Bauer, Pascher and Zawadski, 1992

REVIEW ARTICLE

Magneto-optical properties of semimagnetic lead chalcogenides

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Received 21 February 1992, accepted for publication 9 March 1992

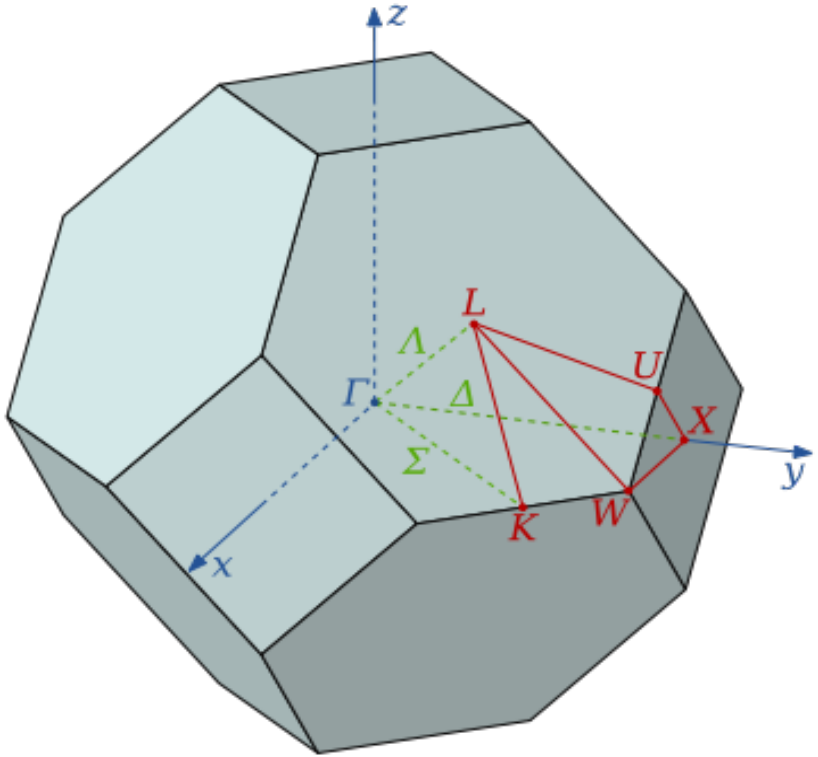
Bauer, Pascher and Zawadski, 1992

Abstract. Magneto-optical properties of PbTe and PbSe alloyed with paramagnetic ions Mn and Eu are reviewed. The $k \cdot p$ theory of the band structure of IV–VI compounds is presented, taking into account the narrow energy gaps and strong spin–orbit interactions in the materials. The exchange interaction between the paramagnetic ions and mobile carriers is included in the framework of the mean-field approximation. The experimental data of various authors on magnetization, interband magneto-optics, intraband magneto-optics and four-wave mixing are presented. All results are successfully described by the theory, treating the exchange integrals as adjustable parameters. It is shown that the exchange interaction is of particular importance for the valence bands. Differences between semimagnetic behaviours of Mn-based and Eu-based systems are emphasized as well as those between the IV–VI and II–VI semimagnetic compounds.

