Ferromagnetic semiconductors with giant blue shift of the absorption edge

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The giant blue shift of the optical absorption edge in certain ferromagnetic semiconductors is attributed to the predominant role of the interband s-d exchange. Certain effects that can be observed in semiconductors (antiferron states etc.,) are predicted.

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As a rule, as the temperature is lowered, the optical-absorption edge of a ferromagnetic semiconductor undergoes a giant red shift (see the review[1]). It can be attributed roughly to Zeeman spin splitting of the electron energy bands in the molecular field of the magnetized crystal. Since one of the conduction subbands shifts downward and one of the valence bands shifts upward, the gap between them becomes narrower with increasing magnetization. The magnetization of the crystal affects the carriers states because of the exchange interaction with localized d or f electrons of the magnetic atoms ("intraband s-d exchange").

It might seem that an effect having so simple a nature should be universal for ferromagnetic semiconductors. The giant blue shift of the absorption edge observed in $CdCr_2S_4$[2] seems therefore to be anomalous. This paper is devoted to an explanation of this effect, based on the fact that in some cases the dominant role is played not by the intraband but by the interband s-d exchange, which causes virtual transitions of the electrons from the valence band to the conduction band. It is known that interaction between two energy terms leads to their repulsion. In analogy with the intraband exchange, the interband s-d exchange becomes stronger when ferromagnetic order is established. Therefore the repulsion between the valence band and the conduction band due to this exchange becomes stronger, i.e., the gap $\mathcal{E}_g$ between them increases. Thus, interband s-d exchange counteracts the intraband exchange.

As a rule, intraband exchange is weaker than s-d exchange in the conduction band, although it is stronger than s-d exchange in the valence band. The reason is that the conduction electrons move mainly along magnetic cations, whereas valence-band electrons move along nonmagnetic anions. Some factors, however, can make the s-d exchange in the conduction band weak (for example, if the conduction band is a hybrid of states having opposite signs of the exchange integral with localized d electrons). It is in such cases that the blue shift should appear. Semiconductors with blue shifts should have unique properties greatly differing from the properties of semiconductors with red shifts. Some of them are indicated below.

In the case considered here, the Hamiltonian of the s-d model is written in the form

$$\mathcal{H} = \Sigma \epsilon_k a^*_{k\sigma} a_{k\sigma} + \Sigma h_k c^*_{k\sigma} c_{k\sigma} - A\Sigma (S_q s)_{\sigma\sigma'} a^*_{k\sigma} a_{k-q\sigma'}$$
$$- G\Sigma (S_q s)_{\sigma\sigma'} [a^*_{k\sigma} c_{k-q\sigma'} + c^*_{k\sigma} a_{k-q\sigma'}] S_q = \frac{1}{N} \Sigma S_g e^{iqg}, \tag{1}$$

where $a^*_{k\sigma}$, $a_{k\sigma}$ and $c^*_{k\sigma}$, $c_{k\sigma}$ are respectively the creation and annihilation operators of the conduction electron in the valence band with quasimomentum k and spin projection σ, s is the electron spin, S_g is the spin of one magnetic atom g, and N is the number of these atoms. It is assumed that the widths W_c and W_v of the conduction and valence bands are large in comparison with the s-d exchange integrals in the conduction band (A) and the interband integral (G), and also with the width $\mathcal{E}_g$ of the energy gap.

Far from the Curie point, in the principal approximation in G/W, it suffices to take into account in the Hamiltonian (1) only the terms with $q = 0$. Such a Hamiltonian can be diagonalized exactly:

$$\tilde{\epsilon}^{\pm}_{k\sigma}(0) = \frac{h_k + \epsilon_{k\sigma}}{2} \pm \sqrt{\left(\frac{h_k - \epsilon_{k\sigma}}{2}\right)^2 + \zeta^2},$$
$$\epsilon_{k\sigma} = \epsilon_k - AS^Z_o \sigma; \quad \zeta = \frac{GS^Z_o}{2} \tag{2}$$

(the upper sign in (2) corresponds to the conduction band and the lower to the valence band). In the case of helicoidal ordering with arbitrary vector Q we obtain from (1) at $A = 0$, independently of σ.

$$\epsilon^{\pm}_k(Q) = \frac{h_k + \epsilon_{k+Q}}{2} \pm \sqrt{\left(\frac{h_k - \epsilon_{k+Q}}{2}\right)^2 + \zeta^2}. \tag{3}$$

According to (3), interband exchange, unlike intraband exchange, does not cause Zeeman splitting of the bands in the case of ferromagnetic ordering ($Q = 0$).

