# The incorporation behaviour of Co impurities in a ZnSe crystal

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**Abstract.** This work is a study on the incorporation phenomena of cobalt magnetic ions in ZnSe. $Zn_{1-x}Co_xSe$ ($x < 0.02$) polycrystals were prepared by the melt growth technique. The influences of Co impurities on the ZnSe crystal were investigated using x-ray diffractometry and Raman spectroscopy. The solid solubility of melt grown crystals is about $x = 0.02(\pm0.0015)$. It was found that the lattice constant of the crystal increases linearly up to $x = 0.0086$ and then saturates as the amount of Co impurities increases. It is also observed that the $TO_2$ and $LO_1$ Raman modes in $Zn_{1-x}Co_xSe$ soften for $x < 0.0086$ by the addition of Co atoms. The oscillator strength, which is calculated using the energies of the $TO_2$ and $LO_1$ phonon modes, decreases as the cobalt content increases. There is a linear relationship between the ionicity and the oscillator strength with a slope of $-7.02 \times 10^{25}$ $s^{-2}$. From these observations, it is clear that the instability of the $Zn_{1-x}Co_xSe$ crystal is mainly due to the ionicity difference between Zn and Co atoms.

## 1. Introduction

Recently, semimagnetic semiconductors (SMSCs) or dilute magnetic semiconductors (DMSs) (i.e. II–VI compounds containing a controlled quantity of magnetic ions, namely Fe, Co, Mn, etc.) have attracted considerable attention because of their interesting magnetic and optical properties [1–3]. For example, $Zn_{1-x}Fe_xSe$ DMSs show extremely large values of the Faraday rotation angle [1] resulting from the strong s–d exchange interaction between band electrons and the localized d electrons of the magnetic ions [2]. Paramagnetic, spin-glass and antiferromagnetic phases have been found for $Cd_{1-x}Mn_xTe$ [4], $Cd_{1-x}Mn_xSe$ [5] and $Hg_{1-x}Mn_xTe$ [6] crystals and others. In the case of the (Zn, magnetic ion)Se DMSs, with common magnetic transition metal ions in the 2+ charge state, the (Zn,Fe)Se DMS is a Van Vleck paramagnet, while (Zn,Mn)Se and (Zn,Co)Se are Brillouin paramagnets [3]. The vibrational properties of $Zn_{1-x}Fe_xSe$, $Zn_{1-x}Co_xSe$ [7] and $Zn_{1-x}Mn_xSe$ [8] are all similar, however, and obey the modified random-element isodisplacement (MREI) model [9].

From the viewpoint of material preparation, $Zn_{1-x}Co_xSe$ is more difficult to grow epitaxially with a high concentration of the transition metal than are (Zn,Fe)Se or (Zn,Mn)Se [3]. Jonker et al [3] argued that this may be due to a clustering of $Co^{2+}$ atoms, which results in a tendency towards localized formation of CoSe. According to them, the formation of CoSe, which has a hexagonal NiAs structure in nature [10], will eventually disrupt the epitaxial growth of zincblende type of $Zn_{1-x}Co_xSe$. The ionicity of the NiAs structure is larger than that of zincblende and the bond length of CoSe is larger than that of ZnSe [10].

In this work, we are particularly interested in the incorporation behaviour of Co atoms in a ZnSe crystal. The influences of Co atoms on the lattice constant and optical phonon modes are studied. The results are interpreted by the effect of the covalent radius and the ionicity of Co atoms.

## 2. Experimental details

$Zn_{1-x}Co_xSe$ ($x < 0.02$) crystals were prepared by the melt growth technique using a horizontal furnace. Stoichiometric quantities of the elements Zn (purity, 99.9999%), Se (purity, 99.999%) and CoSe (purity 99.5%) were sealed under a vacuum of $10^{-5}$ Torr in a quartz ampoule. The sealed ampoules were placed into a horizontal furnace and heated to 1000 °C at a rate of 10–20 °C h$^{-1}$. They were retained at this temperature for about 70 h to obtain the polycrystalline $Zn_{1-x}Co_xSe$ ingots.