Introduction

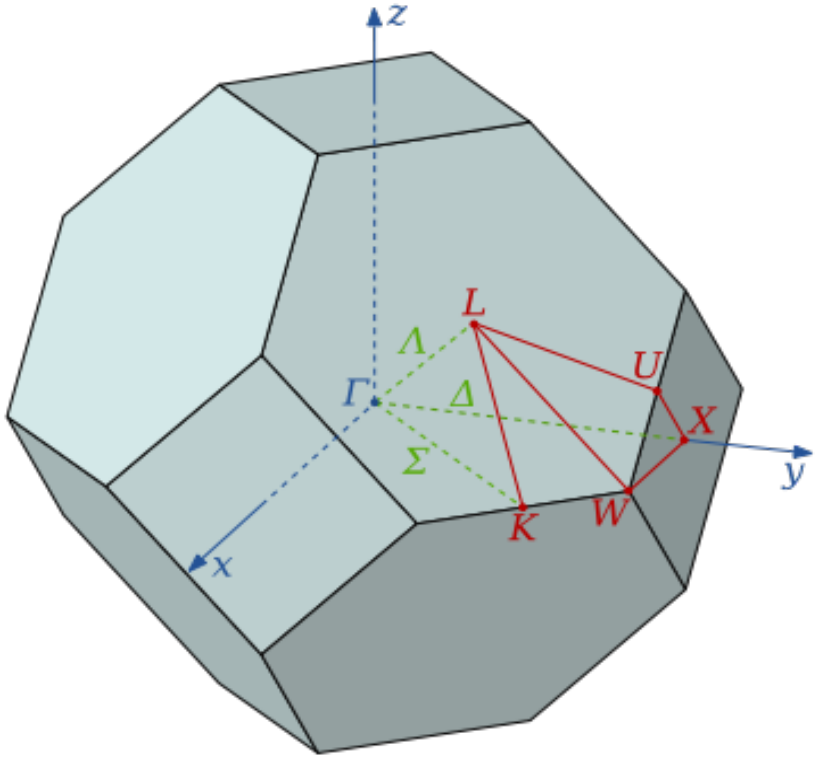
- Lead salts: PbSe, PbTe, etc
- Small energy gaps → strong **k·p** interaction → non parabolic dispersion
- Small electron and hole effective mass
- Large spin orbit coupling effects due to size of Pb nucleus
- Compounds such as PbSe with substitutions of paramagnetic materials such as Mn, Eu
- Paramagnetic ions influence electron/hole mobility

Theory



Geometry of the Brillouin Zone

- Band extrema are at L point
- Choose <111> direction as the z axis

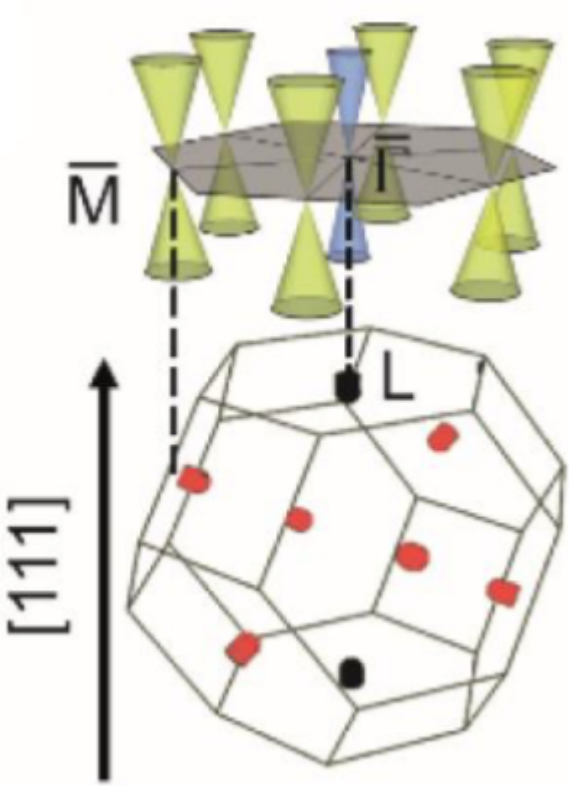


Terminology

- Longitudinal direction is <111>, parallel to the major axis of the central valley
- Transverse direction is in the plane normal to <111>
- Quantities like m_l, m_t refer to longitudinal/transverse
- Isotropy in the transverse plane, anisotropy between longitudinal and transverse directions

Geometry of the Brillouin Zone

- Anisotropy causes Fermi surface to be ellipsoidal at each L point
- These ellipsoids are oriented differently with respect to any fields
- Variable ϕ denotes angle between <111> and external field



