

deren Maxima nach [5] die Grenzenergie ΔE für den Einsatz direkter Interbandübergänge von Zuständen unterhalb der Fermi-Energie in das Leitungsband angeben. Die Tabelle lässt - hier mit stärkerer Streuung - eine monotone Abnahme von ΔE bei Abnahme von p^* erkennen. Damit erscheint eine grobe Abschätzung der Energiedifferenz zwischen der Oberkante des tieferliegenden Valenzbandes und dem unteren Rand des Leitungsbandes möglich; denn aufgrund von Thermokraftmessungen [6-10] sollte das Fermi-niveau für $p^* 770\text{K} = 2.2 \times 10^{20} \text{ cm}^{-3}$ an der Oberkante des unteren Valenzbandes liegen, unabhängig von der Temperatur zwischen 100° und 300°K . Der Tieftemperaturkonzentration von $2.2 \times 10^{20} \text{ cm}^{-3}$ entspricht bei 300°K ein Wert von $1.6 \times 10^{20} \text{ cm}^{-3}$ [9]. Extrapoliert man die Werte für ΔE auf diese Konzentration, so erhält man etwa 0.65 eV. Für die Breite der verbotenen Zone ergaben Untersuchungen an einer $\text{Al-Al}_2\text{O}_3\text{-SnTe}$ -Tunnelodiode 0.18 eV bei 300°K [11]. Damit sollte der energetische Abstand der beiden Valenzbandmaxima etwa 0.47 eV betragen. Dieser Wert ist etwas grösser als die in [7] und [10] zur Erklärung der Thermokraftmessungen angenommenen Energieabstände von 0.38 eV bzw. 0.3 eV.

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OPTICAL ABSORPTION OF SOME FERRO- AND ANTIFERROMAGNETIC SPINELS, CONTAINING Cr^{3+} -IONS

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The optical absorption of CdCr_2S_4 , CdCr_2Se_4 and ZnCr_2Se_4 has been measured above and below the magnetic ordering temperatures. It has been found that the absorption edge shifts towards longer wavelengths when the substances are cooled below their Curie temperatures.

A shift of the absorption edge towards longer wavelengths by cooling a magnetically ordering substance below its transition temperature has been discovered on EuO and EuS by Busch, Junod and Wachter [1] and the work has been extended to the remaining Eu-chalcogenides by Busch and Wachter [2]. It was shown that the shift of the absorption edge is proportional to the magnetization of a domain [2] and therefore gives the possibility to measure the spontaneous magnetization without

an applied magnetic field. Since so far only substances containing ions with unfilled 4f-shells have been investigated, it seemed of interest to know whether substances with unfilled 3d-shells show the same effects. This is the aim of the following investigation.

Much information has been collected concerning the magnetic properties of spinels with the chemical composition $\text{M}[\text{Cr}_2\text{X}_4]$, where M stands for Zn, Cd, Hg and X stands for O, S, Se, Te

Table 1

	Heat treatment	Cell dim. (Å)	T_C (°K)	Θ (°K)	$\Delta E_{G 300^\circ K}$ (eV)	$\Delta E_G^{\max} - \Delta E_G^{\min}$ (eV)
$CdCr_2S_4$	950°C 40 hours	10.242	97 [8] 86 [9]	135 [8] 156 [9]	1.37	--
$CdCr_2Se_4$	640°C 12 days	10.744	142 [8] 130 [9]	190 [8] 210 [9]	1.29	0.186
$ZnCr_2Se_4$	900°C 3 days	10.495	$T_N \approx 20$ [4]	+ 155 [4]	1.285	0.213

[3-9]. Lotgering [5] found a semi-conducting behaviour of the conductivity for the antiferromagnet $ZnCr_2Se_4$ in the paramagnetic temperature range. Similarly Baltzer, Lehmann and Robbins [8,10] concluded from conductivity measurements that the ferromagnets $CdCr_2S_4$ and $CdCr_2Se_4$ are semiconductors above as well as below their Curie temperatures; however the results did not allow the computation of an energy gap. We have prepared polycrystalline samples of $CdCr_2S_4$, $CdCr_2Se_4$ and $ZnCr_2Se_4$ and investigated the optical absorption by means of a diffuse reflectance method *. The preparation of the substances will be described elsewhere.

It has been found [2] that at low temperatures, when the magnetization of a domain is saturated, a magnetic field yields no further shift of the absorption edge; this is the case for $CdCr_2Se_4$, using unpolarized light. Comparing the results of $CdCr_2Se_4$ in fig. 1 with a Brillouin function $B_{J=\frac{3}{2}}(T_C, H)$ matched for saturation magnetization at $T = 0$, shows that the magnetization computed from the absorption edge is always lower than

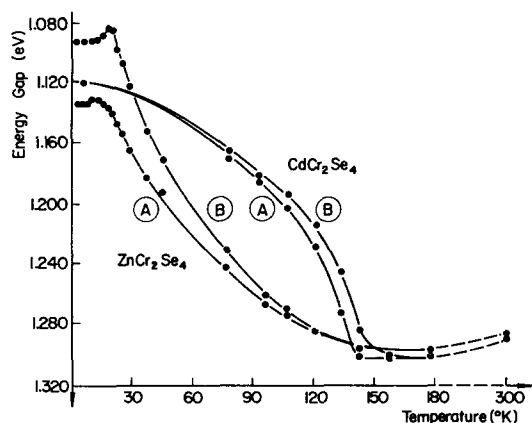


Fig. 1. Energy gap of $CdCr_2Se_4$ and $ZnCr_2Se_4$ as a function of temperature. Curves A without and curves B with an applied magnetic field of 18.5 kOe.

