Anharmonic interactions in the Raman spectrum of ZnGa$_2$Se$_4$ and MnGa$_2$Se$_4$ ordered vacancy compounds

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Abstract. We present a study of anharmonic and local order effects in the Raman spectrum of the ordered vacancy semiconductors ZnGa$_2$Se$_4$ and MnGa$_2$Se$_4$. In MnGa$_2$Se$_4$ the asymmetry of the Se-vacancy breathing like mode and its temperature dependence are satisfactorily explained by a model based on the anharmonic coupling of the phonon with second order phonon excitations. In ZnGa$_2$Se$_4$, however, asymmetry is not fully accounted for with this model. We attribute the discrepancy to short-range order effects in the, on the average, cation disordered structure of ZnGa$_2$Se$_4$. These effects are taken into account by means of the spatial correlation model.

1. Introduction

AB$_2$X$_4$ ordered vacancy compounds (OVC) are a family of tetrahedral semiconductors with a combination of optical and electronic properties that make them promising materials for optoelectronic devices.[1] Some of their technological applications depend on the carrier lifetimes, which can be affected by carrier-phonon or phonon-phonon interactions.[2] Those interactions can be investigated by Raman scattering through their effect on the shape of the Raman peaks.

We present a Raman study of anharmonic interactions in ZnGa$_2$Se$_4$ and MnGa$_2$Se$_4$, two closely related OVC whose main structural difference is their cation distribution. ZnGa$_2$Se$_4$ (space group I-42m) presents a partial cation disorder, with Zn and half of the Ga atoms randomly distributed in the 4d site, whereas in MnGa$_2$Se$_4$ (I-4 space group) cations are totally ordered. In this work we focus on the shape of the Se breathing mode toward the vacancy. A model based on the anharmonic coupling of the phonon to second order phonon excitations is proposed to explain the asymmetry of the mode and its temperature dependence. Short-range order effects are also taken into account in ZnGa$_2$Se$_4$.

2. Experimental details

Raman spectra of MnGa$_2$Se$_4$ and ZnGa$_2$Se$_4$ single crystals have been collected from 4K to room temperature (RT) on a DILOR XY spectrometer with a liquid nitrogen cooled CCD detector. Excitation light was the 514.5 nm line of an Ar$^+$ laser, through a X50 microscope objective lens. Power at the sample was ~1 mW and spectral resolution ~1.6 cm$^{-1}$. The Si mode at 520 cm$^{-1}$ was used for frequency calibration at RT. Single crystals were produced by chemical vapor transport method using iodine as transport agent.[3]
3. Experimental results

Figure 1 shows the RT Raman spectra of MnGa$_2$Se$_4$ and ZnGa$_2$Se$_4$ single crystals recorded in parallel configuration along an arbitrary direction onto a (112) plane. All Raman active modes have been identified in previous works [4].

![Raman Spectra of MnGa$_2$Se$_4$ and ZnGa$_2$Se$_4$ at RT.](image)

We shall focus our attention in the asymmetry of the peaks appearing at $\nu \approx 135$ and 143 cm$^{-1}$ in MnGa$_2$Se$_4$ and ZnGa$_2$Se$_4$, respectively, which are attributed to the anion–vacancy breathing like mode. Their temperature evolution is shown in figures 2a and 2b. Both linewidth and asymmetry decrease with decreasing temperature, but the behavior is different for each compound: in MnGa$_2$Se$_4$ the peak is totally symmetric below 30 K whereas in ZnGa$_2$Se$_4$ asymmetry remains even at 4 K.

![Temperature evolution of Raman spectra in the region of the Se breathing mode.](image)

Figures 3a and 3b show the temperature evolution of the HWHM, deconvoluted from instrumental effects. Data are surprisingly similar for both compounds, and suggest that the width at half height is not the appropriate parameter to discuss line asymmetry. For that purpose, we have worked out the spectrum derivative and calculated the ratio of the left to right maximum slopes. As shown in figure 3, this magnitude varies between one (no asymmetry) and $\approx 1.6$ (maximum asymmetry).

4. Model and discussion

In a previous work [5] we have attributed the asymmetry of the Se-vacancy breathing mode in MnGa$_2$Se$_4$ to the anharmonic coupling of the mode to a continuum of second-order phonon excitations arising from either zone-boundary TA bands or from the zone centre E mode found at $\nu = 77.5$ cm$^{-1}$. The origin of the continuum was discussed in terms of the dispersion relations of the closely related zinc-blende compounds ZnSe and GaAs, in which high two-phonon density of states from 2TA bands is found at 150-160 cm$^{-1}$, close to the position of the Se breathing mode.
In assumption of $\omega$-independent coupling parameter and negligible Raman activity of the continuum (see Ref. [5]), the Raman profile of a discrete state coupled with a continuum of generic shape can be modeled by the expression given by Klein in Ref [6].

$$I(\omega) = \frac{T_d^2}{\pi} \frac{\pi \rho(\omega)V^2 + \gamma}{[\omega_d - \omega + V^2 R(\omega)]^2 + [\pi \rho(\omega)V^2 + \gamma]^2},$$

(1)

where $T_d$ is the Raman activity of the discrete (phonon) state, $\omega_d$ its energy, and $\gamma$ a residual linewidth parameter that accounts for any other line-broadening effects, in particular Se isotope mass fluctuation.[7] $V$ is the coupling parameter between discrete and continuum states. The shape of the continuum is determined by the density of states $\rho(\omega)$ and its Hilbert transform $R(\omega)$. As lattice dynamics of MnGa$_2$Se$_4$ are not available, the two-phonon density of states was modeled with a symmetric function of width $\gamma$ centered at $\omega_d$.

