

## Raman spectroscopy study of ZnSe and $\text{Zn}_{0.84}\text{Fe}_{0.16}\text{Se}$ at high pressures

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The ZnSe powder and  $\text{Zn}_{0.84}\text{Fe}_{0.16}\text{Se}$  crystal were studied by Raman scattering spectroscopy at pressures up to 36.0 and 32.0 GPa, respectively. For ZnSe powder at 4.7 and 9.1 GPa, two phase transitions were observed. However, the resulted phases have not been identified yet. As the pressure was increased to 14.4 GPa, the LO phonon peak disappeared while the TO phonon peak was still visible until the metallization pressure, 17.0 GPa was reached. In addition, three unidentified Raman peaks were still observable above the metallization pressure. For  $\text{Zn}_{0.84}\text{Fe}_{0.16}\text{Se}$  crystal, the structure transition from possible zinc blende to sodium chloride phase ( $B_1$ ) was identified by the disappearance of Fe local mode and longitudinal optical (LO) phonon mode at 10.9 GPa. In addition, an unidentified phase transition at 4.7 GPa was observed. The TO phonon and the split TO phonons were still observable at a pressure above the phase transition pressure up to 32.0 GPa. The existence of Fe impurity in the ZnSe up to a concentration of 0.16 reduced the semiconductor-metal phase transition pressure to 10.9 GPa. According to the calculation of Grüneisen parameters,  $\text{Zn}_{0.84}\text{Fe}_{0.16}\text{Se}$  was found to have a higher ionicity than ZnSe. Reasons for the observation of Raman peaks at a pressure above the metallization pressure are still unknown. [S0163-1829(97)03420-6]

### I. INTRODUCTION

The physical properties of semiconductors at high pressure have attracted much attention.<sup>1-3</sup> Among the numerous semiconductors that have been studied, ZnSe is one of the most important due to its application in the fabrication of blue lasers.<sup>4</sup> In past decades several kinds of high-pressure studies on ZnSe have been performed. Ves *et al.* investigated the band shift of ZnSe as a function of pressure by transmission experiments.<sup>5</sup> The x-ray diffraction experiments were carried out to observe the structure transformations.<sup>3,6</sup> Recently, the luminescence of the deep impurities was measured for the study of pressure effect on the impurity level relative to the valence band edge.<sup>7</sup> The high-pressure experiment for the resistance measurement revealed that ZnSe has undergone a metallization process at a pressure higher than 13.5 GPa.<sup>8,9</sup> Among the works mentioned above, the most popular technique used in the high-pressure study was the Raman scattering.<sup>6</sup>

In addition to the experimental investigations, theoretical studies were also performed by use of the self-consistent pseudopotential approach,<sup>10</sup> the full potential linearly augmented plane wave approach, and numerical atomic orbital band structure calculations within the local-density approximation.<sup>11</sup> Although various experimental and theoretical techniques were employed in the study of ZnSe at high pressure, some of the physical properties of ZnSe at high pressure are still unknown. Moreover, a discrepancy existed among the results obtained by various theoretical works. For example, Smelyansky and co-workers<sup>11</sup> suggested that the metallization occurred when ZnSe transformed from a four-

coordinated zinc-blende (ZB) phase into a six-coordinated rock-salt (RS) phase. However, Andreoni and Maschke<sup>10</sup> indicated that the metallization was due to the band closure.

$\text{Zn}_{1-x}\text{Fe}_x\text{Se}$ , the crystallizes in the zinc-blende structure which is similar to ZnSe for  $0 \leq x \leq 0.22$ ,<sup>12</sup> is a member of the diluted magnetic semiconductor family.<sup>13</sup> Interesting magnetic as well as the magneto-optical properties were investigated on both  $\text{Zn}_{1-x}\text{Fe}_x\text{Se}$  bulk crystals and thin films.<sup>14-16</sup> Recently, the spin superlattice behavior<sup>17</sup> and the spin relaxation process<sup>18</sup> of  $\text{Zn}_{1-x}\text{Fe}_x\text{Se}$  based quantum well structures were observed. Furthermore, the pressure induced phase transition of the  $\text{Zn}_{1-x}\text{Fe}_x\text{Se}$  crystal was also discussed by Qudri *et al.*<sup>19</sup> using the energy-dispersive x-ray-diffraction (EDXD) measurement. It was found that the existence of Fe in the crystal results in a reduction in the transition pressure, and such a reduction was believed to be due to the hybridization of  $3d$  orbitals into the tetrahedral bonds.<sup>20</sup>

