THE ROLE OF JAHN-TELLER EFFECT ON THE MAGNETIC
PROPERTIES OF Fe-BASED SEMIMAGNETIC SEMICONDUCTORS

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We present energy spectrum calculations of ^5E term of Fe^{++} ion taking into account crystal field, spin-orbit interaction, uniaxial stress, magnetic field and dynamic Jahn-Teller effect. Basing on the obtained energy spectra we calculate magnetic properties (specific heat and magnetization) of Fe-based Semimagnetic Semiconductors. We found that presence of the Jahn-Teller effect has very small influence on the magnetic properties at low temperatures.

INTRODUCTION

Energy spectrum of the ground multiplet of the Fe^{++} impurity in II-VI semiconductors is essential for optical and thermodynamic properties of Fe-based Semimagnetic Semiconductors (SMSC) [1,2,3]. Energetical structure of Fe^{++} dopant in II-VI compounds (CdTe, ZnS, ZnO) has been studied for a long time [3-9]. It was found that tetrahedral crystal field splits ^5D ($3d^6$) iron ground term into orbital doublet ^5E and orbital triplet $^5T_2$ (separated from ^5E term by $\Delta \approx 3000cm^{-1}$). Spin-orbit interaction splits furthermore these terms: ^5E into a singlet A_1 (Γ^1), a triplet T_1 (Γ^4), a doublet E (Γ^3), a triplet T_2 (Γ^5) and a singlet A_2 (Γ^2) (with separation roughly $K=15-20cm^{-1}$ between them) [4,5].
The simple model introduced in [5] including crystal field and spin-orbit interaction (denoted as Simple Crystal Field Model - SCFM) provides reasonable description of most of the experimental data of II-IV Fe-based SMSC [2,3,6,7,10,11,12,13,14].
However some experimental results cannot be described by this model. In particular in FIR absorption spectrum of CdTe:Fe too many optical transitions (compared with SCFM) were observed [5,8] and this fact was ascribed to dynamic Jahn-Teller (JT) effect (which increases number of allowed transitions). On the other hand magnetic specific heat of CdFeSe [15] was too large to result from simple 10-level ^5E multiplet [5], as described by SCFM.
In that respect, to check the role of the JT effect we performed model calculations for ^5E ground term of Fe^{++} ion

implementing JT coupling to SCFM in the way suggested in [8]. The obtained energy spectra are subsequently used for determination of magnetic properties (specific heat, magnetization) at low temperatures.

HAMILTONIAN

We assumed the full Hamiltonian of Fe^{++} ion in the form:

$$(1) \quad H = H_0 + H_{cf} + H_{so} + H_B + H_S + H_{osc} + H_{JT}$$

where:
- H_0 is Hamiltonian of free Fe^{++} ion without spin-orbit coupling. The ground term of H_0 is ^5D multiplet.
- H_{cf} describes tetrahedral crystal field splitting of ^5D level into ^5E and $^5T_2$. Energy separation between ^5E and $^5T_2$ is denoted by $\Delta(=10|Dq|)$.
- H_{so} describes spin-orbit coupling.
- H_B is magnetic field term.
- H_S describes uniaxial stress.
- H_{osc} is term describing oscillations of Fe^{++} ion and ligands.
- H_{JT} describes Jahn-Teller coupling.
Usually H_0 together with H_{cf} dominates electronic part of the full H and therefore one can assume basis functions of H in the form $f_i * g_j$ where $\{f_i\}_{i=1...25}$ are eigenfunctions of $H_0 + H_{cf}$ for ^5D multiplet and $\{g_j\}_{j=1,2,...}$ are eigenfunctions of H_{osc} ($\{g_j\}$ is infinite function set).
Due to problems with handling of large Hamiltonian matrices we limited our basis

from one side to ten f_1 eigenfunctions of ^5E term and from the other side to only few vibronic excitations (up to three oscillator levels, including the ground level i.e. $j=1..6$ [16]). The first limitation ($i_{max}=10$) neglects the ^5E, $^5T_2$ terms mixing and consequently Hamiltonians H_{SO}, H_B and H_S must be taken as effective operators [17] to provide correct energy spectrum (in the sense of second order perturbation calculations). The second limitation ($j_{max}=6$) neglects higher phonon excitations and is only important for the highest levels. On the other hand the lowest energy levels, which determine magnetic properties of Fe ion at low temperatures are influenced only slightly by this limitation.
Following [17] we assumed effective operators in the form:

