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References

- [1] G. W. GOBELI and F. G. ALLEN, Phys. Rev. 127, 141 (1962); *ibid.*, 137, A245 (1965).
- [2] J. J. SCHEER and J. VAN LAAR, Phys. Lett. 3, 246 (1963).
- [3] T. E. FISCHER, Phys. Rev. 139, A1228 (1965).
- [4] T. E. FISCHER, F. G. ALLEN and G. W. GOBELI, Phys. Rev. 163, 703 (1967).
- [5] T. E. FISCHER, Phys. Rev. 142, 519 (1966).
- [6] R. K. SWANK, Phys. Rev. 153, 844 (1967).
- [7] T. E. FISCHER, *Proceedings of the Symposium on Semiconductor Surfaces* (San Francisco 1968), to be published in Surface Science.
- [8] A. U. MACRAE and G. W. GOBELI, J. appl. Phys. 35, 1629 (1964).

The Magnetic Red Shift in Europium Chalcogenides

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(13. V. 68)

Abstract. The comparison of optical absorption spectra of Eu^{2+} in Eu-chalcogenides, EuF_2 , KBr, and Sr-chalcogenides suggests the assignment of the absorption edge in Eu-chalcogenides to the $4f \rightarrow 5d$ transition instead of to an indirect transition between valence and conduction bands. The 'magnetic-exciton' model gives a suitable description of the magnetic red shift in this case. In solid solutions between ferromagnetic Eu-chalcogenides and isostructural Sr-chalcogenides the $4f \rightarrow 5d$ absorption band moves toward lower energies with increasing Eu concentration. This indicates the existence of a cation-cation interaction which decreases (as does the ferromagnetic Curie temperature) from EuO to EuTe and which is not observable in paramagnetic EuF_2 .

BUSCH and his collaborators [1-3] discovered the magnetic red shift of the optical absorption edge in Eu^{++} chalcogenide powders by measuring the diffuse reflectance as a function of temperature. Magnetic effects in the optical absorption spectrum of single crystals and evaporated thin films of Eu-chalcogenides have been investigated by several authors [4-6]. We report here additional experimental details which may help to characterize the mechanism of this interesting effect.

There are numerous known examples of magnetic ordering effects in optical spectra and their theoretical interpretations have many uncertainties [7, 8]. The magnetic red shift in the Eu-chalcogenides is of particular interest because the occurrence of a sharp absorption edge is combined with ferromagnetic ordering in a relatively simple crystal lattice.

Two different interpretations of the magnetic red shift have been evolved from different models of the band structure and the nature of magnetic interactions in these materials. BALTENSPERGER and his colleagues [9] relate the absorption edge to an indirect excitation from the valence into the conduction band in agreement with preliminary nonself-consistent APW-band-structure calculations by CHO [10, 11].

The magnetic red shift results then from the influence of spin correlations on electron states at the bottom of the conduction band via intra-atomic $s - f$ exchange.

The other approach, in contrast to the APW-calculations, assumes that the localized $4f$ levels of Eu^{2+} lie above the filled valence band in the energy gap. In this case the absorption edge is assigned to a rather localized $4f - 5d$ transition [12-16] which has a lower energy than the intrinsic excitations between valence and conduction bands¹⁾. The latter lies in the ultraviolet and is very similar in energy and shape to the absorption edge [17-20] of equivalent Sr-chalcogenides. Strontium behaves chemically like europium, but does not contain localized magnetic $4f$ electrons. The $4f - 5d$ transition has an exciton-like character [14] in which the $5d$ orbital of the excited $4f^6 - 5d^1$ configuration overlaps with the 12 nearest Eu neighbors. It can be shown that for this model the red shift is determined by the temperature dependence of the nearest neighbor spin correlation, $\langle S_1 S_2 \rangle / S^2$. KASUYA et al. [21, 22], have treated the model of the 'magnetic exciton' in more detail and find the red shift to be in quantitative agreement with spectroscopic free ion parameters. We believe that the following experimental details support the assumption of a transition to an exciton-like $5d$ state from localized $4f$ states within the forbidden gap above the valence band²⁾.