Recently, the Raman scattering experiment has also been applied to study the pressure effect on  $\text{Zn}_{1-x}\text{Fe}_x\text{Se}$ ,  $\text{Zn}_{1-x}\text{Co}_x\text{Se}$ ,<sup>21</sup> and  $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$  (Refs. 22 and 23) crystals, and two new phases were found at 4.0 GPa and 8.0 GPa in  $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ . However, the cause of the pressure induced phase transitions was not identified. Moreover, the highest pressure used for the Raman study was below 13.0 GPa. Note that zinc blende to sodium chloride ( $B_1$ ) (semiconductor-metal) transition occurs at 13.5 GPa from the resistivity measurement on ZnSe.<sup>8,9</sup> Therefore, the Raman scattering study on  $\text{Zn}_{1-x}\text{Fe}_x\text{Se}$  crystals above the semiconductor-metal transition pressure would be interesting.

In this paper, the Raman scattering was used to investigate the pressure effect on the phase transition of ZnSe powder and  $\text{Zn}_{0.84}\text{Fe}_{0.16}\text{Se}$  crystals at high pressure up to around 36.0 and 32.0 GPa, respectively. We found that ZnSe manifested four phase regions including two unidentified transitions occurred at 4.7 and 9.1 GPa. In addition, three split transverse optical (TO) phonon modes were observed at a pressure higher than the metallization pressure (14.4 GPa) up to 36.0 GPa. As at 4.7 GPa, one unidentified phase transition of  $\text{Zn}_{0.84}\text{Fe}_{0.16}\text{Se}$  was observed, too. In addition, the effect of the Fe element on the phase transition will also be discussed.

## II. EXPERIMENTS

The high pressure, up to 36.0 GPa, was generated in a diamond anvil cell with the culet size of 600  $\mu\text{m}$ .  $\text{Zn}_{0.84}\text{Fe}_{0.16}\text{Se}$  crystal grown by the modified Bridgman method was ground into tiny crystals with the size in the range of 100  $\mu\text{m}$ . The ZnSe powder or tiny  $\text{Zn}_{0.84}\text{Fe}_{0.16}\text{Se}$  crystals and ruby chips (about 1  $\mu\text{m}$  in size) were sealed with the pressure transmitting medium (deionized water) in the sample chamber which was a hole of 130  $\mu\text{m}$  diameter and 50  $\mu\text{m}$  thick drilled on the stainless steel 304 gasket which has an original thickness of 250  $\mu\text{m}$ . The pressure was calibrated by the fluorescence scale method.<sup>24,25</sup> For Raman scattering experiments, a Renishaw 2000 micro-Raman system was used. The 514.5 nm line with a power of 1.5 W from the Coherent INNOVA 5.0 W argon ion laser was focused to about 5  $\mu\text{m}$  on the sample surface. Traditionally, water is considered as a bad pressure medium because it transfers to solid ice VI and VII at 0.6 and 2.1 GPa, respectively. However, previous study has shown that the  $R_1$ - $R_2$  splitting in the ruby fluorescence was maintained well up to 16.7 GPa,<sup>26</sup> therefore, the nonhydrostatic components are not a serious problem below 16.7 GPa. In the present study, such a splitting was well recorded up to 36 GPa as shown in Fig. 1. Hence, water (deionized  $\text{H}_2\text{O}$ ) seems to be a suitable pressure medium in the high pressure study. To verify such a result, we have investigated Raman experiments in both a water and an alcohol solution (4:1 methanol/ethanol solution). We observed that there was no difference in the phase transition pressures, and pressure dependences of Raman shifts in both media were the same. However, in the low Raman frequency range (lower than 500  $\text{cm}^{-1}$ ), a much higher background was found in the alcohol solution experiments, therefore, much longer accumulating time was needed in the case as the alcohol solution was used as the pressure medium. This was the reason that we chose water (deionized  $\text{H}_2\text{O}$ ) as the pressure medium in our normal experimental runs. The Jandel Scientific Peakfit computer program was used in a deconvolution process and determination of the peak position, intensity, and the full width at the half maximum of Raman spectra.

