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PHASE TRANSITIONS OF $Zn_{0.84}Fe_{0.16}Se$ UNDER HIGH-PRESSURE

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The energy-dispersive X-ray-diffraction (EDXD) and Raman spectroscopy were employed to study the pressure induced phase transitions of $Zn_{0.84}Fe_{0.16}Se$ crystal up to 21.0 and 32.0 GPa, respectively. A semiconductor-metal transition was identified by EDXD and Raman spectroscopic methods at 11.4 ± 0.5 GPa. Other two phase transitions were found only in the Raman scattering study below 11.4 GPa. In addition, three unidentified Raman peaks were still observable above the metallization pressure. The existence of Fe impurity in the ZnSe up to a concentration of 0.16 reduced prominently the semiconductor-metal phase transition pressure. For Raman works, the three unidentified Raman peaks of $Zn_{0.84}Fe_{0.16}Se$ above 10.9 GPa are possibly the TO modes in the thin surface of the high pressure metallic phase. © 1998 Elsevier Science Ltd. All rights reserved

Ternary compound semiconductors, especially those containing the transition metal ions, have attracted attentions due to their ability to tune both the band gap and the lattice constant for application in the opto-electric devices as well as for the study of basic physical properties. Among the ternary compounds, diluted magnetic semiconductors (DMS) [1] are the ones of the most interesting types of materials. DMS (also referred to as semimagnetic semiconductors), such as $Cd_{1-x}M_xS$, $Cd_{1-x}M_xSe$, $Cd_{1-x}M_xTe$, $Zn_{1-x}M_xS$, $Zn_{1-x}M_xSe$ and $Zn_{1-x}M_xTe$, etc. (where M is a transition metal like Cr, Mn, Fe and Co) are compound II–VI semiconductor alloys with a fraction of the nonmagnetic cations replaced by the magnetic transition metal ions. Interesting phenomena such as spin glass transition [2], magnetic ordering in a two-dimensional system [3], spin flip Raman scattering [4], observation of polaron [5],

metal insulator transition [6], giant Faraday rotation [7], magnetic tuning of quantum well band alignment [8], spin superlattice structures [9] and novel spin relaxation process [10] have been discovered. Recently, attentions are also focused on the lattice vibration of the DMS [11, 12].

$Zn_{1-x}Fe_xSe$, crystallized in the zinc-blende structure which is similar to ZnSe in the range of Fe content $0 \leq x \leq 0.30$ [13], is a member of the diluted magnetic semiconductor (DMS) family [14]. Interesting magnetic as well as the magneto-optical properties were investigated on both $Zn_{1-x}Fe_xSe$ bulk crystals, thin films and quantum well [7, 13, 15, 16]. Furthermore, the pressure induced phase transition of $Zn_{1-x}Fe_xSe$ crystal was also discussed [17] using the energy-dispersive X-ray-diffraction (EDXD) method. It was found that the existence of Fe in the crystal results in a reduction in the transition pressure; such a reduction was believed to be the result of the hybridization of $3d$ orbitals into the tetrahedral bonds [18]. Recently, the Raman scattering experiment has also been applied to study the pressure effect on $Zn_{1-x}Fe_xSe$ [12], $Zn_{1-x}Co_xSe$ [19] and

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$Zn_{1-x}Mn_xSe$ [20, 21] crystals and two new phases were found at 4.0 GPa and 8.0 GPa which were lower than the semiconductor-metal transition pressure in $Zn_{1-x}Mn_xSe$. In this work, the EDXD measurement combined with the Raman scattering study was used to investigate the pressure effect on the phase transition of $Zn_{0.84}Fe_{0.16}Se$ crystals at high-pressure up to around 25.0 and 32.0 GPa, respectively. A phase transition at 4.7 GPa was found in Raman spectroscopic study, but not in EDXD measurement. The identification of the semiconductor-metal transition pressure for EDXD result is the change of the crystal structure, which is consistent with the disappearance of the Fe local and the longitudinal optical (LO) phonon modes of Raman scattering result.

