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PHOTOTHRESHOLDS OF MAGNETIC SEMICONDUCTORS

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Résumé.- En refroidissant en-dessous du point d'alignement des moments magnétiques, un déplacement du seuil photoélectrique a été observé dans les semiconducteurs EuO + x% La et Gd, CdCr2S4 de type n et Fe0.91O. L'amplitude du déplacement atteint 0,5 eV dans EuO pour une certaine dotation, tandis que dans le cas du Fe0.91O l'effet n'est que de quelques milliélectrons-volts. Des mécanismes expliquant ces déplacements sont discutés.

Abstract.— By cooling below the magnetic ordering temperature changes of the photothreshold have been observed for the semiconductors EuO + x% La or Gd, n-type CdCr2S4 and Fe0.91O. The magnitude of the effect is as large as 0.5 eV for suitably doped EuO, whereas it amounts to only a few milli-eV in the case of Fe0.91O. Possible mechanisms underlying the threshold shift are discussed.

Contrary to metals /1/, no simple model has yet been developed to account for the photothresholds of covalent or ionic semiconductors. For sp-bonded polycrystalline metals the jellium model which contains as the only parameter the conduction electron concentration provides values of the work function accurate to ± 15%. In the case of semiconductors, however, the potential of the ions cannot be neglected nor treated as a perturbation: it must be included from the beginning, and laborious procedures are required to find the self-consistent charge distribution of the valence electrons. Further complications arise due to the often extended geometrical rearrangement of the surface atoms, band bending and surface states. By far the most intensively studied semiconductor surface is the (111)-cleavage plane of silicon /2/.

In this paper experiments are reported dealing with changes of the photothreshold which are related to the magnetic state of the sample. Although the number of investigated materials is still limited, there is sufficient evidence that magnetically induced threshold shifts are a common feature among magnetically ordering semiconductors. The absolute values of the thresholds will not be of any further concern.

In analogy to the work function of metals the ionization energy $I$ is defined as the minimum energy to remove an electron from the semiconductor and to put it at rest far away from the surface. Then

$$ I = (e\phi(\infty) + E_{N-1}^O) - E_N^O $$

(1)

$E_N^O$ and $E_{N-1}^O$ are the ground state energies of the crystal before and after removing the electron, $\phi(\infty)$ is the vacuum potential. In photoemission the crystal left behind is generally in an excited state $E_N^f$ and the photoelectron has kinetic energy $E_{kin}$ in the vacuum. Conservation of energy implies

$$ hv = (E_N^f - E_N^O) + \phi(\infty) + E_{kin} $$

$$ = (E_{N-1}^f - E_{N-1}^O) + I + E_{kin} $$

(2)

For covalent semiconductors with valence electrons occupying broad, delocalized Bloch states the positive hole created by photoemission is distributed over the whole crystal and influences the electron states of the remaining N-1 electrons only very little. At threshold, where the topmost valence electron is just emitted, $E_{N-1}^f = E_{N-1}^O$ and $E_{kin} = 0$. The photon energy at threshold $h\nu_T$ is then equal to the energy difference between the vacuum level and the top of the valence band of the unperturbed N-electron system, see figure 1a.

In the ionic limit the positive hole is strongly localized on the ion from which photoemission took place. In this case the remaining electrons on this particular ion
will rearrange their orbitals and no longer occupy the same states as they did before photoemission.

Then, typical structure is found in the energy distribution of the photoelectrons which reflects the discrete set of ionic final states: this, in fact, is the characteristic feature for emission from localized orbitals [3]. In eq. (2) $E_N^0$ is then equal to the ground state energy of the ion containing $N$ electrons, where $N$ is - 10 and no longer $10^{22}$ as in the case of covalent semiconductors of metals. A schematic picture of the photothreshold of ionic semiconductors is given in figure 1b.

The quantity measured in the present experiments is the quantum yield $Y$ defined as

$$Y(hv) = \frac{\text{number of emitted photoelectrons}}{\text{number of incident photons of energy } hv}$$

The dependence of $Y$ on $(hv - h\nu_T)$ has been discussed by Kane [4] for various types of photoexcitation processes. The experimental set-up is shown in figure 1c. The samples are cleaved and measured in a vacuum of $2 \times 10^{-10}$ torr. The photon flux is determined by a calibrated photocell. The temperature of the sample can be controlled between 20 K and room temperature. The large surface of a surrounding Helium cryostat prevents preferred contamination of the cold sample by condensation of rest gases. Light energies up to 10.8 eV are available.