Hamiltonian

$$\hat{H} = \frac{1}{2m}(\mathbf{p} + e\mathbf{A})^2 + V_0(\mathbf{r}) + H_{SO}$$

- Solutions have form $\psi(\mathbf{r}) = \sum_n f_n(\mathbf{r}) u_n(\mathbf{r})$

- Bloch (Luttinger-Kohn) functions satisfy the hamiltonian
- We want to peel these away and focus on envelope functions only

Effective Hamiltonian

$$\int u_m^* \left(\frac{1}{2m}(\mathbf{p}+e\mathbf{A})^2 + V_0(\mathbf{r}) + H_{SO} \right) \sum_n f_n(\mathbf{r}) u_n(\mathbf{r})\, d\mathbf{r} = \int u_m^* E \sum_n f_n(\mathbf{r}) u_n(\mathbf{r})\, d\mathbf{r}$$

$$\sum_n H'_{mn} f_n = E f_m$$

- We describe effective hamiltonian in terms of **P** and **π**:

$$\mathbf{P} = \mathbf{p} + e\mathbf{A}$$

$$\boldsymbol{\pi} = \mathbf{p} + \frac{\hbar}{4mc^2}(\boldsymbol{\sigma} \times \boldsymbol{\nabla} V)$$

- These are the vector potential and spin orbit couplings of the momentum

Effective Hamiltonian

- The result is the $\mathbf{P}\cdot\boldsymbol{\pi}$ Hamiltonian
- Elements of this matrix can be expressed via band edge valence band functions

$$V^{+} = \mathrm{i}\cos\theta^{+}R\uparrow + \sin\theta^{+}S_{+}\downarrow$$

$$V^{-} = \mathrm{i}\cos\theta^{+}R\downarrow + \sin\theta^{+}S_{-}\uparrow$$

- And similarly the conduction band functions (for PbSe)

$$C^{+} = -\cos\theta^{-}Z\uparrow + \sin\theta^{-}X_{+}\downarrow$$

$$C^{-} = \cos\theta^{-}Z\downarrow + \sin\theta^{-}X_{-}\uparrow .$$

Atomic Orbitals

- $|R\rangle$ = atomic s orbital (spherical symmetry)
- $|X_{\pm}\rangle$, $|Z\rangle$ = atomic p orbitals (oriented along an axis)
- $|S_{\pm}\rangle$ = atomic d orbitals, oriented along an axis but with some in plane components

Effective Hamiltonian

- In this basis, many matrix elements can be simplified to the momentum, vector potential and a velocity term
- The velocity term absorbs tricky features like mixing parameters cos(θ), sin(θ) into something we can treat like an experimental parameter

$$\frac{1}{m_0}\langle V^+|\pi|C^+\rangle \cdot \boldsymbol{P} = v_t P_z$$

$$\frac{1}{m_0}\langle V^+|\pi|C^-\rangle \cdot \boldsymbol{P} = \sqrt{2} v_t P_-$$

$$\frac{1}{m_0}\langle V^-|\pi|C^+\rangle \cdot \boldsymbol{P} = \sqrt{2} v_t P_+$$

$$\frac{1}{m_0}\langle V^-|\pi|C^-\rangle \cdot \boldsymbol{P} = -v_t P_z$$

Effective Hamiltonian

$$\begin{bmatrix} \hat{V}^+ & \frac{1}{2} g_t^+ \mu_B B_x & v_l P_z & \sqrt{2} v_t P_- \\ \frac{1}{2} g_t^+ \mu_B B_x & \hat{V}^- & \sqrt{2} v_t P_+ & -v_l P_z \\ v_l P_z & \sqrt{2} v_t P_- & \hat{C}^+ & \frac{1}{2} g_t^- \mu_B B_x \\ \sqrt{2} v_t P_+ & -v_l P_z & \frac{1}{2} g_t^- \mu_B B_x & \hat{C}^- \end{bmatrix} \tag{13}$$