The influence of Co impurities on the ZnSe crystal was investigated by x-ray diffraction (XRD) analysis and Raman spectroscopy. For XRD, the resolution of the lattice constant is 0.005 Å. The Raman spectra excited by the 4880 Å line from an Ar-ion laser were detected with a cooled photomultiplier (R943-02). The resolution of the spectra is about 0.15 cm$^{-1}$.

## 3. Results and discussion

Figure 1(a) shows the variation in lattice constants in $Zn_{1-x}Co_xSe$ ($x < 0.02$) as the amount of Co atoms is increased. Here the nominal value in the melt was used as the Co concentration of the crystal. The crystal structure of all the grown samples are zincblende. For $x > 0.02$ the peaks which correspond to the hexagonal structure were also found. This aspect is perhaps due to clustering of $Co^{2+}$ impurities [3]. We believe therefore that the solid solubility of Co atoms in ZnSe is limited to about 0.002($\pm$0.0015). This incorporation limit value is about half that of the epitaxial layer grown by the molecular beam epitaxy (MBE) method on GaAs(001) [3]. As can be seen in figure 1, the lattice constant of $Zn_{1-x}Co_xSe$ increases linearly for $x < 0.0086$ and then saturates for $x > 0.0086$. This abrupt change in lattice constant may occur if either a change in symmetry of the solid solutions or a change in the solid solution mechanism occurs [10]. The latter corresponds to our case. For $x < 0.0086$, the solid solution mechanism is thought to involve simply cation replacement. For $x > 0.0086$, a combination of cation replacement and vacancy creation seems to be involved, and the crystals shrink for the $x > 0.0086$ region. An interesting fact is that the lattice constants of $Zn_{1-x}Co_xSe$ for $x > 0.0086$, which remain fixed at $a = 5.68$ Å, correspond to the sum of the octahedral $Co^{2+}$ covalent radius of 1.32 Å and tetrahedral Se covalent radius of 1.14 Å [11]. We believe, therefore, that the size effect of cobalt has an important role in the increase in the lattice constant of melt-grown $Zn_{1-x}Co_xSe$. For $x < 0.0086$, the linear relationship between the content of cobalt and the lattice constant of (Zn,Co)Se is

$$a = 5.661 + 1.602x. \qquad (1)$$

The slope is very large compared with that reported by Jonker *et al* [3]. The observed difference between the solid solubility and composition dependences of the lattice constant in our results and in the results of Jonker *et al* [3] are perhaps due to the difference in the crystal growth mechanisms. In the case of MBE growth at 330 °C [3], the Co atoms are incorporated under non-equilibrium conditions. Thus the microscopic local strain around

Co atoms can be sustained to a relatively high Co concentration and an increase in the lattice constant according to Vegard's law [3] may be quite possible. In crystals grown under equilibrium conditions, however, any local strain must be accommodated by the distortion of the bond. Thus, if too much strain occurs by incorporation of impurity atoms in the matrix crystal, the solid solubility under equilibrium conditions would be low and the lattice constant of the solid solution does not follow Vegard's law [10].
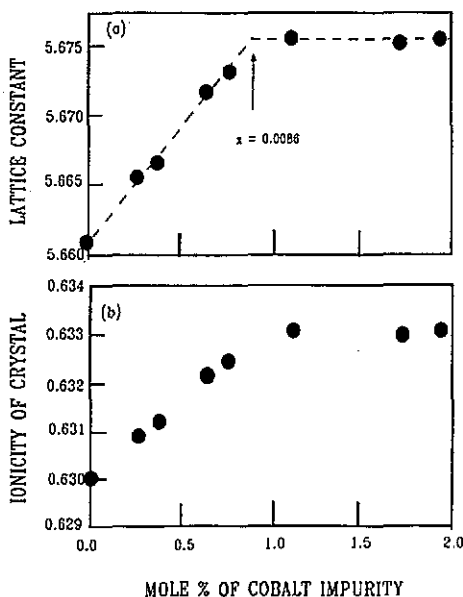


**Figure 1.** (a) Lattice constants of $Zn_{1-x}Co_xSe$ polycrystals for $x < 0.02$. There is a linear relationship between the lattice constant and the cobalt content in the unsaturated region (----). (b) Phillip's ionicities calculated under the assumption of $\partial C/\partial R = 0$ [13].