$Zn_{0.84}Fe_{0.16}Se$ crystals were grown by the modified Bridgman method. The crystals were grounded to 1 μm size for EDXD measurement while in the Raman scattering study, a tiny crystal of 50 μm size was used. We used a Mao-Bell type diamond anvil cell (DAC) with T304 stainless steel gaskets which were preindented to 15.0 GPa; the sample hole was 130 μm in diameter. The anvil parameters were 1/3 carats with a 600 μm culet. Experimental details were described earlier by Xu [22]. For DAC EDXD experiment, pressure up to 21.0 GPa was used. The source is the superconductor wiggler synchrotron beam line X17C of the National Synchrotron Light Source (NSLS) of Brookhaven National Laboratory in U.S.A. The beam size was 50 × 50 μm^2. A Germanium energy dispersive detector was set in the position where the diffracted angle (θ) was 5°. Deionized water and the ruby fluorescence scale method [23, 24] and methanol−ethanol 4 : 1 fluid and the internal gold standard [25] were used as a hydrostatic pressure medium and the pressure determination in Raman scattering and EDXD measurement, respectively. For EDXD, the peak positions were read out by a peak search program provided from the VAX computer in the beam line X17C. The equation of state (EOS) data were fitted to the Murnaghan equation by using a fitting program reported by [26]. The experimental detail on micro-Raman, up to 32.0 GPa and the reason for choosing deionized water as the pressure medium were described earlier [12, 27]. For Raman scattering works, the Jandel Scientific Peakfit computer program for non-linear curve-fitting software produced by AISN Software was used in the deconvolution process and the determination of the peak position, intensity and the full width at half maximum as in the previous work [28]. The component forms of deconvolution process were defined by Lorentzian function as:

$$LORENTZ(x) = \frac{a_0}{1 + \left(\dfrac{x - a_1}{a_2}\right)^2},$$ (1)

where, a_0, a_1 and a_2 are amplitude, center and width, respectively.

$Zn_{0.84}Fe_{0.16}Se$ has a lattice parameter of 5.639 ± 0.001 Å from EDXD measurement at ambient pressure. It is only in the zinc-blende (B3) phase with (1 1 1), (2 2 0) and (3 1 1) peaks below 11.4 GPa. Above 11.4 GPa, the peaks of the B3 phase of $Zn_{0.84}Fe_{0.16}Se$ disappear and an apparent peak in the B1 phase occurs. The B1 peaks, (2 0 0) and (2 2 0), exist up to 21.0 GPa. The d-spacings at 11.4 GPa are 3.112, 2.556 and 1.802 Å for zinc-blende (B3) phase and are 1.861 and 1.634 Å for rock salt (B1) phase. The variation of the interplanar distances $d_{h\,k\,l}$ and equation of state (EOS) relations of $Zn_{0.84}Fe_{0.16}Se$ as a function of pressure are shown in Fig. 1, where V_0 and V are volumes of $Zn_{0.84}Fe_{0.16}Se$ at zero and certain pressure, respectively. The data for the two phases were fitted to the Murnaghan equation by a previously developed fitting process [26]. The Murnaghan equation is defined as:

$$P = (K_0/K_0')[(V_0/V)^{(K_0')} - 1],$$ (2)

where K_0 is the isothermal bulk modulus at zero pressure and K_0' is the pressure derivative of the isothermal bulk modulus evaluated at zero pressure. The values of K_0 and K_0' obtained from the fitting process are 58.85 ± 2.37 and 4.12 ± 0.53, 80.15 ± 1.05 and 3.64 ± 0.55 for B3 and B1, respectively. K_0' values are consistent with the slopes of d-spaces for B3 and B1 in Fig. 1. It is shown that $Zn_{0.84}Fe_{0.16}Se$ in high-pressure region (B1) is less compressible than that in low-pressure region (B3). Figure 1 also shows that there is no two-phase-co-existence ambiguity range and the phase transition occurred at 11.4 GPa. The lattice parameters of zinc-blende (ZB) and rock salt (RS) phases are 5.357 ± 0.001 Å and 5.104 ± 0.001 Å at 11.4 GPa, respectively.