## III. RESULTS AND DISCUSSION

Raman spectra for ZnSe at room temperature and at various pressures are shown in Fig. 2. At ambient conditions, the longitudinal optical (LO) and TO phonons were observed at 250 and 205  $\text{cm}^{-1}$ , respectively, as reported in the previous work.<sup>1</sup> At 4.7 GPa, the TO phonon splits into two peaks

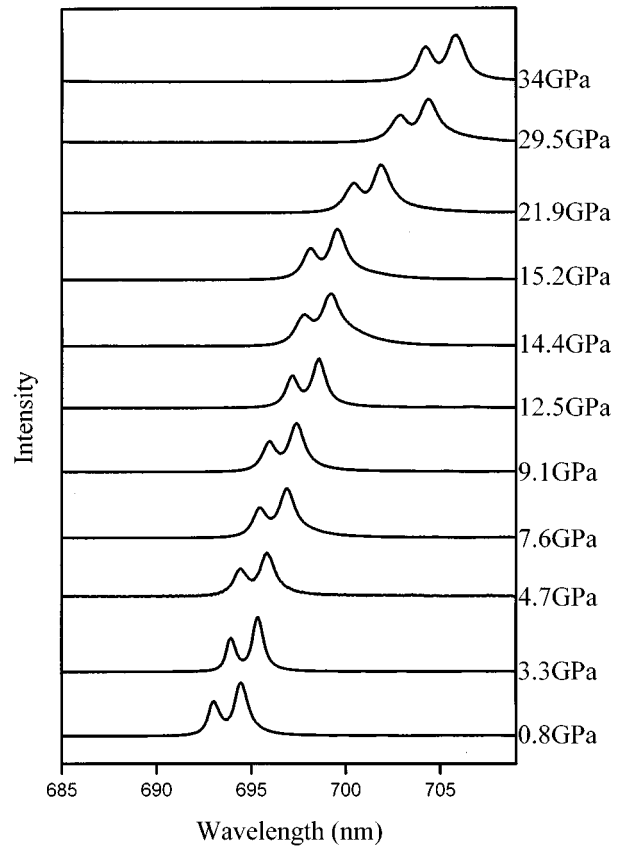


FIG. 1. The ruby fluorescence patterns vs pressure in a pressure medium of deionized water. The left-hand and right-hand side peaks of the plots present  $R_2$  and  $R_1$  peaks of the ruby fluorescence, respectively.

which have different pressure dependences from each other. A mode softening is found for the peak with a lower frequency component. Whereas, the Raman shift of the higher frequency one increases with pressure, and it splits into two components again at around 9.1 GPa. However, for the LO phonon mode, no mode splitting can be found. The Raman shift of the LO phonon increased monotonously with pressure. At pressures higher than 14.4 GPa, the LO phonon became invisible. The disappearance of the LO phonon was attributed to the semiconductor-metal phase transition.<sup>9</sup> On the contrary, all of the TO and TO split phonon modes are still visible above the metallization pressure as shown in Fig. 3. The phase transitions that occurred at 4.7 GPa and 9.1 GPa were ignored in the previous studies of high-pressure phase transition in pure ZnSe, although these two phase transitions were reported in the high-pressure Raman study of the  $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ .<sup>22</sup> In the case of  $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ , one more mode, the Mn impurity mode, was observed. Arora *et al.*<sup>23</sup> reported that the splitting of the impurity mode at 4.0 GPa was caused by the lowering of the crystal symmetry. Later, Arora, and Sakuntala<sup>22</sup> found one more phase transition at 8.0 GPa. At 8.0 GPa, the sample becomes opaque. This transition was considered as a transformation from the direct to indirect band gap. Furthermore, the Raman signal disappeared above 13.5 GPa (our work is 14.4 GPa) because the sample became metallic.

Phase transitions at 4.7 and 9.1 GPa in pure ZnSe observed by Arora and Sakuntala<sup>22</sup> were labeled by using the