The incorporation of Co atoms in a ZnSe crystal can also affect the ionicity of the bond. Figure 1(b) shows the change in the ionicity of the bonds of $Zn_{1-x}Co_xSe$ which is calculated using Phillip's [12] definition of the ionicity. For isoelectronic series of the compounds, the ionicity $f_i$ is defined by

$$f_i = C^2/E_g^2 \tag{2}$$

$$C \sim (X_{Zn} - X_{Se}) \tag{3}$$

where $X_{Zn}$ and $X_{Se}$ are the electronegativities of Zn and Se, respectively. The energy gap $E_g$ has contributions from a homopolar band gap $E_h$ and a charge transfer $C$ between Zn and Se:

$$E_g^2 = E_h^2 + C^2. \tag{4}$$

Here the homopolar energy $E_h$ varies according to $E_h \sim R^{-2.5}$ with the bond length $R$ [12].

Since the amount of cobalt impurities and the difference between the electronegativities of Zn and Co are small, we assume that the change in electronegativity of the crystal is negligible in the impurity region and the assumption of Camphausen *et al* [13] that $\partial C/\partial R = 0$ is valid. Then the change in the ionicity is

$$\Delta f_i = 5f_i(1 - f_i)\,\Delta R/R \tag{5}$$

where $f_i$ and $R$ are the ionicity and lattice constant, respectively, of the pure ZnSe crystal. Equation (5) implies that the change in ionicity of the crystal is proportional to that of the lattice constant of the ZnSe crystal. Taking $E_h$ as the band gap of Ge, the ionicity of the ZnSe crystal varies from 0.630 to 0.633 by the addition of cobalt impurities as shown in figure 1(*b*).

The variation in lattice constant in figure 1 is quite different from Vegard's law behaviour, in which unit-cell parameters change linearly with composition [10], i.e. the lattice constant of $Zn_{1-x}Co_xSe$ for $x > 0.0086$ is determined by the length of the zincblende Co–Se bond. The positive departure from Vegard's law, which is correlated to the occurrence of the immiscibility dome inside the phase diagram of solid solution [10], is quite natural when we note the difference between the natural bonding types of ZnSe (zincblende structure) and Co–Se (NiAs structure). The saturated lattice constant of the (Zn,Co)Se crystal is different from that of ZnSe by 0.25%. The size effect of the Co atom, therefore, cannot contribute much to the lattice strain and the minute difference between the electronegativities of Zn atoms and Co atoms dominates the local strain in $Zn_{1-x}Co_xSe$. This idea of the origin of the local strain in the zincblende Co–Se bond is reinforced from the experimental observations that the growth of $Zn_{1-x}Co_xSe$ by the melt growth technique was difficult for high Co concentrations; for higher Co concentrations the (Zn,Co)Se cannot sustain the zincblende structure by relaxing the local strain. The existence of vacancy defects in the crystal for $x > 0.0086$ also results in local strain. Therefore, the limit of the impurity concentration in solid solution is smaller than that reported by Jonker *et al* [3].
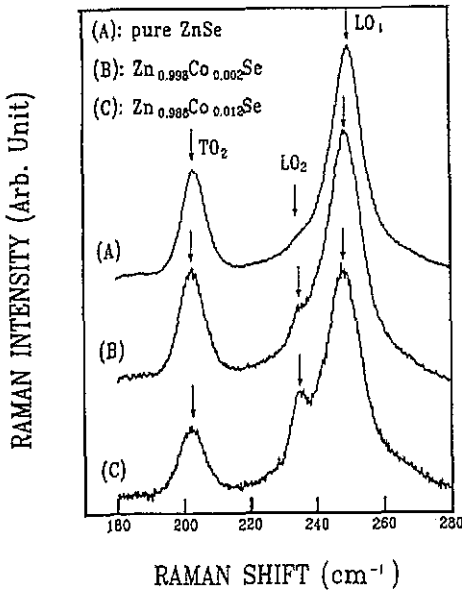