Figure 1 shows the log of optical absorption in EuO single crystals plotted as a function of photon energy for different temperatures. The curves were obtained by

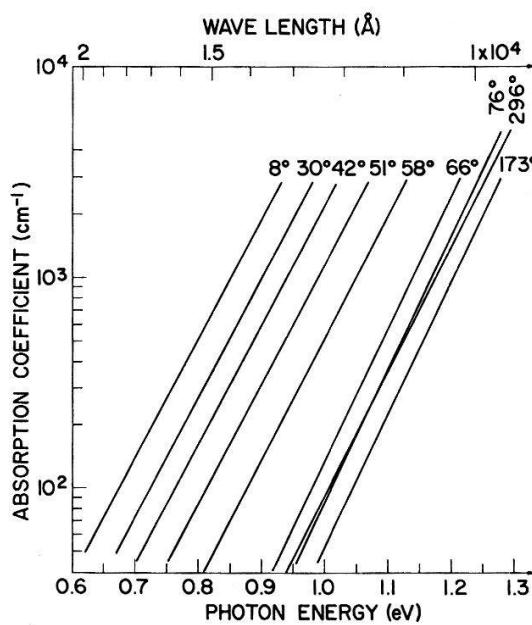


Figure 1

The exponential absorption edge of EuO single crystals as a function of temperature. These curves are the low energy tail of the absorption curves shown in Figure 4 for EuO films.

¹⁾ Note added in proof: Cho's most recent calculations remove this discrepancy and find the position of their $4f$ band extremely sensitive to modifications of the Slater exchange term. A reduction of exchange by 75% moves the $4f$ band up above the top of the valence band, and the indirect excitations from the $4f$ into the $5d$ conduction states now agree with the experimental absorption edges.

²⁾ Note added in proof: The observation of photoconductivity would not conflict with the exciton model (as concluded by R. BACHMANN, P. WACHTER: Phys. Lett. 26 A, 478, 1968). The exciton states can decay into lower lying conducting states.

computer analysis of data recorded by a Cary 14 spectrometer and include reflectivity corrections. The crystals were several mm in diameter and were cleaved and polished to a thickness of 0.01 to 0.1 mm. EuS and EuSe single crystals show similar absorption curves but their slope is steeper ($d \log \alpha / dE > 10.9 \text{ eV}^{-1}$ instead of 5.6 eV^{-1} in EuO). It is remarkable that the absorption edges in all Eu-chalcogenides have an exponential character with constant slope as the edge shifts with decreasing temperature over a wide range of energies. Exponential absorption edges have been found in other materials and have been related to transitions into exciton states [23]. The strong interaction of the excited state with phonons usually results in a strong variation of the slope with temperature. The temperature independent slope in Figure 1 can be understood when we consider the absorption edge in Eu-chalcogenides as the low energy tail of the excitation from the localized $4f^7$ ground state into a $4f^6 - 5d$ state with exciton-like character of the $5d$ wave function. Studies of this excitation for Eu^{2+} in alkaline earth fluorides show that the total width of the resulting absorption band is given by the multiplet width of the excited $4f^6(7F_J)$ configuration which is temperature independent due to the strong localization of the $4f$ electrons [24]. The detailed relationship of the absorption edge in Eu-chalcogenides to the $4f - 5d$ transition in alkaline earth halides is discussed later.