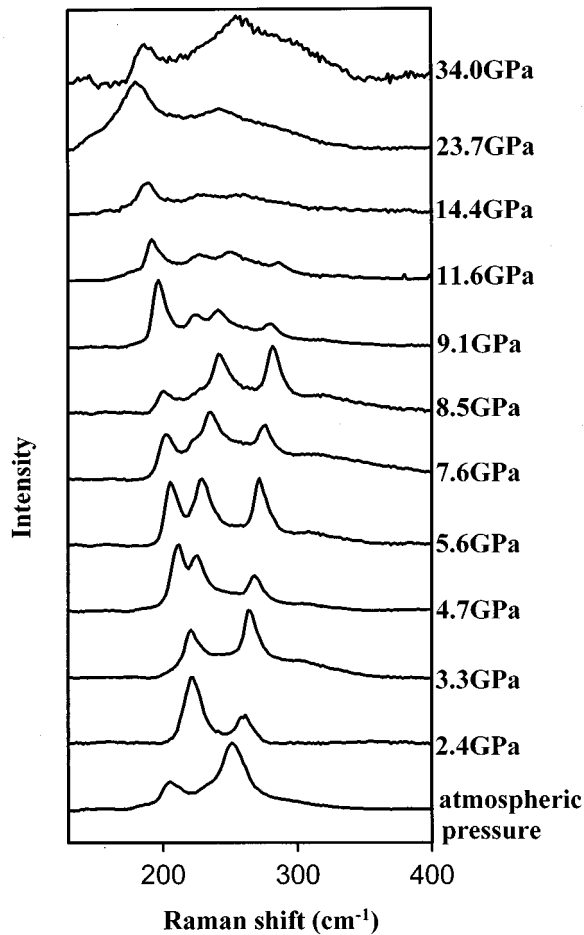


FIG. 2. Pressure dependence of phonon frequencies of ZnSe. Note the lowest frequency component was softened at the high pressure and was continuous to 36 GPa.

splitting of the ZnSe TO phonon instead of the splitting of the Mn impurity mode. A theoretical calculation has been performed by Smelyansky and Tse<sup>11</sup> to study the phase transformations of ZnSe. However, only the phase transition that occurred at 14.4 GPa was considered. The phase transition at 14.4 GPa was attributed to the ZB to RS structure transformation. No calculation was reported for the phase transition at 4.7 and 9.1 GPa. Similar to ZnSe, the semiconductor ZnTe has a ZB crystal structure, but more details were discussed for the calculation of the structure transformations. Recently, Lee and Ihm<sup>27</sup> indicated that ZnTe underwent the structure transformation from the ZB to cinnabar and the orthorhombic (*Cmcm*) to RS phase<sup>3</sup> by use of the *ab initio* pseudopotential calculations within the local-density approximation. Therefore, we suspected that ZnSe might also undergo a similar structure transformation from the ZB through cinnabar and the orthorhombic to the RS structure at 4.7, 9.1, and 14.4 GPa, respectively. As a result, a more detailed theoretical study for the ZnSe structure transformation as well as an x-ray diffraction experiment with higher-pressure resolution at the pressure range around 4.7 to 9.1 GPa should be very useful to clarify our suspicion. Note that in the recent x-ray work of Greene *et al.*,<sup>6</sup> anomaly was also found at a pressure of around 5.0 GPa.

Raman spectra from  $\text{Zn}_{0.84}\text{Fe}_{0.16}\text{Se}$  crystal at various pressures are shown in Fig. 4. At the atmospheric pressure, two

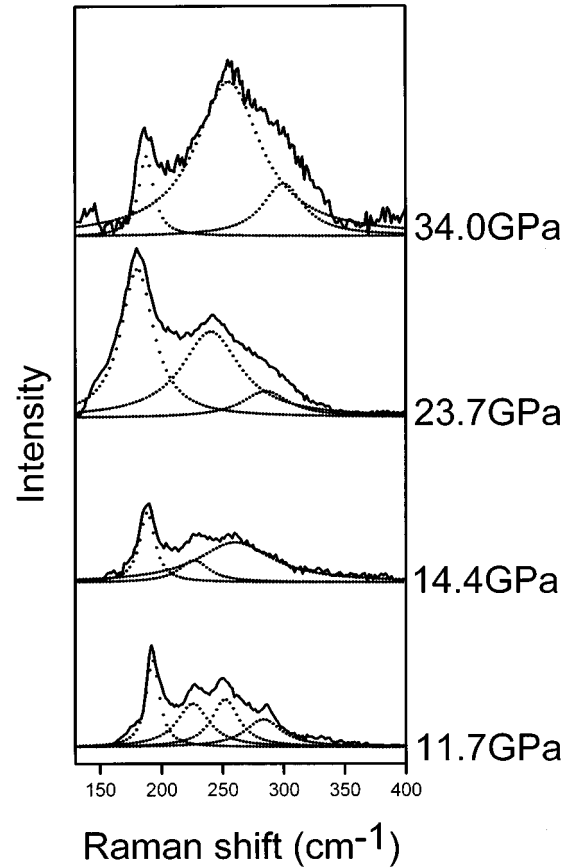


FIG. 3. High pressure, above 14.4 GPa, dependence of phonon frequencies of ZnSe. Note all TO phonon modes were still visible above the metallization pressure, 14.4 GPa.