**Figure 2.** Raman spectra of the $Zn_{1-x}Co_xSe$ crystals: curve (A), pure ZnSe; curve (B), $Zn_{0.998}Co_{0.002}Se$; curve (C), $Zn_{0.988}Co_{0.012}Se$.

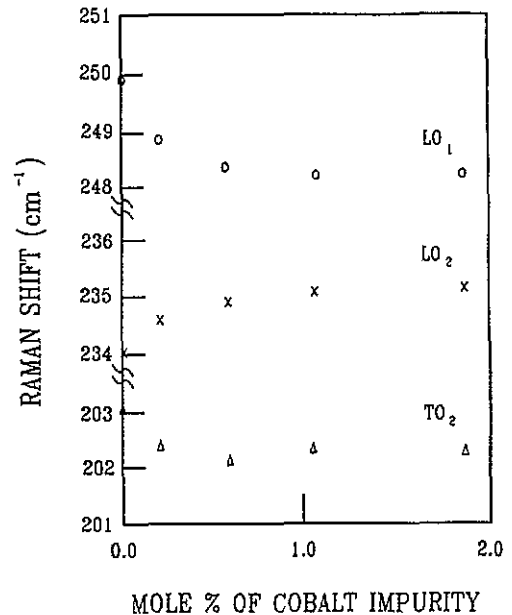**Figure 3.** Frequency variation of the phonon modes of $Zn_{1-x}Co_xSe$.

Figure 2 shows the three Raman spectra of pure ZnSe, $Zn_{0.998}Co_{0.002}Se$ and $Zn_{0.988}Co_{0.012}Se$ polycrystals measured with high resolution at room temperature. For pure ZnSe there are three peaks at 203.0 cm$^{-1}$, 234.0 cm$^{-1}$ and 249.8 cm$^{-1}$, which correspond

to $TO_2(\Gamma)$, $LO_2(\Gamma)$ and $LO_1(\Gamma)$, respectively [7]. These values are in good agreement with the values found by others [7, 14]. The peak at 234.0 cm$^{-1}$, which is labelled $LO_2$ and has the same symmetry as $LO_1$, was also observed by Mak *et al* [7] in the Raman spectra of $Zn_{0.973}Co_{0.027}Se$. However, in our experiment it was observed in all the spectra of $Zn_{1-x}Co_xSe$. Therefore, we believe that this mode is a band mode due to vacancy complexes, which are primary defects in semiconductors [15, 16] or residual defects.

The energy of the $LO_2$ mode hardens as the cobalt content increases, while those of the $TO_2$ and $LO_1$ modes soften as shown in figure 3. These results have the opposite tendency to the results of Mak *et al* [7], who observed that the $LO_2$ mode frequency decreases while the $TO_2$ and $LO_1$ mode frequencies increase as the Co content increases in $(Zn,Co)Se$ ternary compounds. They also showed that such a phenomenon is consistent with the intermediate-mode behaviour of the MERI model in ternary compounds. Our somehow adverse phenomenon seems to be related to the crystal relaxation due to the incorporated Co impurities. In our case, the degree of the crystal relaxation due to the addition of Co impurities is much larger than that of the crystals used by Mak *et al* [7]. Thus the peaks in the Raman spectra move in the opposite direction compared with those in [7].
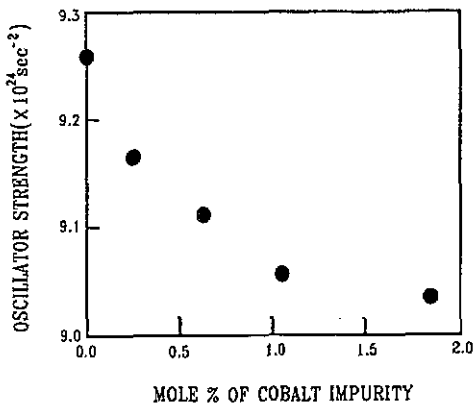


**Figure 4.** Oscillator strength calculated from the frequencies of the optical phonon modes of $Zn_{1-x}Co_xSe$ crystals.