where

$$\hat{V}^{\pm} = \frac{-E_g}{2} - \frac{P_x^2 + P_y^2}{2m_t^+} - \frac{P_z^2}{2m_l^+} \pm \frac{1}{2} g_l^+ \mu_B B_z \tag{14}$$

$$\hat{C}^{\pm} = \frac{+E_g}{2} + \frac{P_x^2 + P_y^2}{2m_t^-} + \frac{P_z^2}{2m_l^-} \pm \frac{1}{2} g_l^- \mu_B B_z \tag{15}$$

Simplified Effective Hamiltonian

$$\begin{pmatrix} -\frac{E_g}{2} & 0 & 0 & 0 \\ 0 & -\frac{E_g}{2} & 0 & 0 \\ 0 & 0 & \frac{E_g}{2} & 0 \\ 0 & 0 & 0 & \frac{E_g}{2} \end{pmatrix}$$

for $\mathbf{B} = \mathbf{0}$, $\mathbf{P} = \mathbf{0}$

Simplified Effective Hamiltonian

- What's left out
  - External Field Effects
  - Spin orbit effects
  - Far band contributions to the effective masses ($m^{\pm}$'s in the diagonal terms)
  - Far band contributions to the gyromagnetic ratios ($g^{\pm}$'s)
  - Anisotropy of velocity terms in transverse vs. longitudinal direction

Summary so far

- Anisotropy gives us ellipsoidal Fermi surfaces at each L point
- Hamiltonian includes vector potential and spin orbit coupling
- Spin orbit coupling makes us mix different spin states for our basis functions

Landau Levels

- **B** = [0, 0, B] → Landau gauge **A** = [0, Bx, 0]
- This gets us x^2 terms from the $\mathbf{P}^2$ terms
- Solutions in x are harmonic oscillator wavefunctions
- Solutions in y, z are free particles
- This method allows us to find energies analytically
- Specifically we find E(B)

$$\psi_n = \exp(ik_z z) \begin{bmatrix} \alpha_1|n\rangle \\ \alpha_2|n+1\rangle \\ \alpha_3|n\rangle \\ \alpha_4|n+1\rangle \end{bmatrix}$$

Landau Levels

- Energy levels are determined as functions of
  - Landau numbers n
  - Cyclotron frequencies ω
  - Spin g-values g

$$E_{V,n,-}^{C,n,+} = \frac{1}{2}(\hbar\omega_l^-(n+\frac{1}{2}) + \hbar\omega_l^+(n+\frac{3}{2}) + \frac{1}{2}\mu_B B(g_l^- - g_l^+))$$

$$\pm\frac{1}{2}\sqrt{(E_g + \hbar\omega_l^-(n+\frac{1}{2}) - \hbar\omega_l^+(n+\frac{3}{2}) + \frac{1}{2}\mu_B B(g_l^- + g_l^+))^2 + 4E_g\hbar\omega_{CV}(n+1)}$$

$$E_{V,n,-}^{C,n,+} = fbc(B) \pm \sqrt{(E_g + fbc(B))^2 + 4E_g * nbc(B)}$$

Landau Levels

- Naming:
  - Landau quantum number n and Kramer pair designation +/-
  - Written $|n, + >$ or n^+
  - Each band (valence and conduction) has this same set of landau levels
- B dependence
  - Large E_g limit → linear in B

Magnetization

- Bulk matrix already accounts for effects of external field **B**
- Paramagnetic ions may also cause an internal magnetic field **H** (assumed to be in xz plane)
- Define $\cos(\phi) = \mathbf{H} \cdot \mathbf{z}$
- Account for these effects with an exchange matrix