peaks identified as the LO and TO phonons were observed at 253 and 215  $\text{cm}^{-1}$ , respectively, as reported previously.<sup>28</sup> Between these two peaks, a weak structure can be labeled through the deconvolution process. The weak structure was attributed to the Fe local (impurity) phonon mode. The Fe local phonon arose from the introduction of the local electric field resulting from the substituting Zn atom by the Fe atom.<sup>28</sup> At 2.6 GPa, the Fe local mode became more intense at a higher pressure and the Raman shift increased with the pressure. The pressure effects on the LO and TO phonons exhibited a blueshift behavior that was similar to the Fe local phonon. As the pressure was increased to 4.7 GPa, two new modes appeared at 219.6 and 205.5  $\text{cm}^{-1}$ , respectively. The phonon energy of the 205.5  $\text{cm}^{-1}$  mode (labeled as TO split mode I) exhibited a redshift and the other 219.6  $\text{cm}^{-1}$  mode (labeled as TO split mode II), as the LO and Fe local mode, exhibited a blueshift as the pressure was increased up to around 32.0 GPa. Although there are no structure transitions identified by Qadri *et al.*<sup>19</sup> at the pressure lower than 10.0 GPa from their EDXD work, however, if one refers to the study of the similar cubic structure of CdTe,<sup>29</sup> before the structure transforms from the four coordinated ZB structure to the six coordinated NaCl structure, one more phase (cinnabar structure) was found. In fact, the CdTe transforms from the ZB to cinnabar, the cinnabar to NaCl, and the NaCl to orthorhombic (*Cmcm*) as the pressure is raised to 10.0 GPa. We therefore attribute the appearance of the new phonon mode to the broken symmetry of the structure transfor-

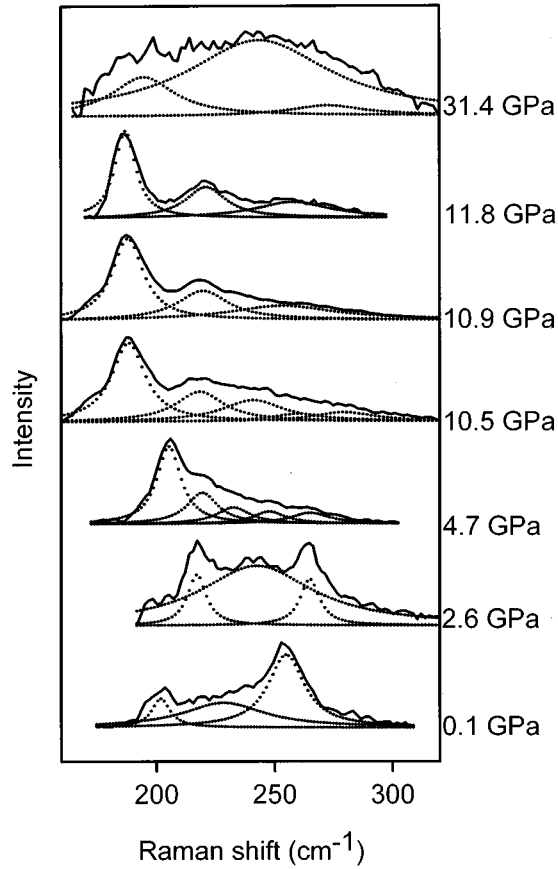


FIG. 4. Pressure dependence of phonon frequencies of  $\text{Zn}_{0.84}\text{Fe}_{0.16}\text{Se}$ . Note the lowest frequency component is softened at the high pressure and was continuous to 32 GPa.

mation. The splitting of the TO phonon at 4.7 GPa could be also due to the structure transition. However, so far, structure transitions that occurred at 4.7 GPa are not confirmed by the x-ray-diffraction work. As the pressure was increased further to 10.9 GPa, the semiconductor-metal transition pressure of  $\text{Zn}_{0.84}\text{Fe}_{0.16}\text{Se}$ , both the LO and the Fe local modes disappeared.