As seen from (2), if intraband exchange predominates, the energy gap $\mathcal{E}_g(T)$ becomes narrower by an amount $A\tilde{S}/2$ when ferromagnetic order is established, where $\tilde{S}$ is the spin of the magnetic atom. In the opposite limit $A \to 0$ it is

necessary to take into account the fact that in a crystal with ferromagnetic order the bottom of the conduction band and the top of the valence band should occur at one and the same value of k. This follows from the requirement that at $T=0$ the energy of the magnetic order produced by the superexchange via the valence band electrons[3]

$$\mathcal{E}_M = \sum_{k\sigma} [\, h_k - \tilde{\epsilon}_k^- (Q)] \tag{4}$$

have a minimum at $Q=0$ ($\tilde{\epsilon}_k(Q)$ is given by (3)). Taking this into account, it follows from (2) and (3) that when complete ferromagnetic order is established (i.e., when the temperature drops from $T=\infty$ to $T=0$) the gap broadens by $\sqrt{1+G^2S^2/4\Delta^2}$ times ($\Delta \equiv \mathcal{E}_g(\infty)$). At the characteristic values of the parameters Δ, $GS \sim 0.1$—1 eV, the blue shift should amount to ~ 0.1 eV, in agreement with the experimental data on $CdCr_2S_4$.[2]

The fact that the bottom of the conduction band drops in our case when the ferromagnetic order is destroyed makes possible in principle the "antiferron" states of the conduction electrons in crystals with a blue shift. They are characterized by the fact that the conduction electrons produce in a ferromagnet regions with destroyed ferromagnetic order and stabilize these regions by becoming localized in them. The superexchange energy consumed in the production of nonferromagnetic regions is offset by the lowering of the electron energy, since such regions are potential wells for the conduction electrons. The antiferron states play a role of states that are inverse relative to the ferron states of the conduction electrons in antiferromagnetic semiconductors, when the conduction electron becomes self-localized in the ferromagnetic region produced by it.[1,4] The results of the theory of ferron states[4,1] can be automatically applied to antiferron states if it is noted that, according to (3), the depth of the potential well is

$$U \approx \frac{1}{2} [\sqrt{\Delta^2 + 4\zeta^2} - \Delta], \tag{5}$$

and the energy loss per atom to the production of an antiferromagnetic microregion at $T=0$ is, taking (3) and (4) into account (a is the lattice constant)

$$D \approx \frac{G^2}{4N} \sum_{k\sigma} \left\{ \frac{1}{\epsilon_k - h_k} - \frac{1}{\epsilon_k - h_{k+\Pi}} \right\} \sim \frac{G^2}{W}; \qquad \Pi \equiv \left(\frac{\pi}{a}, \frac{\pi}{a}, \frac{\pi}{a}\right). \tag{6}$$

Such nonferromagnetic regions can be produced also around donor defects. It is well known that nonionized donors in semiconductors with a red shift increase greatly the paramagnetic Curie temperature Θ without raising the Curie point T_C, since the donor electrons strengthen the ferromagnetic coupling between the atoms in the vicinity of the defect.[1] In semiconductors with blue shifts, such defects, to the contrary, lower Θ, so that the donor electrons weaken the ferromagnetic exchange in the vicinity of the defects or may even reverse the sign of the exchange.

In degenerate ferromagnetic semiconductors with blue shifts, indirect exchange via the conduction electrons should lead to a lowering of T_C. At an electron density $n \gtrsim D/Ua^3 \sim 10^{20}$—$10^{21}$ cm^{-3} the ferromagnetic ordering becomes un-

able in any case. It is possible that at smaller n a crystal state that is energy-ise favored over the ferromagnetic is an inhomogeneous state in which it de-ıys into alternating ferro- and antiferromagnetic regions. In contrast to the ıalogous state of degenerate antiferromagnetic semiconductors, which was in-estigated in[5], all the conduction electrons are concentrated in this case in the ntiferromagnetic and not in the ferromagnetic phase.

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