$Zn_{1-x}Mn_xSe$ — a Diluted Magnetic Semiconductor

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(December 8, 1995)

Abstract

$Zn_{1-x}Mn_xSe$ belongs to the class of diluted magnetic semiconductors (DMS) also known as semimagnetic semiconductors ($SMSC$). These materials have attracted attention due to some unique properties which enhance their potential for use in a wide range of optoelectronic devices. They are semiconductors with a fraction of their constituent ions replaced by transition metal ions or rare earths. The band gap and lattice parameters can be tuned by changing appropriately the concentration of the added magnetic ions and this makes them useful for various device applications. The tunability of the lattice parameter with magnetic ion content also extends their utility into the field of heterostructures where lattice matching is important.

I. INTRODUCTION

The interesting physical properties of Diluted Magnetic Semiconductors (DMS) are due to the exchange interactions induced by the magnetic moments localised at the magnetic ions. DMS are usually compounds in which a fraction of the nonmagnetic cations have been substituted by magnetic transition metal or rare earth ions. In contrast to normal magnetic semiconductors for which the application of an electric field does not produce a marked response by the magnetic ions, the magnetic ions in DMS do respond to an applied magnetic field and change the energy band and impurity level parameters. Much of the interest in DMS is related to the wide range of their magnetic properties such as paramagnetism, ferromagnetism, etc.

The incomplete d-shell (transition metals) or $4f$-shell (rare earths) of the magnetic atoms gives rise to a variety of properties in which their localised magnetic moments play important roles, either individually or collectively through their mutual interactions or through exchange interactions between these localised moments and the spin of the charge carriers.

II. CRYSTAL STRUCTURE

Most research performed on these materials have been devoted to Mn based semimagnetic semiconductors ($SMSC$). The Mn^{++} ground state is a magnetically active spin sextet G_{Al}. The Mn based $SMSC$ are an example of a permanent magnetic moment system called Brillouin-type paramagnetism.

The family of II_{1-x} Mn_x VI alloys along with their crystal structures is presented in $fig.$1. The bold lines indicate ranges of the molar fraction x which homogenous crystals form.

The crystal structures of II VI compounds are zinc blende or wurtzite. They are formed with tetrahedral bonding (sp^3) involving the six valence p electrons of the element VI and the two valence s electrons of the element II. Manganese is a transition metal with valence bond electrons corresponding to $4s^2$ orbital. So it can contribute to the sp^3 bonding by these $4s^2$ electrons and therefore replace the II element in the II VI wurtzite and zinc blende structure, despite the fact that it differs from this element by its $3d$ shell half filled. The exactly half filled $3d$ orbitals play a role in the existence of solid solutions. Mn is more miscible than other transition metals because all five spins are aligned and it would require large energy to add an electron with antiparallel spin. In this way the $3d^5$ orbit behaves as a complete one and so Mn is like a group II element.

Except exchange interactions and magnetic properties, the physical properties of $ZnMnSe$ are deduced from the properties of the starting II VI ($ZnSe$) compound. Therefore it is useful to review its structural properties. Zinc blende is a cubic structure with two interpenetrating fcc lattices ($fig.$2). Anions and cations are shifted with respect to each other by one fourth the body diagonal. The wurtzite struture is formed by two interpenetrating fcc sublattices shifted along the c-axes.

The nearest cation-cation distance d and the bond length b (cation-anion distance) are the same in the two structures. From geometrical considerations

$$d = \frac{\sqrt{8}}{3} b \qquad (1)$$

In the case of ZB the lattice parameter

$$a = \sqrt{2} d = \frac{4}{\sqrt{3}} b \qquad (2)$$

In wurtzite the two lattice parameters a (separation between like atoms of the sublattices in the hexagonal plane) and c (distance between repeating planes) are

$$a = d \tag{3}$$

$$c = \frac{\sqrt{8}}{3} d \tag{4}$$

The maximum solubility of $MnSe$ in $ZnSe$ is about 0.57. The solid solution $ZnMnSe$ exhibits the ZB structure upto 35% mole of $MnSe$ and then wurtzite form in the $0.35 < x < 0.57$ range. For $x > 0.57$, two phases with wurtzite and rocksalt are observed in the mixture.

The microscopic structure is expected to be similar to that of the parent binary compound with cation sites occupied randomly by two species of ions.

III. ELECTRONIC STRUCTURE

The photoemission spectra reveal strong hybridization between the Mn $3d$ and the host anion p-band states as well as the multielectron satellite features. These results are interpreted consistently by the configuration-interaction theories, in which both the p-d hybridisation and the electron correlation at the Mn site are exactly treated with Mn impurity models. Such an approach can describe the localised Mn $3d^5$ multiplet and the strongly hybridised photoemission spectra on the same ground, reconciling the localised behaviour of the Mn $3d$ electrons with their strong hybridisation with host band states.