The variation of the mode energies as a function of the pressure can be shown in Fig. 4. The open symbols correspond to the LO, TO, and TO split Raman modes of ZnSe, respectively. Simultaneously, the solid symbols correspond to the LO, Fe local, TO, and TO split Raman modes of

$\text{Zn}_{0.84}\text{Fe}_{0.16}\text{Se}$ , respectively. The relationships of the mode frequencies versus the pressure of ZnSe can be obtained by the quadratic polynomial fitting by the following formulas:

$$\omega_{\text{LO mode}} = 251.9 + 3.44p - 0.02p^2, \quad (1)$$

$$\omega_{\text{TO mode}} = 204.2 + 4.98p - 0.07p^2, \quad (2)$$

$$\omega_{\text{TO split mode(I)}} = 207.2 + 2.01p - 0.02p^2, \quad (3)$$

$$\omega_{\text{TO split mode(II)}} = 222.9 - 3.12p + 0.06p^2, \quad (4)$$

and were plotted as the dashed curves as shown in Fig. 4.

Similarly, the solid lines are the fitting results by the following formulas for  $\text{Zn}_{0.84}\text{Fe}_{0.16}\text{Se}$ :

$$\omega_{\text{LO mode}} = 254.353 + 3.370p - 0.133p^2, \quad (5)$$

$$\omega_{\text{Fe local mode}} = 228.293 + 6.138p - 0.313p^2, \quad (6)$$

$$\omega_{\text{TO mode}} = 202.644 + 5.603p - 0.111p^2, \quad (7)$$

$$\omega_{\text{TO split mode(I)}} = 216.532 + 0.149p + 0.021p^2, \quad (8)$$

$$\omega_{\text{TO split mode(II)}} = 215.948 - 3.565p + 0.099p^2, \quad (9)$$

where  $\omega_i$  was the wave number in  $\text{cm}^{-1}$  and  $p$  was the pressure in GPa. The Grüneisen parameter ( $\gamma_i$ ) for a quasi-harmonic mode  $i$  of frequency  $\omega_i$  was defined by<sup>30</sup>

$$\gamma_i = - (d \ln \omega_i / d \ln V) = \frac{1}{\beta} \frac{\partial \ln \omega_i}{\partial p} = (K_0 / \omega_i) (d \omega_i / d p), \quad (10)$$

where  $K_0$  (Ref. 5) is the bulk modulus for ZnSe, and was taken as 62.4 GPa. The same  $K_0$  value was used in the  $\text{Zn}_{0.84}\text{Fe}_{0.16}\text{Se}$  system. The  $\beta$  parameter is the isothermal volume compressibility, and  $V$  is the molar volume in  $\text{cm}^3/\text{mol}$ . The effects of the pressure on various Raman vibrational modes of ZnSe and  $\text{Zn}_{0.84}\text{Fe}_{0.16}\text{Se}$  at room temperature (298 K) were listed in Tables I and II, respectively. As a comparison with previous works,<sup>1</sup> some conclusions can be obtained: (i) the  $\gamma_{\text{LO}}$  values of ZnSe and  $\text{Zn}_{0.84}\text{Fe}_{0.16}\text{Se}$  are 0.85 and 0.827, respectively. They are very close to one; (ii)  $\gamma_{\text{TO}} > \gamma_{\text{LO}}$  for both systems (for ZnSe is  $1.52 > 0.85$  and for  $\text{Zn}_{0.84}\text{Fe}_{0.16}\text{Se}$  is  $1.725 > 0.827$ ); (iii) the ratios  $\gamma_{\text{TO}}/\gamma_{\text{LO}}$  for ZnSe and  $\text{Zn}_{0.84}\text{Fe}_{0.16}\text{Se}$  are 1.788 and 2.086, respectively.

TABLE I. Effect of pressure on various Raman vibrational modes of ZnSe at room temperature (298 K). The values of mode frequencies  $\omega_i$ , pressure dependence  $d\omega_i/dp$ , mode Grüneisen parameter  $\gamma_i$ , and  $d\gamma_i/dp$  were extrapolated at ambient conditions.

Mode	$\omega_i$ ( $\text{cm}^{-1}$ )	$\frac{d\omega_i}{dp}$ ( $\frac{\text{cm}^{-1}}{\text{GPa}}$ )	$\gamma_i$	$\frac{d\gamma_i}{dp}$ ( $\frac{1}{\text{GPa}}$ )
LO	251.9	$3.44 - 0.04p$	0.85	$-0.02 + 3.2 \times 10^{-4}p$
TO	204.2	$4.98 - 0.14p$	1.52	$-0.06 + 1.14 \times 10^{-4}p$
TO split (I)	207.2	$2.01 - 0.02p$	0.60	$-0.02 + 2.02 \times 10^{-4}p$
TO split (II)	222.9	$-3.12 + 0.12p$	-0.87	$0.03 + 5.25 \times 10^{-4}p$

TABLE II. Effect of pressure on various Raman vibrational modes of  $\text{Zn}_{0.84}\text{Fe}_{0.16}\text{Se}$  at room temperature (298 K). The values of mode frequencies  $\omega_i$ , pressure dependence  $d\omega_i/dp$ , mode Grüneisen parameter  $\gamma_i$ , and  $d\gamma_i/dp$  are extrapolated at ambient conditions.