The intrinsic linewidth $\gamma$ can be determined by fitting the data of figure 3 to the expression $\Gamma = \gamma + \Gamma_0(I + n(\omega_b, T) + n(\omega_a, T))$ that gives the broadening due to third order anharmonic decay of the phonon to a pair of phonons $a$ and $b$ fulfilling $\omega_d = \omega_a + \omega_b$, where $\Gamma_0$ is a parameter proportional to the coupling strength and the residual linewidth parameter $\gamma$ has been introduced. A good fit is obtained with $\omega_d = \omega_a = \omega_b/2$ for both compounds with $\omega_d$ fixed at the phonon frequency at low temperatures (137.5 and 145 cm$^{-1}$ for MnGa$_2$Se$_4$ and ZnGa$_2$Se$_4$, respectively). The remaining parameters are $\Gamma_0 = 0.295$ and $\gamma = 0.19 \pm 0.03$ cm$^{-1}$, for MnGa$_2$Se$_4$, and $\Gamma_0 = 0.291$ and $\gamma = 0.12 \pm 0.03$ for ZnGa$_2$Se$_4$.

The Raman profile of MnGa$_2$Se$_4$ was simulated by means of eq. (1) with $\gamma = 0.2$ cm$^{-1}$. Good agreement with experimental data was reached, as shown in figure 2. The bare phonon frequency varies from 138.5 cm$^{-1}$ at 4K to 138.1 cm$^{-1}$ at RT. The temperature dependence of the coupling parameter $V$ obtained from the fitting is plotted in figure 4, and $\omega_d$ is found at values of 150-160 cm$^{-1}$. We note that, as it is defined, $V$ includes the temperature dependence arising from Bose factors.

The attempt to fit the temperature evolution of the breathing mode in ZnGa$_2$Se$_4$ with eq. (1) was unsuccessful. As shown in figure 3 the asymmetry in ZnGa$_2$Se$_4$ is high even at 4 K, and it can not be reproduced with Klein’s expression. This suggests that there is another mechanism contributing to the line asymmetry. Since ZnGa$_2$Se$_4$ is partially cation disordered, with Zn and half of Ga cations randomly distributed in the 4d crystallographic site, we attribute the additional effects to structural disorder, in particular to the formation of locally ordered domains.
In semiconductor alloys and finite size systems, the asymmetry of the Raman peaks is explained with the spatial correlation model (SCM). According to this model, local order or finite size lead to the relaxation of the Raman selection rule $\Delta q = 0$. Assuming a gaussian space/momentum correlation function, the Raman profile is given by

$$I'(\omega) = \frac{1}{\sqrt{2\pi}} \exp\left(-\frac{q^2 L^2}{4}\right) I(\omega, q) dq^3$$

Figure 4. Temperature evolution of the coupling parameter $V$ in MnGa$_2$Se$_4$ (a) and ZnGa$_2$Se$_4$ (b) to the relaxation of the Raman selection rule $\Delta q = 0$. Assuming a gaussian space/momentum correlation function, the Raman profile is given by

$$I'(\omega) = \frac{1}{\sqrt{2\pi}} \exp\left(-\frac{q^2 L^2}{4}\right) I(\omega, q) dq^3$$

where $I(\omega(q), q)$ is the intrinsic Raman line shape, $q$ is expressed in units of the Brillouin zone dimensions and $L$ is the space correlation length, related to the size of the ordered regions. Line broadening and asymmetry arises from the dispersion of the phonon frequency $\omega(q)$, for which we have used the expression $\omega(q) = \sqrt{A + \sqrt{A^2 - B(1 - \cos \pi q)}}$ (Ref. [9]) with $A$ varying from 10380 to 10420 cm$^{-2}$ between 4 and 300 K and $B = 4 \times 10^8$ cm$^{-4}$.

The temperature dependence of the asymmetry of the Se breathing mode in ZnGa$_2$Se$_4$ is explained as the combined effect of anharmonic decay and short-range order effects. Since the anharmonic contribution decreases with decreasing temperature, short-range effects show up mostly at low temperatures, which explain the non-vanishing asymmetry at 4K. Good agreement is reached at all temperatures, as seen in figure 2b. A value of $L = 27.9$ unit cells has been obtained. As shown in figure 5b, $V(T)$ has the same behaviour as in MnGa$_2$Se$_4$, which indicates that the anharmonic decay mechanism is similar in both compounds. The bare frequency is found to be almost constant at 145 cm$^{-1}$. In agreement with the negligible cation mobility expected below 300 K, the parameters of the SCM are found to be temperature independent.

References

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