Pressure-induced metallization and resonant Raman scattering in Zn$_{1-x}$Mn$_x$Te


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Pressure-induced resonant Raman scattering is adopted to analyze the zone-center optical phonon modes and crystal characteristics of \( \text{Zn}_{1-x}\text{Mn}_x\text{Te} \) \((0 \leq x \leq 0.26)\) thin films. The pressure \((P_t)\) at which the semiconducting undergoes a transition to the metallic phase declines as a function of \( \text{Mn} \) concentration \((x)\) according to the formula \( P_t(x) = 15.7 - 25.4x + 19.0x^2 \) (GPa). Pressure-dependent longitudinal and transverse optical phonon frequencies and the calculated mode Grüneisen parameters were adopted to investigate the influence of \( \text{Mn}^{2+} \) ions on the iconicity. The experimental results indicate that the manganese ions tend to increase the iconicity of \( \text{ZnTe} \) under ambient conditions, whereas an external hydrostatic pressure tends to reduce the iconicity and the bond length of \( \text{Zn}_{1-x}\text{Mn}_x\text{Te} \). © 2008 American Institute of Physics. [DOI: 10.1063/1.2949707]

I. INTRODUCTION

Dilute magnetic semiconductor (DMS) \( \text{Zn}_{1-x}\text{Mn}_x\text{Te} \), in which a fraction of \( \text{Zn} \) element is replaced by \( \text{Mn} \) atoms, crystallizes in the zincblende (ZB) structure for \( x \leq 0.8 \) under ambient conditions.\(^1\) The magnetic properties of \( \text{Zn}_{1-x}\text{Mn}_x\text{Te} \)-related materials are currently a focus of research activities in numerous interesting investigations.\(^2\)\(^-\)\(^6\) Magnetic ordering in semiconductors can arise from the superexchange interaction or free-carrier-mediated exchange interaction between magnetic ions. Long-range ferromagnetic orderings, mediated by holes, were observed in \( \text{Ga}_{1-x}\text{Mn}_x\text{As} \) (Ref. 7) and \( \text{In}_{1-x}\text{Mn}_x\text{As} \),\(^8\) in which manganese ions act as acceptors. Alternatively, \( p \)-doped \( \text{Zn}_{1-x}\text{Mn}_x\text{Te} \), in which magnetic ions are not dopants, exhibits ferromagnetism that is induced by the exchange interaction of free holes with the localized spins of \( \text{Mn}^{2+} \) ions.\(^3\)\(^-\)\(^6\) Moreover, our recent high pressure study of \( n \)-doped \( \text{ZnSe}:\text{Cl} \) demonstrated that the hydrostatic pressure tends to reduce the carrier concentration, and that doping influences the metallic phase transition.\(^9\) Therefore, the effect of applied pressure on the physical properties of DMS \( \text{Zn}_{1-x}\text{Mn}_x\text{Te} \) will be of interest in future studies of the pressure-dependent magnetic properties of this material.