Exchange Matrix

- Exchange hamiltonian depends on ion spin and charge carrier spin:

$$\hat{H}_{ex} \sim \mathbf{S} \cdot \boldsymbol{\sigma}$$

$$\hat{H}_{ex} \sim |\mathbf{S}|(\sigma_x \sin\phi + \sigma_z \cos\phi)$$

$$\langle V^+|\sigma_z + \sigma_x|V^+\rangle = \langle V^+|\sigma_z|V^+\rangle + \langle V^+|\sigma_x|V^+\rangle$$

Exchange Matrix

- Nonzero z spin terms are diagonal

$$\langle V^+|J\sigma_z|V^+\rangle = a_1 - a_2 \qquad \langle C^+|J\sigma_z|C^+\rangle = b_1 - b_2$$

$$\langle V^-|J\sigma_z|V^-\rangle = a_2 - a_1 \qquad \langle C^-|J\sigma_z|C^-\rangle = b_2 - b_1$$

- Z spin only couples bands to themselves
- a_1, a_2 etc. can be considered input parameters

Exchange Matrix

- Physical meaning of the exchange terms

$$a_1 = (1/\Omega_0)\langle R|J|R\rangle \cos^2\theta^+$$

$$a_2 = (1/\Omega_0)\langle S_\pm|J|S_\pm\rangle \sin^2\theta^+$$

$$b_1 = (1/\Omega_0)\langle Z|J|Z\rangle \sin^2\theta^-$$

$$b_2 = (1/\Omega_0)\langle X_\pm|J|X_\pm\rangle \cos^2\theta^-$$

Exchange Matrix

- Nonzero x spin terms are off diagonals of diagonal blocks

$$\langle V^+ | J\sigma_x | V^- \rangle = a_1$$

$$\langle C^+ | J\sigma_x | C^- \rangle = -b_1$$

- Z spin only couples valence to its valence counterpart, conduction to its conduction counterpart

Exchange Matrix

$$\begin{bmatrix} A\cos\phi & a_1\sin\phi & 0 & 0 \\ a_1\sin\phi & -A\cos\phi & 0 & 0 \\ 0 & 0 & B\cos\phi & b_1\sin\phi \\ 0 & 0 & -b_1\sin\phi & -B\cos\phi \end{bmatrix}$$

- Diagonalized exchange matrix for $\phi = 0$ has eigenvalues A, -A, B, -B
- These are linear shifts to the previously determined energies
- In general levels are shifted by AB^*

Exchange Matrix

- B^* is the modified Brillouin function
- Can be determined from the magnetization curve M(B), which also depends on it

$$B^* = \tfrac{1}{2} S_0 x B_S\left(\frac{2S\mu_B|B|}{k_B(T+T_0)}\right)$$

Summary so far

- Can determine energy levels of bulk **k·p** hamiltonian
  - Use Landau Level method
  - Depend on cyclotron frequencies which are B dependent
    - Far band contributions and near band contributions
  - Depend on energy gap which is B independent
- Exchange matrix modifies energy levels
  - Depends on $\sigma_{x,z}$ matrix elements a_1, b_1, etc
  - These can be treated as adjustable parameters
  - Depends on modified Brillouin function B^*

Experiment

Magnetization

- Magnetization vs field measurements allow determination of parameters S_0, T_0 in the Brilloun function