IV. EXCHANGE INTERACTION EFFECTS ON OPTICAL PROPERTIES

The effect of the exchange interaction between the spin of the s-like (p-like) conduction (valence) band electrons and the localised moment of the d-like Mn^{2+} electrons in the wide gap $SMSC$ $A^{II}_{1-x}Mn_xB^{VI}$ alloys like $ZnMnSe$ is large. This large sp-d exchange interaction affects the energy bands of these materials resulting in interesting effects like extremely large Zeeman splitting of electronic levels and giant Faraday rotation. Only few investigations have been devoted on the band structure far from the Brillouin zone center. At the L point magneto-optical measurements clearly indicate that the magnitude of the effect is much less spectacular than at the Γ point. Another magneto-optical effect observed is Spin Flip Raman Scattering ($SFRS$) and studies have established the nature of $SFRS$ lines observed in σ^+ and σ^- circular polarised light in a magnetic field associated with spin flip transition of electrons bound to donors in $SMSC$.

V. TRANSPORT PROPERTIES

The influence of magnetic atoms on transport properties is ultimately related to the energetic position of d or f like open shells with respect to the Fermi level and band edges. This, as well as the degree of electron localisation on magnetic shells, are known to reflect competition between the on-site Coulomb repulsion between electrons (which tend to conserve the local character of d or f shells) and the delocalising influence of the hybridisation between extended states and magnetic orbitals. The nature of the magnetic ground state is determined by local distortions and spin-orbit coupling. $Fig.4$ shows the distances between energy levels of different transition metals in various hosts together with distances to the band edges of various II-VI semiconductors.

The exchange interaction causes spin-disorder scattering, spin splitting of electronic states and formation of magnetic polarons. Still another effect is the existence of ferromagnetic clouds around singly occupied local electronic states. These complexes known as bound magnetic polarons enhance binding energy and shrink the localisation radius of localised electrons.

VI. MAGNETIC POLARON EFFECT

This feature is ascribed to the magnetisation of DMS samples like $ZnMnSe$ and is magnetised by the motion of Bloch electrons through the crystal even in the absence of an applied magnetic field. If there is some donor impurity at some other site of the crystal, the Bloch electron can bind to this impurity in hydrogen like orbits. The radius of these orbits is very large and may encompass a large number of magnetic ions. The motion of the bound electron in its orbit across these magnetic ions presents similar magnetic effects as the free electron and the energy required to flip its spin by an antiferromagnetic polarisation of magnetic ions is called bound magnetic polaron energy.

