

Collective light-mediated magnetoexciton transition in the transparency band of a crystal

É. L. Nagaev and É. B. Sokolova

(Submitted 16 May 1978)

Pis'ma Zh. Eksp. Teor. Fiz. **28**, No. 3, 105–108 (5 August 1978)

The ground state of a semiconductor containing ions with partially filled d or f shells becomes unstable to production of Frenkel excitons on these ions when illuminated by light having a frequency in the transmission band.

PACS numbers: 78.50.Ge, 75.10.Dg, 71.35.+z

The energy spectrum of a number of semiconductors that contain ions of transition or rare-earth elements includes low-frequency Frenkel excitons on these ions. They are due to the effect of the crystal field on the states of the partially filled d or f shells. The production of such excitons can be accompanied by a change of the crystal magnetization. For example, in some materials ions with even number of d or f electrons are diamagnetic in the ground state, but only a small amount of energy can change them into a state with nonzero angular momentum (this corresponds usually to production of a triplet exciton). The situation is different in the so-called singlet magnets, where the angular momentum J of the ions in the ground state differs from zero, but its average projections are equal to zero. A nonzero magnetization of the ion sets in when an excited state is mixed with the ground state.

The main result of the present paper is that low-frequency Frenkel excitons can be collectively excited by light whose frequency lies in the crystal transmission band. This non-absorptive excitonic transition is due to the fact that the light intermixes the electron states in the conduction and valence bands, and by the same token enhances the interaction of the excitons with the valence-band electrons. As a result, if the light is intense enough, the ground state of the ions can become unstable to exciton production, and spontaneous magnetization appears in the crystal.

Photo-enhancement of the electron-exciton interactions occurs when the valence band is made up of states of anions with completely filled electron shells, and the conduction band is made up of the outer orbits of cations with partially filled d or f shells. Since this is mainly an exchange interaction, it is short-range and is therefore enhanced by the light-mediated virtual transitions of the electrons from the anions to the cations.

The calculation that follows corresponds to the standard model of a singlet magnet: both the ground term $|0\rangle$ of the cation and the first excited term $|1\rangle$ are singlet, so that $\langle 0|J|0\rangle = \langle 1|J|1\rangle = 0$. The diagonal component $\langle 0|J_z|1\rangle = C$, however, differs from zero, so that the cation acquires a magnetic moment as a result of the mixing of the ground and excitonic states. This mixing can arise also in the absence of light, as a result of exchange of the cation with the neighbors, if the intensity K of the latter exceeds a certain critical value, and then the light merely enhances the exchange.

The Hamiltonian of the considered system is

$$\mathcal{H} = \mathcal{H}_{ep} + \mathcal{H}_{ex} + \mathcal{H}_i. \quad (1)$$

Here \mathcal{H}_{ep} is the Hamiltonian of the conduction electrons and of those from the valence band, interacting with the photons:

$$\mathcal{H}_{ep} = \sum_{\mathbf{k}i} \epsilon_{\mathbf{k}i} a_{\mathbf{k}i\sigma}^* a_{\mathbf{k}i\sigma} + \sum_{\mathbf{q}j} \nu_{\mathbf{q}} c_{\mathbf{q}j}^* c_{\mathbf{q}j} + \sum \{ g_{\mathbf{k}c, \mathbf{k}-\mathbf{q}v, \mathbf{q}j} (c_{\mathbf{q}j} + c_{-\mathbf{q}j}^*) \times a_{\mathbf{k}i\sigma}^* a_{\mathbf{k}-\mathbf{q}v\sigma} + \text{conj.} \},$$

$$\epsilon_{\mathbf{k}c} = \frac{k^2}{2m^*}, \quad \epsilon_{\mathbf{k}v} = -E_g - \frac{k^2}{2m^*}, \quad (\hbar = 1)$$

$$g_{\mathbf{k}c, \mathbf{k}-\mathbf{q}v, \mathbf{q}j} = \sqrt{\frac{2\pi}{V\nu_{\mathbf{q}}}} \frac{e}{m} \langle \mathbf{k}c | e^{i\mathbf{q}\mathbf{r}} (l_{\mathbf{q}j} \hat{\mathbf{p}}) | \mathbf{k}-\mathbf{q}v \rangle,$$

where $a_{\mathbf{k}i\sigma}^*$, $a_{\mathbf{k}i\sigma}$ and $c_{\mathbf{q}j}^*$, $c_{\mathbf{q}j}$ are respectively the electron and photon operators, $i=v$ or c is the index of the valence or conduction band, $l_{\mathbf{q}j}$ is the photon polarization vector. It is assumed that the extrema of both bands are located near $k=0$ and that the effective masses m^* are equal in both bands (m is the true mass).