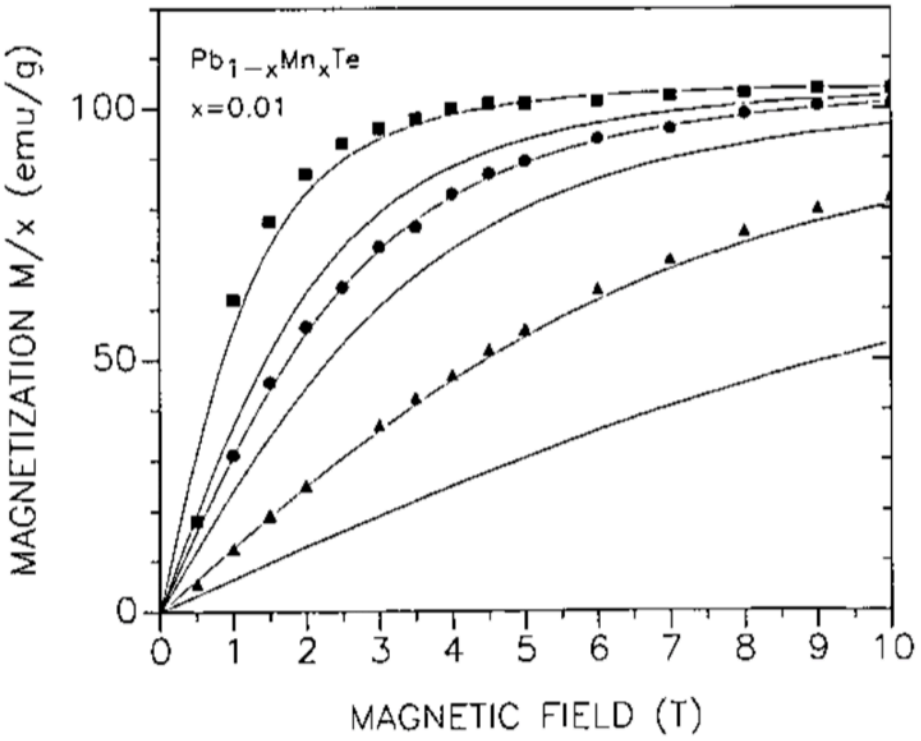


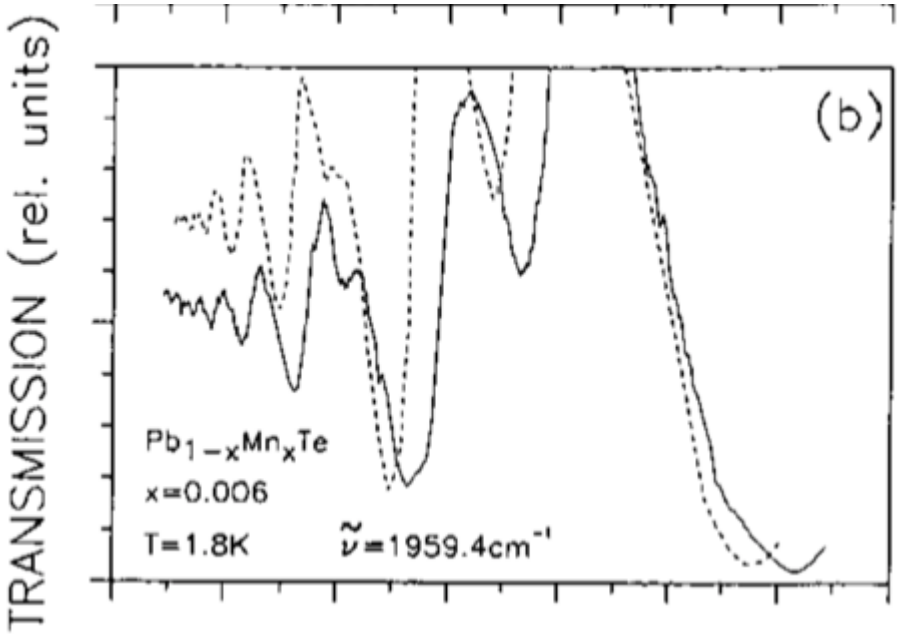
Figure 6. Magnetization of epitaxial $Pb_{1-x}Mn_xTe$ versus magnetic field with T as parameter. Experimental data ■ ($T = 2$ K), ● ($T = 4.2$ K), ▲ ($T = 15$ K). Full curves:

Experiment

- Many of the Hamiltonian parameters mentioned can be determined experimentally
- Bauer's method is to use magneto-optical measurements to measure interband transition energies as a function of field (ie E(B))