The first material where a significant change of the quantum yield upon magnetic ordering has been observed was La$^{3+}$-doped EuO [5]; in contrast, for undoped EuO the yields above the ferromagnetic Curie temperature $T_C = 70$ K and at $T < T_C$ are identical, see figure 2.

From threshold up to 6 eV the photoelectrons are emitted exclusively from the half filled 4f-shell. The energy of the 4f-level lies in the band gap, about 1.5 eV below the bottom of the conduction band. Above 6 eV the increase of $Y$ is due to the valence electrons (oxygen 2p-derived). The $Y$-minimum around 6 eV is independent of sample and temperature: It is an effect of the energy scheme of EuO: at $hv < 6$ eV, photoexcited 4f-electrons have enough energy to scatter inelastically with the valence electrons thereby promoting them into the conduction band. However, the secondaries created by this process have not enough energy to escape into the vacuum. This
scattering mechanism causes a reduction of the mean free path of the 4f-photoelectrons which then gives rise to the observed decrease of the quantum yield.

Fig. 2: Quantum yield of undoped and 2% La-doped EuO at room temperature ($T > T_c$) and 10 K ($T < T_c$).

The constant position of the Y-minimum indicates that the energy scheme of EuO is quite insensitive to the magnetic state of the sample. The well known splitting of the conduction band below $T_c$ is too small to produce a measurable displacement of the Y structure.

The yield curve of the doped sample at $T < T_c$ is then interpreted as being shifted to lower light energies by about 0.4 eV with respect to the paramagnetic yield. The fact that the Y's of the undoped sample and the Y of the doped sample at $T < T_c$ coincide is considered as accidental. The important conclusion from figure 2 is that a shift of the photothreshold occurs for La$^{3+}$-doped EuO when going from the paramagnetic to the ferromagnetic state.

Further experiments with Gd$^{3+}$-doped EuO showed similar shifts of the photothreshold, see figure 3. The essential property of the dopant is that it is trivalent and thus furnishes an extra electron compared to the replaced Eu$^{2+}$.

Fig. 3: Temperature dependence of quantum yield of 4.3% Gd-doped EuO.

Several proposals have been made to explain the surprisingly large effect of the magnetic transition on the photothreshold of trivalently doped EuO /6,7/. Vigren /6/ makes use of the experimental finding that the surface of doped or undoped EuO is not magnetically saturated even at low temperature $T < T_c$. This has been shown by measurements of the spin polarization of the photoemitted 4f-electrons /8/. As a model the EuO surface is considered to consist of a paramagnetic layer whose thickness is an adjustable parameter. Adjacent to this layer is the ideal bulk crystal. The extra electrons introduced by the trivalent ions occupy conduction band states for dopant concentrations $> 1\%$, i.e. the doped EuO is then metallic. Below $T_c$ the conduction band in the bulk splits up into a spin "up" and "down" subband. The bottom of the spin "up" band moves towards the 4f-level, the spin "down" band in the other direction. If the splitting is large enough conduction elec-
trons from the paramagnetic surface layer will leak into the energetically favorable spin-up subband, thereby decreasing the negative charge in the surface and setting up a dipole layer. Due to this dipole layer the vacuum level of doped EuO is lowered in the ferromagnetic state with respect to the paramagnetic state. The second parameter in Vigren's model is the magnitude of the exchange splitting of the spin subbands. Taking a value of 0.4 eV the experimental data for a 2% La-doped sample are fitted best by assuming a paramagnetic surface layer 25 Å thick. This value seems rather large in view of the spin polarized photoemission experiments. Interestingly, for heavily doped samples the magnetically induced surface dipole and correspondingly also the threshold shift become smaller if the thickness of the paramagnetic layer is held constant. The reason is that the conduction band splitting for heavily doped samples becomes small.

In another model the threshold shift is interpreted as a bulk effect. Below $T_C$ the conduction electrons become polarized due to the conduction band splitting. This is accompanied by a change of their effective potential such that the work function decreases. Note that the work function of doped EuO is the energy difference between the Fermi level (some few tenths of an eV above the bottom of the conduction band) and the vacuum level. Using the experimental fact that 4f- and valence levels remain fixed with respect to the conduction band- except for the magnetic splitting - a corresponding change of the threshold for 4f and valence-band emission is expected. Although this model does not require the possibly unrealistically thick paramagnetic surface layer, it seems difficult to visualize how the valence level structure is coupled to the effective potential of the conduction electrons.