–H_{SO} is taken to split the ^5E orbital into five equally spaced spin-orbital sublevels denoted as Γ^1, Γ^4, Γ^3, Γ^5, Γ^2 [8].

$$-H_B = \mu_B g_1 \mathbf{SB} + \tfrac{1}{2}\mu_B g_2 \{[3S_z B_z - (\mathbf{SB})]U_u +$$

$$+ \sqrt{3}[S_x B_x - S_v B_v]U_v\}$$

where μ_B is Bohr magneton, factor $g=2.0023$, $g_1 = g - (4\lambda/\Delta)$, $g_2 = -4\lambda/\Delta$, U_u and U_v are orbital operators defined to have matrix elements with respect to orbital electronic states ϕ_u, ϕ_v of ^5E term [8]

$$(2)\quad U_u = \begin{vmatrix} -1 & 0 \\ 0 & +1 \end{vmatrix} \qquad U_v = \begin{vmatrix} 0 & +1 \\ +1 & 0 \end{vmatrix}$$

–The form of effective uniaxial stress operator H_S depends on strain direction. For stress parallel to [001] it has symmetry of E representation and Hamiltonian [17]:

$$H_{S\_tetr} = C_P[(e_{zz}-\tfrac{1}{2}e_{xx}-\tfrac{1}{2}e_{vv})U_u + \sqrt{3}/2(e_{xx} -$$

$$+ e_{vv})U_v],$$

where e_{ij} denote strain tensor components [17], C_P is material dependent factor proportional to the applied stress, U_u and U_v are defined in Eq. (2).
For stress parallel to [111] H_S has symmetry T_2 and the form [17]:

$$H_{S\_trys} = C_P(2\lambda/\Delta)(S_x e_{vz}+S_v e_{zx}+S_z e_{xv})A_2,$$

where A_2 is orbital operator analogous to U_u, U_v:

$$A_2 = \begin{vmatrix} 0 & -i \\ +i & 0 \end{vmatrix}$$

We notice that trigonal distortion (i.e. stress along [111] direction) can be used to simulate hexagonal environment of the Fe ion.
–H_{osc} is Hamiltonian of two dimensional harmonic oscillator with energy $\hbar\omega_E$. We

use its eigenfunctions ($\{g_J\}$) $|F^m_u F^n_v\rangle$ (u, v denotes rows of the irreducible representation E and m, n are non-negative integer values such that $m+n<3$). H_{osc} has eigenenergies:

$$H_{osc}|F^m_u F^n_v\rangle = \hbar\omega_E(n+\tfrac{1}{2}+m+\tfrac{1}{2})|F^m_u F^n_v\rangle.$$

–The dynamic JT Hamiltonian was assumed in the following form [8]:

$$H_{JT} = A(U_u Q_u + U_v Q_v),$$

where U_u, U_v are operators given by Eq. (2) Q_u, Q_v are linear combinations of the ion displacements classified according to rows of E representation.
We considered coupling between ^5E orbital doublet and vibration of E symmetry ($\in$ mode). We used in calculations coupling constant $V_{JT} = A/(m\omega_E/\hbar)^{1/2})$ (m is effective mass of vibrational mode).
We mention that for $V_{JT}=0$ electronic and oscillator systems are decoupled and the eigenenergies of Eq. (1) are just the sum of the electronic energies and vibrational energies of H_{osc}. Electron-oscillator vibronic state $\Gamma^K|F^m_u F^N_v\rangle$ is called m+n-phonon exited Γ^K state.