Mode	$\omega_i$ ( $\text{cm}^{-1}$ )	$\frac{d\omega_i}{dp}$ ( $\frac{\text{cm}^{-1}}{\text{GPa}}$ )	$\gamma_i$	$\frac{d\gamma_i}{dp}$ ( $\frac{1}{\text{GPa}}$ )
LO	254.353	$3.370 - 0.266p$	0.827	$-0.0761 + 1.7397 \times 10^{-3}p$
Fe local	228.293	$6.138 - 0.626p$	1.727	$-0.2125 + 8.1888 \times 10^{-3}p$
TO	202.644	$5.603 - 0.222p$	1.725	$-0.0989 + 2.4740 \times 10^{-3}p$
TO split (I)	216.532	$0.149 + 0.042p$	0.043	$-0.0121 + 1.6106 \times 10^{-5}p$
TO split (II)	215.948	$-3.565 + 0.198p$	-1.030	$0.0127 + 4.1160 \times 10^{-3}p$

This manifests that  $\text{Zn}_{0.84}\text{Fe}_{0.16}\text{Se}$  has a higher ionicity than ZnSe. We suggest that the higher ionicity resulted from the Fe impurity.

In Fig. 5, it is clear that the pressure effect on the Raman shift for the ZnSe and  $\text{Zn}_{0.84}\text{Fe}_{0.16}\text{Se}$  is almost the same, except the phase transition pressures are different, and no local mode could be observed in the ZnSe. The disappearance of the LO phonon can be understood as a

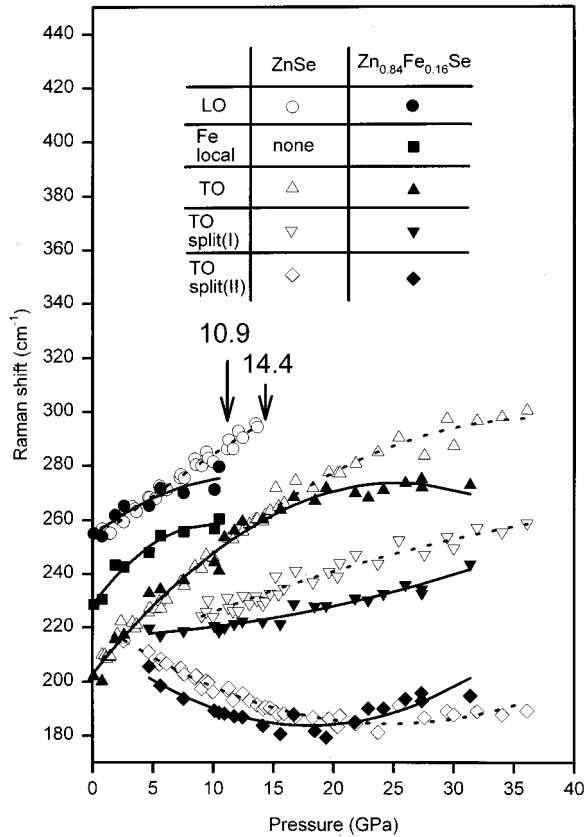


FIG. 5. Pressure dependence of Raman peaks in the  $\text{Zn}_{0.84}\text{Fe}_{0.16}\text{Se}$  crystal (black symbols) and ZnSe powder (opened symbols). The solid lines and dashed lines are quadratic polynomial fitting curves for  $\text{Zn}_{0.84}\text{Fe}_{0.16}\text{Se}$  crystal and ZnSe powder, respectively. The arrows at 10.9 and 14.4 represent the semiconductor-metal phase transition pressure of  $\text{Zn}_{0.84}\text{Fe}_{0.16}\text{Se}$  and ZnSe, respectively.