Pressure-induced phase transitions of \( \text{ZnTe} \) bulk crystal have been widely studied.\(^10\)\(^-\)\(^13\) So far, all of the evidence has shown that the application of pressure to a semiconducting \( \text{ZnTe} \) exhibits a unique transition sequence. As the pressure is increased, the semiconducting ZB \( \text{ZnTe} \) phase (\( \text{ZnTe} \) I) first transforms to the other semiconducting cinnabar phase (\( \text{ZnTe} \) II), and then undergoes a transition to a metallic orthorhombic (\( Cmcm \)) phase (\( \text{ZnTe} \) III). These high-pressure phase behaviors differ from those of most II-VI semiconductors,\(^14\)\(^-\)\(^16\) which transform from ZB (or wurtzite) first to the cinnabar structure and then to the rock-salt (\( \text{NaCl} \)) structure as external pressure is applied. Even though the \( \text{NaCl} \) phase is unstable and has not been observed in \( \text{ZnTe} \) at room temperature under any pressure, it has been revealed to be stable only at high temperature.\(^17\) This result is attributed to the fact that \( \text{ZnTe} \) is the lowest ionic semiconductor in the II-VI family.\(^18\) The transition pressure from nonmetallic \( \text{ZnTe} \) to metallic \( \text{ZnTe} \) III (\( Cmcm \) phase) is controversial. Optical-absorption measurements yield a transition pressure of 11.9 GPa.\(^10\) The electrical resistance approach yields a transformation of 13–15 GPa.\(^11\) The metallic phase of \( \text{ZnTe} \) as revealed by Raman scattering, forms at above 14.2 GPa.\(^1\) Moreover, the crystalline structure of the \( \text{ZnTe} \) phase III is determined to be 16 GPa using angle-dispersive powder-diffraction techniques with synchrotron radiation.\(^15\) To resolve these unusual and controversial phase transitions at high pressure, \( \text{ZnTe} \) scattering under high pressure was performed to investigate \( \text{ZnTe} \) and \( \text{Zn}_{1-x}\text{Mn}_x\text{Te} \) thin films up to 17.0 GPa. Furthermore, resonant Raman scattering (RRS) was adopted to enhance the Raman signal to identify more clearly the semiconductor-to-metal phase transition pressure. The crystalline stability, iconicity, and Grüneisen parameters \((\gamma)\) of \( \text{Zn}_{1-x}\text{Mn}_x\text{Te} \) \((0 \leq x \leq 0.26)\) thin films were also studied.

II. EXPERIMENT

\( \text{Zn}_{1-x}\text{Mn}_x\text{Te} \) samples with various \( \text{Mn} \) contents \((0 \leq x \leq 0.26)\) were deposited at 300 °C by molecular beam epitaxy on \((001)\) oriented semi-insulating \( \text{GaAs} \) substrates. The samples’ thicknesses were fixed at about 0.7 \( \mu \text{m} \), and the \( \text{Mn} \) composition was determined by energy-dispersive x-ray analysis. Raman spectra under ambient pressure were all recorded at 300 K and excited using the 514.5 nm line of an \( \text{Ar}^+ \) laser, while the 488.0 nm line from the \( \text{Ar}^+ \) laser was used in high-pressure experiments. High-pressure Raman measurements were all made at room temperature using a
ruby-calibrated diamond anvil cell (DAC). A liquid methanol-ethanol 4:1 mixture was utilized as the pressure-transmitting medium, and the pressure gradient was less than 0.2 GPa throughout the sample chamber. Before loading the Zn$_{1-x}$Mn$_x$Te crystal into the DAC, the GaAs substrate was removed by mechanical polishing and chemical etching. Spectra were all obtained in backscattering configuration and analyzed by a SPEX 1404 double grating spectrometer equipped with a multichannel LN$_2$-cooled charge coupled device. The high-pressure experiments are reproducible for each specimen. The photoluminescence device. The high-pressure experiments are reproducible for each specimen. The photoluminescence (PL) energies were obtained at 300 K, using the 488.0 nm line of an Ar$^+$ laser.

III. RESULTS AND DISCUSSION

Figure 1 presents the zone-center Raman spectra of Zn$_{1-x}$Mn$_x$Te ($x=0.00$, 0.09, 0.14, 0.22, and 0.26), measured at room temperature and ambient pressure under $z(x+y,x+y)$ backscattering geometry. In this configuration, transverse optical (TO) phonons are forbidden and longitudinal optical (LO) phonons are allowed. As the Mn content increases, the 1LO and its overtone (2LO) phonon frequencies increase. Figure 2 plots the dependence of the 1LO phonon frequency and the PL energy on the Mn concentration ($x$). The increase in the LO phonon frequency with Mn content is due to the difference between atomic masses, $m_{35b}(55)<m_{Zn}(65)$. As the Mn concentration increases, the PL energy is blueshifted and slowly approaches the incident laser energy. When the energy of the electronic transition energy is sufficiently close to the incident laser energy, the RRS effect occurs, enhancing the intensity of LO phonons. Based on the RRS condition,