RESULTS

The model described above needs some material parameters to be inserted: crystal field parameter Δ, spin-orbit parameter λ, energy of the coupled phonon $\hbar\omega_E$ and JT strength coupling parameter V_{JT}.
For our model calculations we have chosen $\Delta = 2570\text{cm}^{-1}$ and $\lambda = -82.5\text{cm}^{-1}$ producing $K = 15.9\text{cm}^{-1}$ i.e the value close to the gravity center of the energy gaps A_1-A_2, E for CdFeSe [18]. Both $\hbar\omega_E$ and V_{JT} are parameters known with poor accuracy and were treated as fitting parameters in previous papers [8, 22, 25].
Typical energy spectrum is shown in Fig.1, where vibronic energy levels for ^5E term of Fe^{++} ion are plotted versus JT coupling parameter V_{JT}. Generally speaking JT coupling leads to vibronic energy levels splitting. The common behaviour of the energy spectrum is decrease of energy separation between Γ^1 and $\Gamma^1+\hbar\omega_E$ levels (i.e. E(Γ^1, $\Gamma^1+\hbar\omega_E$)) as well as energy distance between Γ^1 and Γ^4 levels with increasing JT coupling. For high phonon energy ($\hbar\omega_E \gg K$) the primary effect of JT coupling is reduction of the intervals between ^5E states. However this effect can be also accounted for decrease of K parameter. Large splittings can be seen even for small coupling when phonon exited states are close to other levels (see $\Gamma^1+\hbar\omega_E$ and Γ^3).
We note that JT coupling influences only slightly the ground term field and stress dependencies. This situation is shown in Fig.2, where we display energy spectrum as a function of magnetic field (in the presence of trigonal strain, simulating
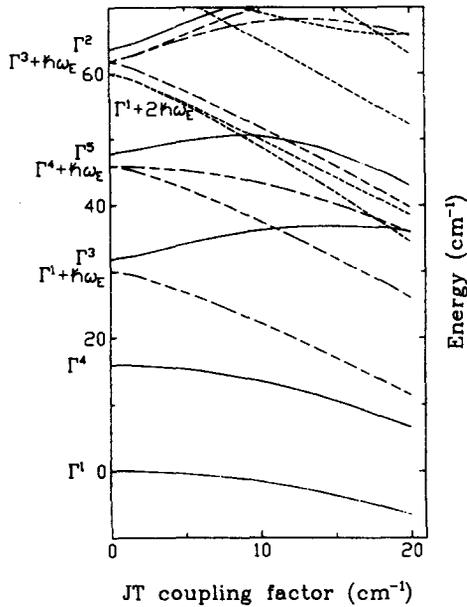
Fig.1 The lowest energy levels for ^5E term of Fe++ ion in cubic crystal field as a function of Jahn-Teller coupling. Five 0-phonon excited levels (Γ^1, Γ^4, Γ^3, Γ^5, Γ^2) are marked with the solid lines. Dashed lines denotes 1- and 2- phonon excited levels. Crystal field parameter $\Delta=2570cm^{-1}$, spin-orbit parameter $\lambda=-82.5cm^{-1}$ (i.e. parameter $K=15.9cm^{-1}$) energy of the coupled phonon $\hbar\omega_E=30cm^{-1}$.
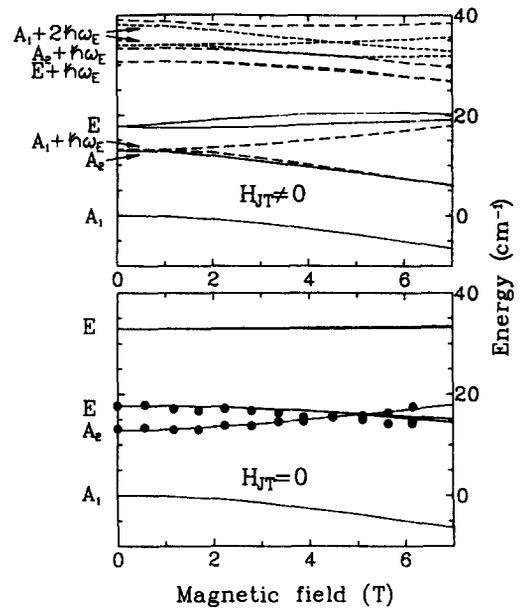

Fig.2 Low energy levels of ^5E term of Fe++ ion in hexagonal crystal for $V_{JT}=0$ (down) and $V_{JT}=20cm^{-1}$ (up) versus magnetic field. Levels are marked according to C_{3v} irreducible representations. Phonon-exited states are marked with dashed lines (for $V_{JT}=0$ phonon exited states are not plotted). Parameters (for $V_{JT}=0$: $C_P=115cm^{-1}$, $\lambda=-83.2cm^{-1}$; for $V_{JT}=20cm^{-1}$: $C_P=174cm^{-1}$, $\lambda=-95.3cm^{-1}$, $\hbar\omega_E=20cm^{-1}$; in both cases $\Delta=2570cm^{-1}$) are set to fit energy separation A_1-A_2, A_1-E [18]. . Circles represent experimental data from Raman experiment for CdFeSe [23].