A shift of the photothreshold similar to EuO has been observed for the ferromagnetic n-doped semiconductor CdCr$_2$S$_4$, see figure 4. Again the photocurrent increases drastically when cooling below $T_C$. In view of the models this points to a conduction band splitting as for EuO. In fact, direct proof of this splitting has been obtained by measuring the spin polarization of the photoemitted conduction electrons. Because of an apparent blue-shift of the optical absorption edge at low temperatures for CdCr$_2$S$_4$ speculations have been made about a magnetic splitting of the valence band instead of the conduction band. Our evidence is that CdCr$_2$S$_4$ shows a conduction band splitting analogous to that of all other magnetic semiconductors.

![Fig.4: Temperature dependence of quantum yield of n-type CdCr$_2$S$_4$.](image_url)

A much less pronounced variation of the photocurrent upon magnetic ordering is observed for antiferromagnetic Fe$_x$O, $T_N = 193$ K, see figure 5. It is well known that in many magnetically ordered insulators the electrons of the magnetic shell form the top-most electronic level. At photothreshold the quantum yield curves are very steep, varying by orders of magnitude over a few tenths of an eV. As the magnetic level experiences the Weiss-field its energy with respect to the vacuum level changes by the corresponding magnetic energy when going from the paramagnetic to the fully ordered magnetic state. Although the energy change
typically amounts to no more than a few milli-ev, it should produce a measurable variation of the photocurrent near threshold.

Using eq.(1), the difference between the photothresholds or ionization energies in the para- and antiferromagnetic state is

\[ \hbar \nu_T(p) - \hbar \nu_T(a) = I(p) - I(a) + (e_{N-1}^0 - e_{N-1}^0(a)) + (E_N^0(p) - E_N^0(a)) \]

In the ground state the Fe^{2+} ion has the configuration 3d^5 giving a spin moment of 4 \( \mu_B \). Then the energy of the initial state at \( T << T_N \) is

\[ E_N^0(a) = E_N^0(p) - 4 \mu_B H_{\text{eff}} \]

The lowest lying final state has a spin moment 5 \( \mu_B \):

\[ E_{N-1}^0(a) = E_{N-1}^0(p) - 5 \mu_B H_{\text{eff}} \]

assuming that the Weiss-field is constant. Then

\[ \hbar \nu_T(p) - \hbar \nu_T(a) = + \mu_B H_{\text{eff}} \]  

i.e. in the fully ordered antiferromagnetic state the effect of the Weiss-field is to reduce the photothreshold by \( \mu_B H_{\text{eff}} \) with respect to the paramagnetic state. Obviously this should result in an increase of the photocurrent when cooling below \( T_N \). In the experiment, however, not an increase but a decrease of the photocurrent is observed.

Unfortunately, in the original report on this effect (12) the quantity \( \mu_B H_{\text{eff}} \) in eq.(3) appeared with the wrong sign, namely instead of +. Therefore it was concluded that the change of the photocurrent were exclusively due to the direct spin interaction with the magnetic molecular field. Having recognized this error it is now inevitable to invoke other magnetic effects in order to account for the observed temperature dependence of the photocurrent. Although it is difficult to make quantitative estimates a likely cause is a crystal field splitting of the electronic levels due to the spontaneous magnetostrictive distortion of the cubic Fe\(_x\)O lattice below \( T_N \).

The change of the photocurrent is measurable only near threshold where the \( Y \)-curve has a large gradient. At higher photon energies \( Y \) levels off and the effect is no longer discernible, see figure 5.

It should be noted that the variation of the photocurrent is nearly a linear function of temperature for \( T < T_N \), see figure 6. Interestingly, the surface magnetization of a Heisenberg antiferromagnet has been shown to exhibit the same \( T \)-dependence. Therefore it is tempting to interpret the observed threshold shift in terms of the surface magnetization. The simple experimental set up for measuring photo-yields could then be used as a sensitive surface magnetometer.

In conclusion we note that the photothreshold of magnetic semiconductors is sensitively dependent on the magnetic state of the material. As relative changes of the photocurrent are easily measured, we believe that this technique should be
further developed to investigate the magnetic properties of semiconductor surfaces.

Fig. 6: Plot of $\Delta i(T)/\Delta i(0) = (i(T) - i(250 K))/(i(0K) - i(250 K))$. The dashed curve labelled "Bulk" indicates the Brillouin-function $M(T)/M(0)$ for $S=4/2$. The tail of $\Delta i(T)/\Delta i(0)$ is due to spin correlation above the ordering temperature.

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References

1/ For a recent review, see Hölzl, J., and Schulte, F.K., Springer Tracts Mod. Phys. 85 (1979) 1 and references cited therein.


