Raman study of $Zn_{1-x}Mn_xGa_2Se_4$ diluted magnetic semiconductors at room temperature: disorder and resonance effects.

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The Raman spectrum of the diluted magnetic semiconductor compounds $Zn_{1-x}Mn_xGa_2Se_4$ ($0 \leq x \leq 1$) has been measured and interpreted at RT. These compounds have a tetragonal structure related to that of defect chalcopyrite, with a unit cell consisting of two zinc-blende type unit cells. Recent neutron scattering studies [1] have allowed the determination of the crystal structure as being $I\bar{4}2m$ for $0 \leq x < 0.5$ and $I\bar{4}$ for $0.5 \leq x \leq 1$. Single crystalline samples were produced by the iodine transport method [1]. In most cases as-grown samples were found to be oriented in a tetragonal (112) plane, but (001) orientation was also encountered in $MnGa_2Se_4$.

First order Raman peaks are observed from 50 to 280 cm^{-1} while second order bands are detected between 500 and 600 cm^{-1}. In first order, 12 Raman active modes are expected for $I\bar{4}2m$ space group ($2A_1 + 3B_2 + 2B_1 + 5E$) and 13 modes for $I\bar{4}$ space group ($3A + 5B + 5E$). The spectrum of $MnGa_2Se_4$ contains up to 20 peaks appearing selectively according to the experimental polarization configuration. The availability of samples oriented in different crystallographic planes has allowed a complete assignment of the mode symmetries and polar behavior. In particular, a discussion concerning the origin and symmetry of the highest frequency band ($\nu \approx 280$ cm^{-1}) in isostructural compounds such as $CdGa_2Se_4$ has been elucidated.

Except in the case of $x = 1$ ($MnGa_2Se_4$), disorder effects are seen in the spectra of all other compounds due to the disordered distribution of Zn, Mn and Ga cations. Those effects are greatest in the region close to $x = 0.5$, but even for $x = 0$ ($ZnGa_2Se_4$) the bands are broadened and much resolution is lost compared with $MnGa_2Se_4$. Our results for $ZnGa_2Se_4$ are similar to those previously reported for this compound [2].

Upon variation of the excitation wavelength (an Ar^+ laser was used) resonance effects are observed depending on x and are in agreement with the reported evolution of the optical gap [3] which is found to be close to 2.3 eV for $x = 0$, ≈ 2.2 eV for $x = 0.5$ and 2.5 eV for $x = 1$, all at RT.

[1] M. C. Morón et al., to be published.
[2] P. P. Lottici and C. Razzetti, Sol. State Commun. **46**, 681 (1983).
[3] A. Millán and M. C. Morón, J. Appl. Phys. **89**, 1687 (2001).