The Hamiltonians \mathcal{H}_{ex} of the excitons and \mathcal{H}_i of the electron-exciton interaction are given by

$$\mathcal{H}_{ex} = \omega \sum_{\mathbf{f}} b_{\mathbf{f}}^* b_{\mathbf{f}} - \frac{K}{2} \sum \langle 0 | \mathbf{J}_{\mathbf{f}} | 1 \rangle \langle 1 | \mathbf{I}_{\mathbf{f}+\Delta} | 0 \rangle (b_{\mathbf{f}}^* + b_{\mathbf{f}})(b_{\mathbf{f}+\Delta}^* + b_{\mathbf{f}+\Delta}),$$

$$\mathcal{H}_i = - \frac{A}{N} \sum \langle 0 | \mathbf{J}_{\mathbf{f}} | 1 \rangle (s)_{\sigma\sigma'} (b_{\mathbf{f}}^* + b_{\mathbf{f}}) e^{i\mathbf{q}\mathbf{R}_{\mathbf{f}}} a_{\mathbf{k}c\sigma}^* a_{\mathbf{k}+\mathbf{q}c\sigma'},$$

where $\mathbf{R}_{\mathbf{f}}$ is the coordinate of the cation \mathbf{f} , N is the number of cations, $(s)_{\sigma\sigma'}$ are Pauli matrices, and $\mathbf{J}_{\mathbf{f}}$ is the angular momentum of the \mathbf{f} ion.

In our case, the excitation should be accompanied by changes in the crystal magnetization M . At $T=0$ we obtain for the magnetization from (1), the self-consistent-field approximation, a system of equations that are valid when $AC \ll W = 6/m^*a^2$:

$$M^2 \left(\frac{\omega}{4} + h^2 \right) = h^2 C^2, \quad M = C \langle b_{\mathbf{f}}^* + b_{\mathbf{f}} \rangle,$$

$$h = \frac{AC}{2} (\theta_{\uparrow} - \theta_{\downarrow}) + KCM, \quad (2)$$

$$\theta_{\sigma} \approx 8\pi g^2 / 15W^{3/2} (E_g - \nu_{\mathbf{q}} + AM_{\sigma})^{1/2}, \quad g \equiv g_{0, -\mathbf{q}, \mathbf{q}j},$$

where the angle brackets denote averaging over the ground state of the crystal at a density n of photons having a linear polarization j and a momentum q , and a is the lattice constant. The effect of the light on the magnetization is due to the fact that, owing to the Zeeman splitting of the conduction band in the molecular field of the crystal, the average number of the virtual electrons in the conduction band θ_σ depends on the spin.

From (2) follows the condition for the presence of magnetization

$$KC^2 + 2A^2C^2n g^2/15W^{3/2}(E_g - \nu_q)^{3/2} \geq \frac{\omega}{2}, \quad (3)$$

At $AC=0.5$ eV, $W=3$ eV, $gn^{1/2}=0.01$ eV (with allowance for the fact that $g \sim (mE_g)^{1/2}$, corresponding to field intensity $\sim 10^6$ V/cm in the laser beam) and $E_g - \nu_q = 0.01$ eV magnetization appears in a crystal with $K=0$ if the exciton frequency ω is less than 6 K, and this corresponds exactly to the characteristic exciton frequencies in singlet magnets. After the magnetization has set in at $n=n_0$, it increases further with increasing light intensity like $(n-n_0)^{1/2}$, i.e., just as in a second-order phase transition.

If $2KC^2 > \omega$, on the other hand, and the crystal had according to (3) a magnetization prior to illumination, then the magnetization increases at $\theta_1 \gg \theta_0$ under the influence of the light by an amount

$$\delta M = \frac{A\theta_1}{2K} \left(\frac{C^2}{M^2} - 1 \right). \quad (4)$$

At the parameter values used above [with the only difference that $E_g - (AM/2) - \nu_q = 0.01$ eV] and at $KC^2 = 10$ K the value $\delta M/M$ should amount to 15% if $M = C/2$, and to 50% if $M = C/3$, i.e., the effect is quite substantial.

Illumination changes the width of the forbidden band. Were there no change in the magnetization, the gap would always increase, since the field of the wave, by coupling the states of the valence band and the conduction band with each other, leads to repulsion of the corresponding terms. However, with increasing M the lower Zeeman subband of the conduction band tends to drop lower, so that the total change in the gap is

$$\delta E_g = 2g^2n \left(E_g - \frac{AM}{2} - \nu_q \right)^{-1} - \frac{A}{2} \delta M.$$

The sign and magnitude of δE_g depend substantially on the magnetization. At the parameter values indicated above, we have from (2), (4), and (5) $\delta E_g = 0.01$ eV at $M=C/2$ and -0.05 eV at $M=C/3$. If the light frequency at low intensity lies close enough to the absorption edge in the transmission band, then when the intensity is increased the frequency can land in the absorption band; this can give rise to photoconductivity.

The transition of a diamagnet to the magnetic state is similar to a first-order phase transition. Unfortunately, the only presently known materials have $\omega > 0.01$ eV, whereas the transition calls for $\omega < 0.001$ eV.