$$h\nu_{laser} - mh\nu_{LO}(x,p) \approx E_{exc}(x,p),$$

where $h\nu_{laser}$ is the photon energy of the incident laser, $E_{exc}(x,p)$ and $h\nu_{LO}(x,p)$ are the electronic transition energy and the LO phonon energy, respectively, as functions of Mn content ($x$) and applied pressure ($p$). The $m$ denotes the overtone order of LO phonons. Under ambient conditions, when the laser is fixed at 2.41 eV, the Raman scattering of the larger overtone phonon comes into resonance first (Fig. 1). As shown in Fig. 1, besides the LO mode, an impurity ($I$) mode and its overtone ($2I$) at the lower-frequency side of the LO phonon in Zn$_{1-x}$Mn$_x$Te ($x>0$) are also visible. As the Mn content increases, the impurity ($I$ and $2I$) modes shift to lower frequencies and become intense. Similar phenomena are also found in Zn$_{1-x}$Mn$_x$Se (Ref. 15) and Zn$_{1-x}$Cd$_x$Se (Ref. 16) II-VI ternary compounds. Since the impurity mode discussed herein lies between the LO and TO modes and can also be apparently observed at high pressures, it can be identified as the impurity mode of Mn in ZnTe. Accordingly, the zone-center optical phonon mode of Zn$_{1-x}$Mn$_x$Te can be concluded to exhibit mixed mode behavior. This finding is consistent with an earlier work.  

Figure 3 shows the up-stroke pressure-dependent Raman spectra of the ZnTe thin film at up to 17.0 GPa. The TO mode, which is not allowed under ambient conditions before pressurization, appears at high pressures. The emergence of the TO mode can be attributed to the pressure-induced RRS enhancement and the deviation of the sample chip from the perfect backscattering geometry in the DAC. The LO and TO phonons both shift to higher frequencies with increasing pressure, wherein the shift is accompanied by clear changes in their intensities. The reduction in the lattice constant and the crystal volume under external pressure increases the LO and TO phonon frequencies. The pressure-driven RRS effect, according to Eq. (1), causes the intensity of the LO phonon to increase abruptly at first and then to decline smoothly. As the pressure increases, the LO phonon disappears and the sample becomes opaque at 15.7 ± 0.2 GPa, indicating a semiconductor-to-metal phase transition.  

This phenomenon is distinct from that revealed by the Raman results of...
Camacho et al., in which the LO phonon was invisible above 9.6 GPa—far below the critical pressure obtained under the RRS condition discussed herein. The metallic phase transition pressure of ZnTe, measured by the RRS experiment, is consistent with the experimental results of Nelmes et al. who determined, using angle-dispersive diffraction techniques with synchrotron radiation source, which crystal structure changed to the ZnTe phase III at 16 GPa. Recently, Shchennikov et al. revealed that the sharp drop in resistance from 10^6 to 10^1 Ω in ZnTe at about 13.0–15.0 GPa is related to the transformation into the orthorhombic Cmcm phase. The difference between the phase transition pressures obtained by x-ray and electrical resistance methods is attributable to the fact that x-ray techniques determine the phase transition pressure closer to the completion of the transformation, whereas the electrical resistance measurements reveal the beginning of the transition. In Fig. 3, the TO mode does not disappear until at about 17.0 GPa. Other II-VI compounds exhibited a similar phenomenon because transverse surface lattice vibration is allowed in both semiconductor and metal, even though the skin depth (or penetration depth) of the metal for a laser is only several tens of angstroms. In the down-stroke high-pressure process, only hysteresis is observed and no additional phonon appears.