hexagonal crystal case; magnetic field is parallel to the crystal hexagonal axis). The behaviour of low lying levels in the absence as well as in the presence of JT effect ($\hbar\omega_E=20cm^{-1}$, $V_{JT}=20cm^{-1}$) is shown. The constant K and stress coefficient were chosen to fit CdFeSe data ($E(A_1, A_2)=12.8$, $E(A_1, E)=17.6cm^{-1}$) [18]) in both cases ($V_{JT}=0$ and $V_{JT}>0$). On the other hand drastic influence of the JT effect on excited states can be noticed. For $V_{JT}=0$ levels A_2 and E do cross, whereas for $V_{JT}>0$ noncrossing of the levels is observed due to the interaction with $A_1+\hbar\omega_E$ level (essential is here such small phonon energy $\hbar\omega_E$ that $A_1+\hbar\omega_E$ level lies between A_2 and E).
Basing on the calculated energy spectrum magnetic moment of the Fe++ ion and thus SMSC crystal magnetization can be determined [19]. Fig.3 shows magnetization versus magnetic field for hexagonal crystal (simulated by trigonal stress) for B parallel and perpendicular to the crystal c axis. Both cases: zero and nonzero JT coupling (h $_E=20cm^{-1}$, $V_{JT}=20cm^{-1}$) are shown. We notice that for $V_{JT}=0$ magnetization does not depend on phonon energy h $_E$. Parameter K and strain coefficient are the same as for Fig. 2.

One can notice that low temperature magnetization is practically JT coupling independent which is the consequence of very weak ground state magnetic field dependence on JT effect, as mentioned above.
Specific heat C_V for an electron-vibrational system (Fe++ ion and ligands) is for $V_{JT}=0$ a sum of specific heat of electronic levels (C_M, magnetic specific heat) and specific heat of vibrational levels (C_{osc}): $C_V=C_M+C_{osc}$. For $V_{JT}>0$ we use still the same formulae and therefore magnetic contribution to specific heat is obtained as $C_M=C_V-C_{osc}$. Results of C_M calculated in this way are shown in Fig. 4 (solid lines). Parameter K is set to fit the energy separation $E(\Gamma^1, \Gamma^3)=15.9cm^{-1}$ for $V_{JT}=0$ as well as for and $V_{JT}>0$ [20].
At low temperatures specific heat C_M depends mostly on the energy gap between the ground and the first excited states. Since we keep the same energy distance $E(\Gamma^1, \Gamma^3)$ for both cases $V_{JT}=0$, $V_{JT}>0$, the presence of JT coupling does not influence C_M significantly at low
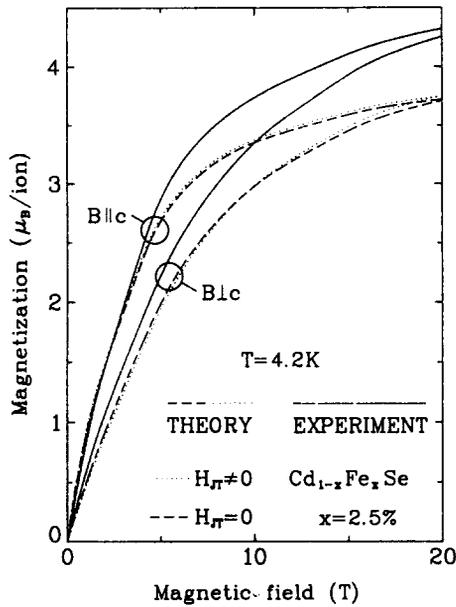
Fig.3 Magnetization of Fe++ ion in hexagonal crystal versus magnetic field (parallel and perpendicular to crystal c axis). Dashed and dotted lines represent theoretical predictions (T=4.2K, parameters Δ, λ, C_P, $\hbar\omega_E$ as in Fig.2). Solid lines denotes experimental results for $Cd_{.975}Fe_{.025}Se$ [24].
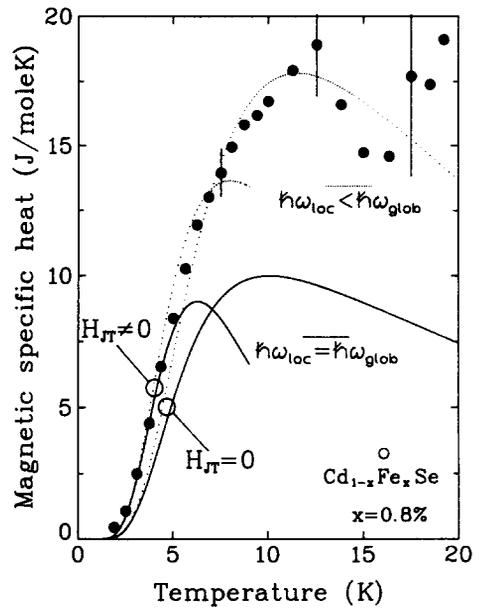