Raman spectra for $Zn_{0.84}Fe_{0.16}Se$ crystal at various pressure were reported by Lin et al. [12]. The variation of the mode energies as a function of the pressure is shown in Fig. 2. The solid symbols correspond to the LO, Fe TO local, TO and TO split Raman modes of $Zn_{0.84}Fe_{0.16}Se$, respectively. The relationship of the mode frequencies vs pressure of $Zn_{0.84}Fe_{0.16}Se$ is plotted as the dash curves in Fig. 2. These curves are obtained by a quadratic polynomial fitting using the equations listed in Table 1, where ω_i is the wavenumber in cm^{-1} and p is the pressure in GPa. At atmospheric pressure, two peaks labelled as LO and TO phonons were reported previously [29]. Between these two peaks, a Fe TO local (impurity) phonon mode could be labelled through the deconvolution process [29]. The phonon energy of Fe TO local and the LO and TO modes are increased with the pressure. As pressure rises up to 4.7 GPa, two new modes appear. The phonon mode labelled as TO split mode I exhibits red shift and the other mode labelled as TO split
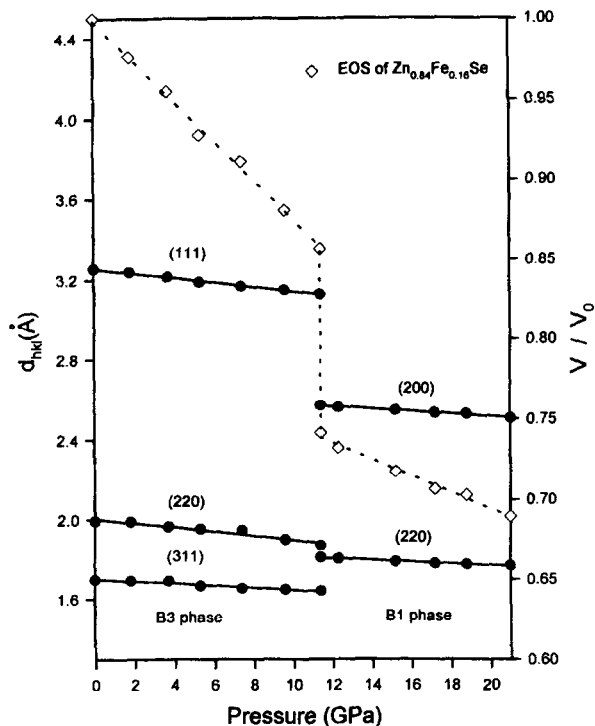
Fig. 1. The variation of $d_{h\,k\,l}$ (Å) of $Zn_{0.84}Fe_{0.16}Se$ with pressure (GPa) and the V/V_0 vs pressure for the B3 and B1 phases of $Zn_{0.84}Fe_{0.16}Se$.
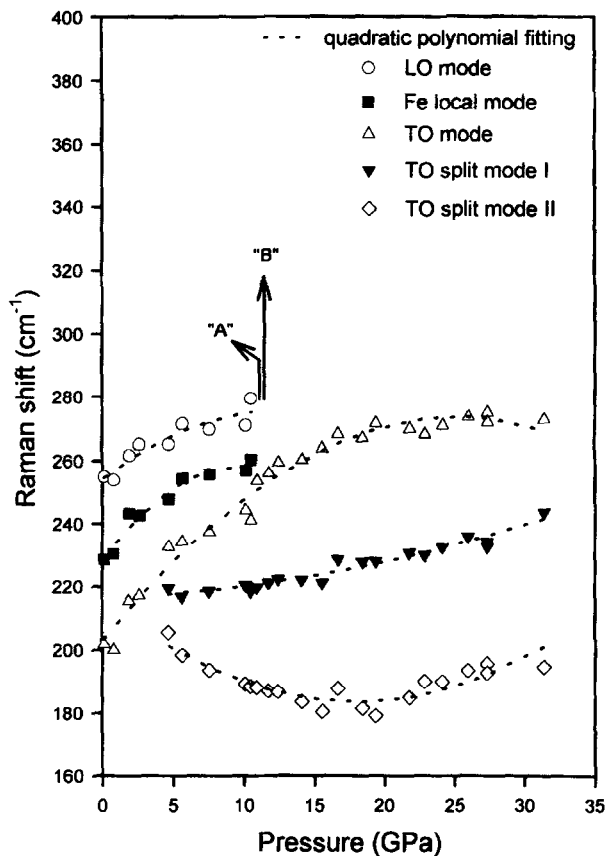

Fig. 2. Pressure dependence of Raman peaks in the $Zn_{0.84}Fe_{0.16}Se$ crystal. The dash lines are quadratic polynomial fitting curves for $Zn_{0.84}Fe_{0.16}Se$ crystal. The semiconductor-metal phase transition pressure of $Zn_{0.84}Fe_{0.16}Se$ can be well identified.

mode *II*, as well as the LO phonon and Fe TO local mode, exhibits blue shift as pressure is increased up to around 32.0 GPa. Although no structure transitions could be identified in the EDXD works of ours and Qadri *et al.* [17] for a pressure below 10.0 GPa, Michel *et al.* [30] reported that ZnSe follows the structural transition sequence: zinc-blende → cinnabar → NaCl → CmCn with increasing pressure by using the *ab initio* pseudopotential calculations method. Ahuji *et al.* [31] also indicated that CdTe follows the structural sequence: zinc-blende → cinnabar → NaCl → orthorhombic with increasing pressure by using the full-potential linear muffin-tin-orbital (EPLMTO) calculations in the studying of the structural phase transition of CdTe under high-pressure. Similar study of the ZB structure of CdTe [32] showed that one more phase exists below the structure