Figure 4 displays the up-stroke pressure-dependent Raman spectra of Zn_{0.91}Mn_{0.09}Te. In addition to the LO and TO modes, a Mn-related impurity mode (I) and a double structure associated to LO+TA (transverse acoustic) phonon appear between the LO and TO phonons and at the higher-frequency side of the LO phonon, respectively. As the pressure increases, the impurity mode, the LO phonon, and the TO phonon shift to high frequencies which can be fitted by a quadratic polynomial, as listed in Table I. Since Zn is partially replaced by Mn, the intensity of the Raman spectra is lower than that of ZnTe because the 3d orbital of Mn^{2+} ions hybridizes into tetrahedral bonds, causing distortions and altering the overall ZnMnTe crystal symmetry. Furthermore, the LO phonon becomes opaque and disappears at 13.6 ± 0.2 GPa. When the pressure is 15.7 GPa, the TO and I modes become invisible. As the Mn content is increased from 0 to 0.09, the semiconductor-to-metal phase transition pressure falls from 15.7 to 13.6 GPa.

Figure 5 plots the phase transition pressure as a function of the Mn content. A decline in the semiconductor-to-metal phase transition pressure (Pr) versus x is shown and is fitted using a quadratic curve, given by \( P_{\text{t}}(x) = 15.7 - 25.4x + 19.0x^2 \) (GPa). As the Mn content increases from 0 to 0.26, the phase transition pressure falls from 15.7 to 10.3 GPa (Table I), indicating that the substituted Mn^{2+} ions tend to reduce the stability of the crystal. The Mn^{2+} ions in Zn_{1-x}Mn_xTe may alter the overall symmetry and soften the lattice by generating large distortions. As the substituted element content increases, the structure becomes less stable. This dependence is similar to other DMS II-VI ternary compounds. Yang et al. found that for Zn_{1-x}Mn_xSe compounds, as x is increased from 0.07 to 0.24, the pressure of the metallic phase transition falls from 11.8 to 9.9 GPa. For the Zn_{1-x}Fe_xSe semiconductor, the existence of Fe ions (x = 0.16) in the ZnSe reduces the semiconductor-metal phase transition pressure from 14.4 to 10.9 GPa. Table I summarizes the pressure-dependent LO, TO, and I phonon frequencies derived from quadratic polynomial fits to our measurements. Moreover, the pressure dependence of a mode frequency \( \omega_i \) can be defined using the dimensionless Grüneisen parameters \( \gamma_i \).

\[
\gamma_i = -\left( \frac{d \ln \omega_i}{d \ln V} \right) = \frac{1}{\beta} \frac{\partial \ln \omega_i}{\partial p} = \left( K_0 \right) \left( \frac{d \omega_i}{d \rho} \right),
\]

where \( K_0 \) is the bulk modulus, defined as the reciprocal of the isothermal volume compressibility (\( \beta \)), and \( V \) is the molar volume in cm\(^3\)/mol. Since the bulk modulus (\( K_0 \)) of
Zn$_{1-x}$Mn$_x$Te is unavailable, $K_{\text{ZnTe}}=50.5$ GPa is used. As shown in Table I, several conclusions can be drawn. At ambient pressure ($p \sim 0$), (i) the LO phonon frequency increases and the TO phonon frequency decreases as the Mn content increases: the LO-TO splitting increases with Mn content; (ii) $\gamma_{\text{LO}}<\gamma_{\text{TO}}$ is observed throughout all the specimens, and the ratio $\gamma_{\text{TO}}/\gamma_{\text{LO}}$ rises from 1.38 to 1.77 as the Mn concentration increases from 0 to 0.26. At high pressure, (iii) $d\omega_{\text{TO}}/dp<d\omega_{\text{LO}}/dp$, such that the LO-TO splitting falls under external pressure for all samples herein; and (iv) $d\omega_{\text{TO}}/dp$ and $\gamma$ follow no consistent trend over the entire Mn range of interest $(0.09 \leq x \leq 0.26)$. These results demonstrate that under ambient conditions, the manganese ions slightly increase the iconicity of ZnTe. Nevertheless, an externally applied pressure reduces the iconicity and bond length of Zn$_{1-x}$Mn$_x$Te crystals.