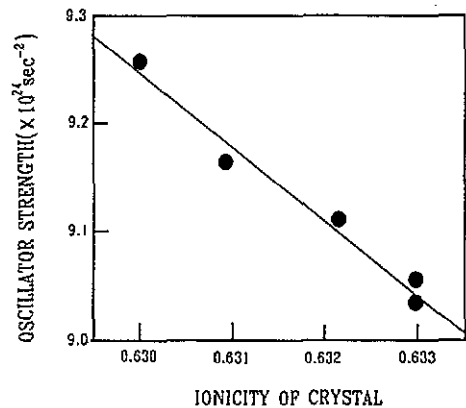**Figure 5.** The linear relationship between Phillip's ionicity and the oscillator strength of the $Zn_{1-x}Co_xSe$ crystal. The equation of the full line is $Y = 3.14 - 7.02X(\times 10^{25})$. The two points at $f_i = 0.633$ arise because $Zn_{0.988}Co_{0.012}Se$ and $Zn_{0.982}Co_{0.018}Sr$ have the same lattice constant.

The changes in optical phonon mode energies are related to changes in the oscillator strength which decreases as the lattice constant increases. From the TO and LO mode energies, the oscillator strength $\rho$ can be calculated as follows [17]:

$$\epsilon(0) = \epsilon(\infty) + 4\pi\rho/\omega_{TO}^2 \tag{6}$$

$$\left(\omega_{LO}/\omega_{TO}\right)^2 = \epsilon(0)/\epsilon(\infty). \tag{7}$$

Here the value of 6.1 is used for $\epsilon(\infty)$ [18]. Figure 4 shows the change in the oscillator strength due to the addition of Co impurities. The oscillator strength decreases for $x < 0.0086$ and saturates for $x > 0.0086$. This behaviour is opposite to that of the ionicity of the crystal and can be understood from the fact that the effective charge of atoms in

crystals tends to reduce the transverse optical frequency $\omega_{TO}$ and thus the spring constant of the crystals decreases [19]. Figure 5 shows that there is a linear relationship between the oscillator strength and the ionicity of crystal. The two points at $f_i = 0.633$ arise because the lattice constants of $Zn_{0.988}Co_{0.012}Se$ and $Zn_{0.982}Co_{0.018}Se$ are the same. The equation for this relationship is

$$Y = 3.14 - 7.02X \left( \times 10^{25} \right) \tag{8}$$

where $Y$ and $X$ are the oscillator strength and Phillip's ionicity of the crystal, respectively.

## 4. Conclusion

$Zn_{1-x}Co_xSe$ ($x < 0.02$) polycrystals were grown by the melt growth technique. The effects of Co impurities on the ZnSe crystal were investigated by XRD analysis and Raman spectroscopy. The solid solubility of this crystal is about $x = 0.02(\pm0.0015)$. The ionicity of $Zn_{1-x}Co_xSe$ crystals increases linearly from 0.630 for $x < 0.0086$ and saturates at 0.633 for $x > 0.0086$ because the addition of Co impurities results in a size effect. We observed that the energies of $TO_2$ and $LO_1$ phonon modes decrease with increasing impurity content in the unsaturated region. This means that the oscillator strength decreases as the lattice constant of the ZnSe crystal increases. The oscillator strength which is calculated using the frequencies of the optical phonon modes is linearly related to the ionicity of the crystal with a slope of $-7.02 \times 10^{25}$ s$^{-2}$.

## Acknowledgment

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