semiconductor-metallic transition from the high-pressure resistivity<sup>31</sup> and Raman spectroscopy measurements on the ZnSe powder. The Fe local phonon in  $\text{Zn}_{0.84}\text{Fe}_{0.16}\text{Se}$  behaves the same way as the LO phonon instead of the TO phonon which splits into three components and is still visible at the highest pressures achieved in our experiments. Furthermore, it was found the semiconductor-metal transition pressure for the  $\text{Zn}_{0.84}\text{Fe}_{0.16}\text{Se}$  is 10.9 GPa, which is 3.5 GPa lower than that of the ZnSe. The reduction in the transition pressure is due to the existence of Fe which results in the hybridization of  $3d$  orbitals into the tetrahedral bonds.<sup>20</sup> Our result is consistent with the study of pressure-induced phase transition of  $\text{Zn}_{0.83}\text{Fe}_{0.17}\text{Se}$  by the energy-dispersive x-ray-diffraction measurement.<sup>19</sup>

The other significant result obtained in this work is that at a pressure higher than 10.9 GPa, the metallic RS structure transformation pressure of  $\text{Zn}_{0.83}\text{Fe}_{0.17}\text{Se}$ , the LO and Fe local phonon disappeared, but all the TO and split TO phonon modes were still clearly visible. The high-pressure Raman scattering experiments up to  $\sim 6.0$  GPa have also been carried out by Arora *et al.*<sup>23</sup> to study ZnSe and  $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ . However, no Raman signals above 13.5 GPa have been reported yet. We note that the onset of the metallization occurs at 13.5 GPa. According to the data provided by Itkin and co-workers,<sup>9</sup> at that pressure the resistance drops abruptly from  $10^{21}\Omega$  to  $10^4\Omega$ . Assuming the sample size is about  $100\ \mu\text{m}$  in diameter and  $10\ \mu\text{m}$  in thickness, then the calculated resistivity at 13.5 GPa is about  $10^9\ \mu\Omega\ \text{cm}$ , which is the intermediate of those of silicon ( $6.4 \times 10^{10}\ \mu\Omega\ \text{cm}$ ) and copper ( $1.7\ \mu\Omega\ \text{cm}$ ). Itkin *et al.* suggested that at the pressure of 13.5 GPa, where the RS structure first appeared, a new semiconducting phase was formed and was able to exist in a pressure range of about 13.5–17.0 GPa. Beyond that range, metallization occurred due to gap closure. However, we have found that three Raman peaks on ZnSe powder at  $260.0\ \text{cm}^{-1}$ ,  $230.0\ \text{cm}^{-1}$ , and  $191.0\ \text{cm}^{-1}$  were still visible at the highest pressure (36.0 GPa) we achieved. One can recall that the skin depth (or penetration depth)  $\delta$  can be expressed as

$$\delta \approx \frac{c}{\sqrt{2\pi\mu\omega\sigma}}, \quad (11)$$

where  $c$ ,  $\mu$ ,  $\omega$ , and  $\sigma$  are the speed of light, permeability, angular frequency of excitation laser beam, and the conduc-

tivity, respectively. The permeability of the metallized ZnSe is about the same as the permeability in vacuum and the wavelength of the excitation laser beam is 5145 Å. The resistivity above 18.6 GPa is reported to be smaller than  $12 \mu\Omega \text{ cm}$ .<sup>9</sup> Then the calculated skin depth at a pressure above 18.6 GPa was only about several tens of an Å. It may be very interesting to study which mechanism makes the number of scattered photons become large enough to be detected for such a thin penetration depth.

#### IV. CONCLUSIONS

We have carried out high-pressure Raman scattering experiments on ZnSe powder and  $\text{Zn}_{0.84}\text{Fe}_{0.16}\text{Se}$  crystal up to 36.0 and 32.0 GPa, respectively. The existence of the Fe element results in a reduction in the semiconductor-metal phase transition pressure. The disappearance of the LO and Fe local phonons are attributed to the metallization of the

ZnSe powder and the  $\text{Zn}_{0.84}\text{Fe}_{0.16}\text{Se}$  crystal. Visible TO phonon splitting into three components in ZnSe and  $\text{Zn}_{0.84}\text{Fe}_{0.16}\text{Se}$  systems was observed up to 36.0 and 32.0 GPa, respectively. The calculated Grüneisen parameter implied that  $\text{Zn}_{0.84}\text{Fe}_{0.16}\text{Se}$  has a higher ionicity than ZnSe. A complete theoretical study and detailed x-ray work are needed to fully understand the current experimental results.

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