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FIGURES

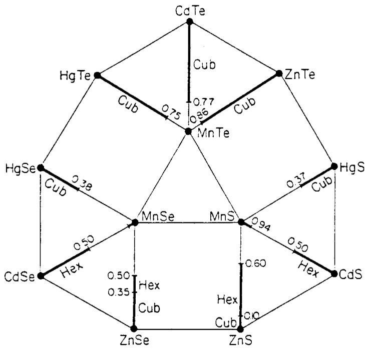

FIG. 1. $A^{II}_{1-x}Mn_xB^{VI}$ *alloys and their crystal structure*

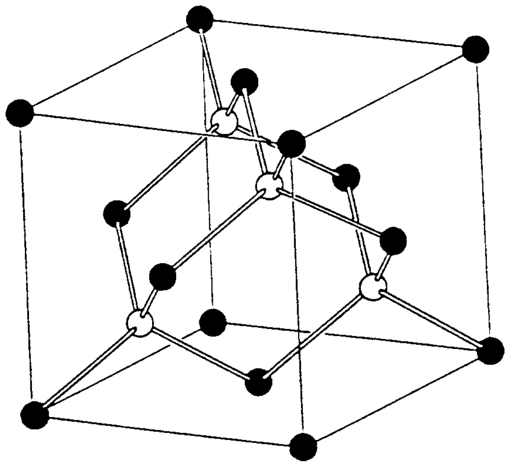

FIG. 2. *Zinc Blende Structure*

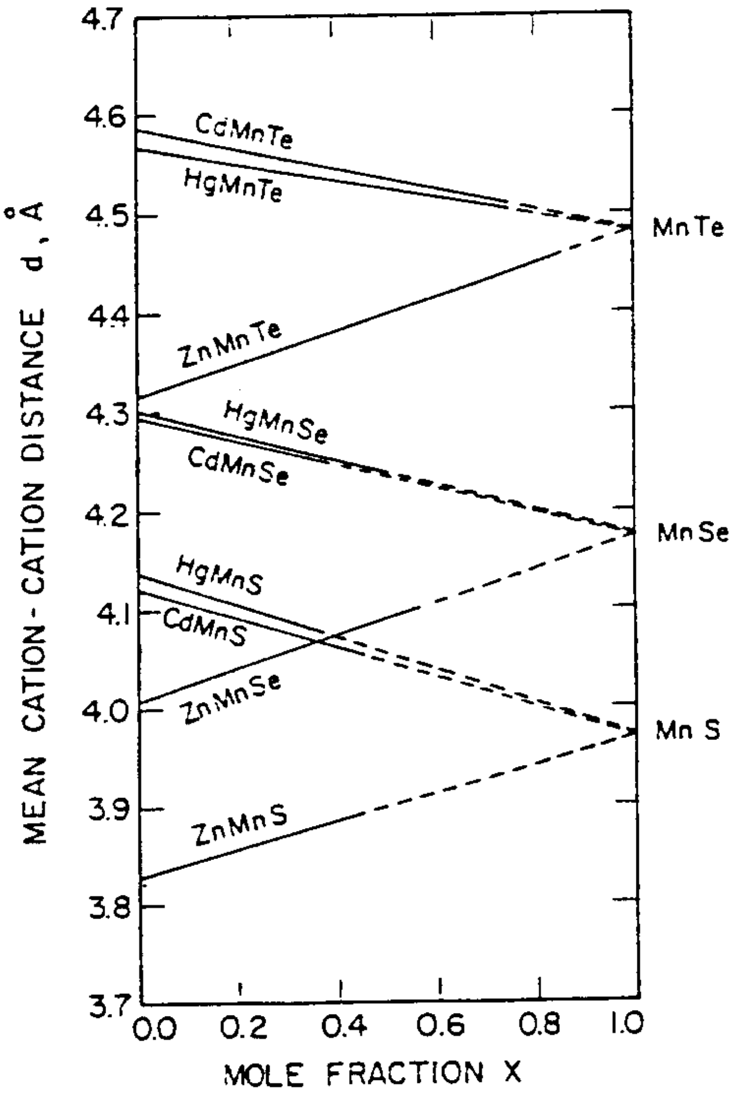

FIG. 3. *Mean cation-cation distance vs. Mn mole fraction*

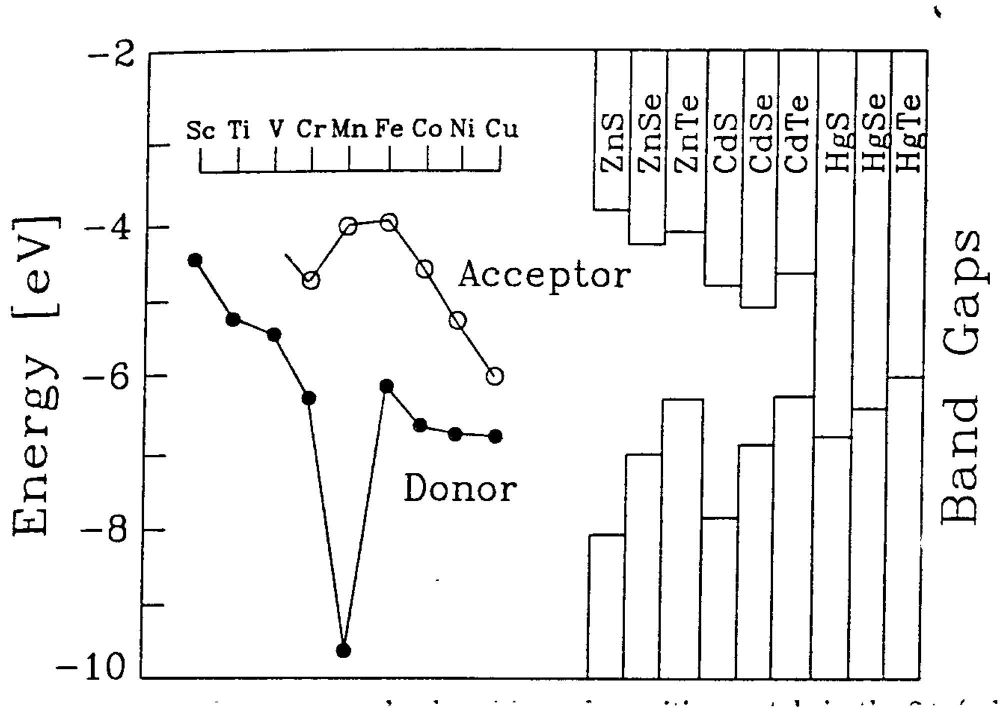

FIG. 4. *Approximate energy level positions o ftransition metals in the 2+(solid symbols) and 1+(open symbols) charge states relative to band edges of* $II-VI$ *compounds*