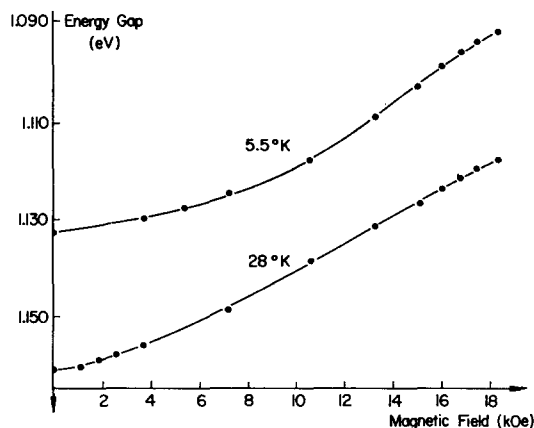


Fig. 2. Energy gap of $ZnCr_2Se_4$ as a function of an applied magnetic field at 5.5 and 28°K.

predicted by molecular field theory. This is in good agreement with measurements of the magnetization alone [8,9]. Curve A in fig. 1 indicates that the shift of the absorption edge continues well above the Curie point of 142 or 130°K respectively [8,9]. Similar effects were found with the Eu-chalcogenides and were attributed to near dering [2].

At room temperature $CdCr_2S_4$ has an energy gap of 1.37 eV, which is larger than that of $CdCr_2Se_4$. This is in agreement with a steeper slope of the conductivity-temperature function for $CdCr_2S_4$ [10]. Below the Curie temperature only a small portion of the absorption curve of $CdCr_2S_4$ shifts in the expected way towards longer wavelengths, however two new absorption bands appear. We feel that this problem needs further investigation.

* By private communication we learned that G. Harbeke, Laboratories RCA Ltd., Zürich, has performed transmission measurements on single crystals of $CdCr_2S_4$ and $CdCr_2Se_4$ with similar results.

Antiferromagnetic ZnCr_2Se_4 has a positive asymptotic Curie temperature of 115°K and a Néel point of about 20°K , measured with a field of 20 kOe [5]. Below the Néel temperature the spin configuration is a helix which propagates in the [001] direction [6]. Lotgering [5, 7] assumed a positive Cr-Se-Cr interaction and a negative Cr-Se-Se-Cr interaction. A positive ferromagnetic exchange is in our opinion a necessary condition for a substance to exhibit a shift of the absorption edge in the described way; as an example antiferromagnetic EuSe may be obtained [2, 11].

Contrary to CdCr_2Se_4 , where the curves taken with and without a magnetic field yield the same saturation magnetization at $T=0$, this is not the case for ZnCr_2Se_4 as shown in fig. 1. Below the Néel point and without a magnetic field the helical arrangement of the ion spins is saturated [6]. However a field of about 20 kOe produces another antiferromagnetic spin order, which is confirmed by Plumier [12]. The Néel point is found with a field of 18.5 kOe at 19°K , with zero field at 10°K . Since ZnCr_2Se_4 is magnetically anisotropic, powder measurements yield only an average value of the magnetization. In the propagation direction of the helix a linear increase of the magnetization with field is to be expected. However perpendicular to this direction, up to a critical field, only a small magnetization exists, while above this

field the spin structure is changed. The curve at 5.5°K is in good agreement with magnetization measurements by Lotgering [7]. Yet at 28°K , which is above the Néel point, the necessary critical field to change the spin structure is already reached at a much lower field strength.

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BROAD BAND U. V. EXCITATION OF Sm^{3+} -ACTIVATED PHOSPHORS

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The possibility of exciting Sm^{3+} -activated phosphors in the charge transfer band of the Sm^{3+} -centre is discussed. A number of examples is given.

Rare-earth activated phosphors can be excited in three different ways: (a) in the narrow 4f levels of the rare-earth ion; (b) in the broad levels of the rare-earth ion centre by 4f \rightarrow 5d processes (e.g. Tb^{3+}) or ligand \rightarrow 4f processes (e.g. Eu^{3+}); (c) in the host lattice, if effective energy transfer from host lattice to rare-earth ion is possible.

These three types of excitation have been realized in the case of Eu^{3+} [1]. For Sm^{3+} -activated phosphors only the excitation mechanisms (a) and

(c) have been reported [e.g. 2]. The charge transfer absorption (ligand \rightarrow 4f) of the Eu^{3+} oxygen centre in mixed metal oxides extends from 31 to 45 kK [3]. We have now tried to realize this type of excitation for Sm^{3+} -activated phosphors, by the following reasoning: if the charge transfer band of the Eu^{3+} ion in a certain host lattice is at relatively low energy, the host lattice can be considered to be weakly electronegative, so that the charge transfer band in the case of Sm^{3+} will