**IV. CONCLUSIONS**

RRS can enhance the LO and TO phonon intensities in studying pressure-dependent vibrational spectra of Zn$_{1-x}$Mn$_x$Te thin films. Intermediate optical phonon mode behavior was identified. The disappearance of the LO phonon, which accompanies a semiconductor-to-metal phase transition in ZnTe, occurs at about $15.7 \pm 0.2$ GPa. As the Mn content increases from 0 to 0.26, the metallic phase transition pressure falls from 15.7 to 10.3 GPa. Based on the pressure-dependent LO and TO phonon frequencies and Grüneisen parameters ($\gamma$), externally applying pressure reduces the iconicity of Zn$_{1-x}$Mn$_x$Te compound semiconductors.

**ACKNOWLEDGMENTS**

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<table>
<thead>
<tr>
<th>Mn content (x)</th>
<th>Mode</th>
<th>$\omega_1$ (cm$^{-1}$)</th>
<th>$d\omega_1/ dp$ (cm$^{-1}$/GPa)</th>
<th>Grüneisen parameter ($\gamma_1$)</th>
<th>Phase transition pressure (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>LO</td>
<td>203.6+3.42$p-0.10p^2$</td>
<td>3.42–0.20$p$</td>
<td>0.85</td>
<td>15.7±0.2</td>
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<tr>
<td></td>
<td>TO</td>
<td>179.2+4.16$p-0.11p^2$</td>
<td>4.16–0.22$p$</td>
<td>1.17</td>
<td></td>
</tr>
<tr>
<td>0.09</td>
<td>LO</td>
<td>206.3+3.34$p-0.11p^2$</td>
<td>3.34–0.22$p$</td>
<td>0.82</td>
<td>13.6±0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.14</td>
<td>LO</td>
<td>207.4+3.29$p-0.10p^2$</td>
<td>3.29–0.20$p$</td>
<td>0.80</td>
<td>12.4±0.2</td>
</tr>
<tr>
<td></td>
<td>TO</td>
<td>176.1+4.30$p-0.06p^2$</td>
<td>4.30–0.12$p$</td>
<td>1.24</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$i$</td>
<td>193.4+3.15$p-0.08p^2$</td>
<td>3.15–0.16$p$</td>
<td>0.82</td>
<td></td>
</tr>
<tr>
<td>0.22</td>
<td>LO</td>
<td>208.7+3.15$p-0.03p^2$</td>
<td>3.15–0.06$p$</td>
<td>0.76</td>
<td>11.2±0.2</td>
</tr>
<tr>
<td></td>
<td>TO</td>
<td>175.5+4.43$p-0.14p^2$</td>
<td>4.43–0.28$p$</td>
<td>1.27</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$i$</td>
<td>189.7+3.02$p-0.05p^2$</td>
<td>3.02–0.10$p$</td>
<td>0.80</td>
<td></td>
</tr>
<tr>
<td>0.26</td>
<td>LO</td>
<td>209.7+3.06$p-0.08p^2$</td>
<td>3.06–0.16$p$</td>
<td>0.74</td>
<td>10.3±0.2</td>
</tr>
<tr>
<td></td>
<td>TO</td>
<td>174.8+4.55$p-0.07p^2$</td>
<td>4.55–0.14$p$</td>
<td>1.31</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$i$</td>
<td>187.4+3.18$p-0.08p^2$</td>
<td>3.18–0.16$p$</td>
<td>0.85</td>
<td></td>
</tr>
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</table>

FIG. 5. Mn concentration (x)-dependent semiconductor-to-metal phase transition pressure of Zn$_{1-x}$Mn$_x$Te. The solid curve is a quadratic polynomial fit, given by $P(x)=15.7-25.4x+19.0x^2$ (GPa).

(2007).


