered but anharmonic crystal while the other interpretation was based on a harmonic but disordered crystal. Anharmonicity will couple different phonons and if the selection rules for infrared and Raman scattering are satisfied, multiphonon process can produce additional structures. From the temperature dependence of far-infrared reflection, the structure near 80 cm\(^{-1}\) was assigned to a TA + LA combination mode which is infrared active. The second interpretation was based on defects and has been proposed by Burns. It was shown by quantitative calculations that these defects give rise to a structure near 80 cm\(^{-1}\) in far infrared and Raman spectra. Generally, nanoparticles are considered to have a defect structure. Also, in nanostructured materials, the effective anharmonicity of the vibrations increase due to the contribution from surface atoms. Hence the appearance of the structure in the infrared transmission spectrum of AgI nanoparticles in the present study can be attributed to the combined effect of anharmonicity and the defect structure of the nanoparticles. The observed shift of the peak to the higher energy side (\(-87\) cm\(^{-1}\)) may be attributed to the increased polarization charge at the surface of the nanoparticles.
The far-IR spectrum of nanoparticles of CuI showed two bands at 125 and 131 cm\(^{-1}\) with nearly equal intensities (Fig. 4.2). Plendl et al\(^{26}\) had reported the far-IR transmission and reflection spectra of CuI thin films. They observed a single band at 124 cm\(^{-1}\) at room temperature which was found to shift to higher energy side with decrease in temperature. In the reflection spectrum, maximum reflection occurred at 130 cm\(^{-1}\) at room temperature which, according to the authors, corresponded to the 124 cm\(^{-1}\) mode of the transmission spectrum. The maximum of reflection shifted to higher energy side as the temperature was lowered. Raman spectrum of CuI has also been reported.\(^{32,33}\) The main feature of the room temperature Raman spectrum reported by Potts et al\(^{35}\) was the peak at 124 cm\(^{-1}\) which was assigned as the TO mode. The Raman spectrum revealed a shoulder at 140.5 cm\(^{-1}\) which had the polarization characteristics of an LO mode. The Raman lines were found to shift to higher energy side with decrease in temperature. High pressure Raman spectra of CuI was studied in detail by Brafman et al.\(^{33}\) At 6.3 kbar, with two atoms per unit cell of the zinc blende structure, a relatively strong TO mode at 131 cm\(^{-1}\) and a weak LO line at 144 cm\(^{-1}\), which appeared as a shoulder on the intense TO line, were observed. The mode observed at 125 cm\(^{-1}\) in the infrared spectrum of nanoparticles of CuI in the present study (Fig. 4.2) can be identified as the TO mode based on the above results. The slight shift of the mode to the higher energy side compared to the 124 cm\(^{-1}\) mode of the CuI thin films may be attributed to the increased polarization charge at the surface of the nanoparticles.\(^{4}\) The mode observed at 131 cm\(^{-1}\) could not be explained on the basis of the bulk spectrum. This new feature can be considered as the surface mode.

In very small particles, the effective anharmonicity of the vibrations increase due to the contributions from surface atoms.\(^{2}\) The high temperature far-IR spectra of polycrystalline Ag\(_2\)HgI\(_4\) has been reported earlier\(^{34}\) and it was shown that the vibrational lines shift to lower frequencies with increasing temperatures in the \(\beta\) phase. This was explained on the basis of the anharmonicity. In the present study the two bands at 105 and 120 cm\(^{-1}\) in the infrared spectra of Ag\(_2\)HgI\(_4\) have been observed to have shifted to lower frequencies. This may be due to the increased anharmonicity of the vibrations.
4.5 Conclusion

The FTIR spectra of nanoparticles of AgI, Ag₂HgI₄ and Cul were recorded and analysed in comparison with the corresponding spectra of bulk material. The changes in frequencies are attributed to the surface properties of the nanoparticles.

4.6 References

6. R Englman and R Ruppin, J Phys. C 1, 630 (1968)