Experiment

- Geometry of the interband transition measurements (thin epitaxial samples)
  - Faraday: **k** || **B**
    - **B** || **E**
    - **B** ⊥ **E**
  - Voigt: **k** ⊥ **B**
    - **B** || **E**
    - **B** ⊥ **E**
- Need to probe all these geometries because each has different selection rules



Fan charts

- Show interband magnetooptical transitions
- Data points ▲ come from transmission peaks at a given B, energy (previous graph)
- Linear fits of these provide energy level parameters

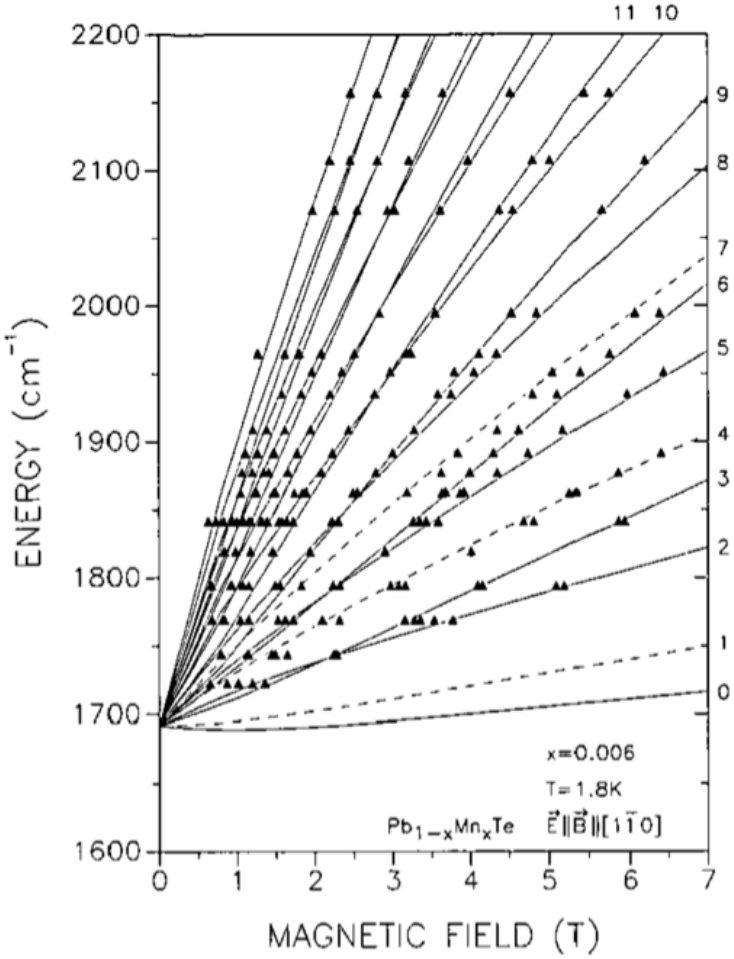


Figure 9. Fan chart for interband magneto-optical transition in the Voigt geometry for $Pb_{1-x}Mn_xTe$, $\boldsymbol{E} \| \boldsymbol{B} \| [1\bar{1}0]$. Experimental data, ▲, in $\boldsymbol{E} \| \boldsymbol{B}$ polarization. Full curves: calculated values for $\phi = 90°$; broken curves: $\phi = 35.26°$. 0: $0^- \rightarrow 0^-$ ($\phi = 90°$); 1: $0^- \rightarrow 0^-$ ($\phi = 35.26°$); 2: $0^+ \rightarrow 0^+$ ($\phi = 90°$); 3: $1^- \rightarrow 1^-$ ($\phi = 90°$); 4: $0^+ \rightarrow 0^-$ ($\phi = 35.26°$); 5: $1^+ \rightarrow 1^+$ ($\phi = 90°$); 6: $2^- \rightarrow 2^-$ ($\phi = 90°$); 7: $0^+ \rightarrow 0^+$ ($\phi = 35.26°$); 8: $2^+ \rightarrow 2^+$ ($\phi = 90°$); 9: $3^- \rightarrow 3^-$ ($\phi = 90°$); 10: $3^+ \rightarrow 3^+$ ($\phi = 90°$); 11: $4^- \rightarrow 4^-$ ($\phi = 90°$). (After Pascher *et al* 1989.)