Fig.4 Magnetic specific heat per mole of Fe++ ions (cubic environment) versus temperature. Solid lines: C_H calculated assuming only global phonons ($V_{JT}=0$: $\lambda =-82.5cm^{-1}$, $V_{JT}=20cm^{-1}$: $\lambda =-94.7cm^{-1}$, $\hbar\omega_E =20cm^{-1}$)). Dotted lines represent calculations including local and global phonons ($\hbar\omega_{LOC}=20cm^{-1}$, $\hbar\omega_{GLOB}=40cm^{-1}$, for $V_{JT}=0$ $\lambda =-82.5cm^{-1}$, for $V_{JT}=20cm^{-1}$ $\lambda =-94.7cm^{-1}$). Points: experimental data for $Cd_{.992}Fe_{.008}Se$ [15].

temperatures [21]. It shifts the maximum of $C_H(T)$ to lower temperatures but does not change very much its maximum value.

DISCUSSION

Previous calculations of the JT effect for the ^5E term of the Fe++ ion were compared to CdFeTe FIR absorption data. Vallin [8] and Vogel [22] have shown that one can improve the description of the spectroscopic data taking into account JT effect, although not all optical transitions were fully explained. Present calculations are more concentrated on vibrational coupling effects in the presence of magnetic field and external stress.

Spectroscopic data of CdFeSe (Raman experiment) [23], in particular observed crossing of E and A_2 levels, are in good agreement with Simple Crystal Field Model (Fig.2). Therefore in this case Jahn-Teller effect does not seem to play important role (or the phonon energy is appreciably higher than used by us, see preceding section).

Moreover we found that even for apreciable JT coupling magnetic specific heat (its maximum value) is rather weakly influenced by JT effect (Fig. 4). Thus it is evident that problems in describing magnetic specific heat of CdFeSe [15] (Fig.4) can not be explained by JT effect. We believe this problem was

rather due to incorrect procedure of extracting C_H from total heat capacity. Magnetic specific heat was obtained by subtracting C_{latt}(CdFeSe) from total heat capacity C_v(CdFeSe):

(3) $C_m(CdFeSe)=C_v(CdFeSe)-C_{latt}(CdFeSe)$

where C_{LATT}(CdFeSe) is specific heat of "nonmagnetic" CdFeSe lattice [15]. C_{LATT} was modelled by CdSe and ZnSe lattices specific heat [15]. This method accounts only for global vibrations of the lattice and obviously neglects the presence of local phonons (associated with Fe impurity) in doped material. In the case of pronounced differences in energies of local (CdFeSe) and global (CdSe) phonons magnetic specific heat determined by formula (3) can substantially differ from the proper value. In particular if $\hbar\omega_{glob}>\hbar\omega_{loc}$ the true CdFeSe phonon spectrum is more dense than the spectrum resulting in C_{latt} used in (3), which leads to overestimation of C_m. We believe this is actually our case.

For low temperature magnetization the difference between experimental data in high magnetic field and SCFM theory prediction is shown in Fig.3. However one can notice that this difference does not result from JT effect. We think it is

rather due to neglection of large clusters of Fe ions in the theoretical model [24].

CONCLUSIONS

We calculate Fe^{++} ion energy spectrum using Simple Crystal Field Model including Jahn-Teller effect. No appreciable influence of JT coupling on magnetic properties in low temperatures is found. This reflects the fact that JT coupling affects mostly orbital part of wavefunctions but orbital momentum of Fe ion ^5E ground term is mostly quenched. It seems that FIR spectroscopy is much more appropriate to trace the JT effect in our case. We conclude that as far as no precise optical experiments for considered materials (CdFeSe, CdFeTe) are performed, Jahn-Teller coupling need not to be included into description of magnetic properties of Fe-based Semimagnetic Semiconductors.

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19. We assume here that only isolated Fe ions contribute to magnetization, which is reasonable approximation for low x [12].
20. Specific heat $C_H(T)$ is plotted only in the temperature ranges were finite vibrational wavefunctions base does not influence C_H significantly.
21. For $\hbar\omega_E=20$, $V_{JT}=20cm^{-1}$ vibronic coupling moves $\Gamma^1+\hbar\omega_E$ level below first exited Γ^4 state
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