transformation from ZB to RS structure. We therefore attribute the appearance of the new phonon mode to the broken symmetry of the structure transformation. The splitting of TO phonon at 4.7 GPa could be also due to the structure transition as zinc-blende phase transforms into cinnabar phase. As the pressure increases further to 10.9 GPa, the semiconductor-metal transition pressure of $Zn_{0.84}Fe_{0.16}Se$, both LO and Fe TO local modes disappear. The arrows at 10.9 and 11.4 GPa labelling as "A" and "B" symbols in Fig. 2 indicate the transition pressures of B3 to B1 identified by Raman scattering and EDXD measurement, respectively. The effects of pressure on various Raman vibrational modes of $Zn_{0.84}Fe_{0.16}Se$ at room temperature (298 K) are listed in Table 2. The Grüneisen parameter (γ_i) for a quasi-harmonic mode *i* of frequency ω_i was defined by Cardona *et al.* [33]. From the comparison of the values of γ_{LO}, γ_{TO} and γ_{TO}/γ_{LO} of ZnSe [12] and $Zn_{0.84}Fe_{0.16}Se$, we may conclude that $Zn_{0.84}Fe_{0.16}Se$ has higher ionicity than ZnSe. The Fe TO local mode in $Zn_{0.84}Fe_{0.16}Se$ behaves the same way as the LO mode instead of the TO mode

Table 1. The quadratic polynomial fitting equation of the $Zn_{0.84}Fe_{0.16}Se$

Raman modes	Quadratic polynomial fitting equation
LO	$254.4 + 3.37p - 0.133p^2$
Fe local	$228.3 + 6.14p - 0.313p^2$
TO	$202.6 + 5.60p - 0.111p^2$
TO split (I)	$216.5 + 0.15p + 0.021p^2$
TO split (II)	$216.0 - 3.57p + 0.099p^2$

Table 2. Effect of pressure on various Raman vibrational modes of $Zn_{0.84}Fe_{0.16}Se$ at room temperature (298 K). The values of mode frequencies ω_i, pressure dependence $d\omega_i/dp$, mode Grüneisen parameter γ_i are extrapolated at ambient conditions

Mode	ω_i (cm^{-1})	$d\omega_i/dp$ (cm^{-1}/GPa)	γ_i [$(K_0/\omega_i)(d\omega_i/dP)$]	$d\gamma_i/dp$ (1/GPa)
LO	254.4	$3.37 - 0.266p$	0.668	$-0.0761 + 1.7397 \times 10^{-3}p$
Fe local	228.3	$6.14 - 0.626p$	1.395	$-0.2125 + 8.1888 \times 10^{-3}p$
TO	202.6	$5.60 - 0.222p$	1.394	$-0.0989 + 2.4740 \times 10^{-3}p$
TO split (I)	216.5	$0.15 + 0.042p$	0.043	$-0.0121 + 1.6106 \times 10^{-5}p$
TO split (II)	216.0	$-3.57 + 0.198p$	-0.832	$0.0127 + 4.1160 \times 10^{-3}p$

which splits into three components. These three components are still visible at the highest pressure achieved in our experiments. Furthermore, it was found the semiconductor-metal transition pressure for Raman scattering measurement of the $Zn_{0.84}Fe_{0.16}Se$ is 10.9 GPa which is 3.5 GPa lower than that of our previous ZnSe Raman works. The reduction in the transition pressure might be attributed partially to the hybridization of $3d$ orbitals of Fe ion into the tetrahedral bonds [18] and partially to the percentage of the volume change, $\Delta V/V_0$, of B3-to-B1 phase transition [34]. Our result was consistent with the study of pressure-induced phase transition of $Zn_{0.83}Fe_{0.17}Se$ by the EDXD measurement [17].

According to the data of resistance of ZnSe measured Itkin and co-workers [35], the onset of the metallization occured at 13.5 GPa. The calculated skin depth above phase transition pressure could be found to be about several tens Å [12]. Therefore, we suggest that the possible reason for the disappearance of LO phonon and Fe local phonon modes and the existence of TO and split TO phonon modes above metallization pressure may due to a thin skin depth could only sustain the propagation of transverse EM wave but forbid the longitudinal EM wave. In addition, the disappearance of the LO-TO splitting may be due to screening of the longitudinal phonon field by metallic electrons.

In summary, both Raman scattering and EDXD measurements show that the existence of the Fe element results in a reduction of phase transition pressure in the semiconductor-metal phase transformation. The disappearance of the LO and Fe local phonons above the transition pressure is attributed to the metallization of the $Zn_{0.84}Fe_{0.16}Se$ crystal. The calculated Grüneisen parameter implies that $Zn_{0.84}Fe_{0.16}Se$ has higher ionicity than ZnSe. Three visible TO phonon splitting components in $Zn_{0.84}Fe_{0.16}Se$ system are observed from a pressure below metallization transition up to 32.0 GPa for Raman scattering measurement. Structure transitions occur below the semiconductor-metal phase transition, which are obtained by Raman scattering, however, they are not observed in the EDXD measurement.

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