Fan charts

- Intercept gives energy gap
- Splitting (low n values) gives far band effects and exchange parameters
- For large energy gaps, expect linear behavior in B after Taylor expansion
- Slope gives velocity like terms

Band parameters

- Most of the important features of the bulk Hamiltonian can be determined by fitting this kind of experimental data from interband transitions

Parameter	Sample			
	PbSe $x = 0$	$Pb_{1-x}Eu_xSe$ $x = 0.012$	$Pb_{1-x}Eu_xSe$ $x = 0.0142$	$Pb_{1-x}Eu_xSe$ $x = 0.024$
E_g (meV)	146.3 ± 0.3	181.1	189.1	219.0
$2P_\perp^2/m_0$ (eV)	3.6 ± 0.1	3.6	3.6	3.6
$P_\perp/P_\parallel$	1.35 ± 0.02	1.40	1.40	1.40
m_t^-/m_0	0.27 ± 0.05	0.27	0.27	0.27
m_l^-/m_0	0.95 ± 0.2	0.95	0.95	0.95
m_t^+/m_0	$+0.29 \pm 0.05$	+0.29	+0.29	+0.29
m_l^+/m_0	$+0.37 \pm 0.1$	+0.37	+0.37	+0.37
g_t^-	-4.0 ± 1	−4.0	−4.0	−4.0
g_l^-	-8.1 ± 1	−8.1	−8.1	−8.1
g_t^+	5.4 ± 1	5.4	5.4	5.4
g_l^+	7.3 ± 1	7.3	7.3	7.3

Exchange parameters

- Exchange parameters can also be deduced in this way

Table 3. Exchange parameters.

	T (K)	A (meV)	a_1 (meV)	B (meV)	b_1 (meV)
Mn content					
$x = 0.010$	1.8	-182 ± 15	-288 ± 15	-33 ± 10	27 ± 5
$x = 0.008$	1.8	-192 ± 15	-315 ± 15	-66 ± 10	55 ± 5
$x = 0.006$	1.8	-225 ± 15	-314 ± 15		50 ± 5
$x = 0.006$	3.5	-142 ± 15	-279 ± 15	-41 ± 10	50 ± 5
$x = 0.006$	4.4	-124 ± 15	-279 ± 15	-51 ± 10	51 ± 5
$x = 0.006$	12.0	-51 ± 15	-288 ± 15		59 ± 5
Eu content					
$x = 0.0142$	1.7	32 ± 3	30 ± 3	6.6 ± 1.6	7.5 ± 1.6
$x = 0.024$	1.7	24.4 ± 3	20 ± 3	6 ± 1.6	2.5 ± 1.6
$x = 0.024$	6.0	24 ± 3	18 ± 3	7.8 ± 1.6	0.9 ± 1.6
$x = 0.024$	12.0	22 ± 3	17.5 ± 3	9.7 ± 1.6	2.2 ± 1.6

Further Experiments

- Temperature dependence of the exchange interaction
- Temperature dependence of the effective gyromagnetic ratios
- Composition dependence of the effective gyromagnetic ratios

Discussion

- Valence bands are more affected by exchange effects
- g-factors are also affected by the exchange parameters
  - Magnitude
  - Sign
  - Anisotropy
  - As compared to when calculated from energy gaps and momentum matrix elements alone
- It is impossible to extract the pure exchange integrals $a_1 = (1/\Omega_0)\langle R|J|R\rangle \cos^2\theta^+$

  because of the confounding effects of $\cos(\theta)$, $\sin(\theta)$