The red shift of the absorption edges with temperature for EuO and EuS single crystals are shown in Figure 2. These curves are derived from point-by-point measurements with magnetic fields applied parallel to the polarization plane of linearly polarized light. The small magnetic field removes domains which can affect the absorption measurements in the ferromagnetic state by scattering light [25] out of the aperture of the spectrometer and can produce magnetic dichroism. The shift of the

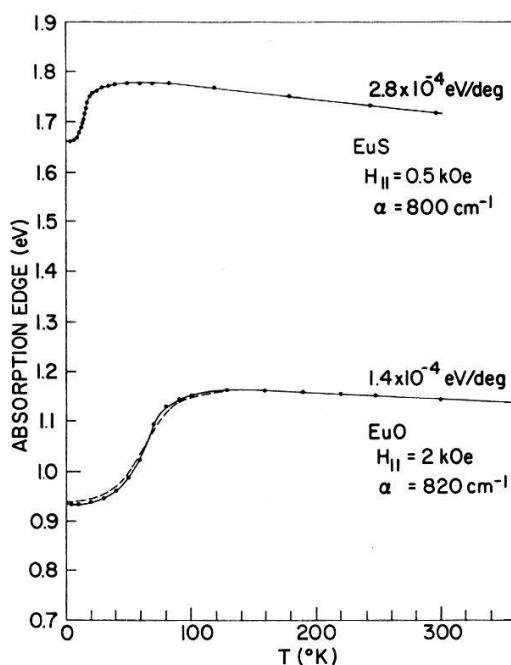


Figure 2

The magnetic red shift in single crystals of EuO and EuS. The photon energy where the absorption coefficient is 800 or 820 cm^{-1} is taken as the absorption edge. The blue shift at higher temperatures is given in eV/deg . The dashed line is proportional to the experimentally determined spin correlations in EuO.

absorption edge with temperature is consistent with the earlier observed [6, 9] proportionality to the spin correlation function. The temperature dependence of the spin correlation in Figure 2 was obtained from specific heat³) and magneto-elastic investigation on EuO single crystals [26].

Figure 3 demonstrates the influence of magnetization direction and light polarization on absorption edges observed in EuO single crystals near the Curie temperature at 77°K. A component of the magnetization parallel to the light beam adds a Faraday contribution to the red shift which is proportional to the magnetization. Magnetization components in the plane of the sample produce a quadratic Cotton-Mouton contribution by magnetic dichroism for light polarizations perpendicular to the magnetization. These polarization effects are comparable in magnitude with the orientation independent red shift, which is directly observable only with linear polarized light in a parallel magnetic field.

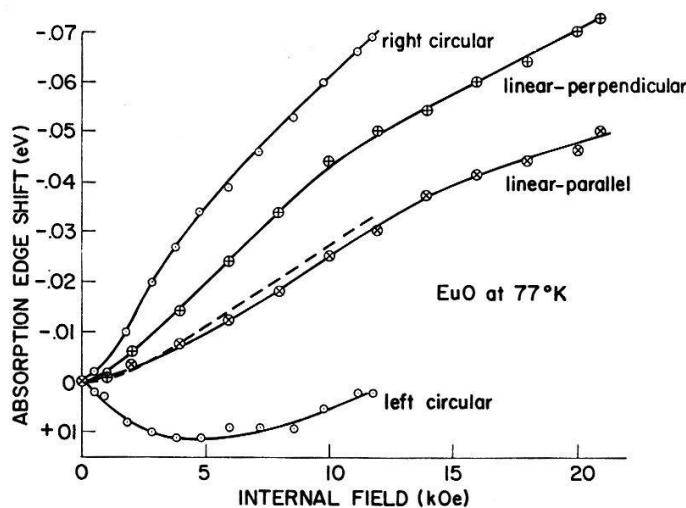


Figure 3

Absorption edge shift of EuO at 77°K for different magnetization directions and light polarizations as function of the internal magnetic field. The dotted line gives the red shift in circular polarized light obtained by averaging the right-circular and left-circular measurements. It agrees with the linear-parallel measurements which are free of dichroism.

In order to demonstrate the consistent character of the absorption spectrum of Eu⁺⁺ in the solid state, and of our identification of the principal features of the spectrum with $4f - 5d$ transitions, we have assembled in Figure 4 absorption curves for a variety of materials containing Eu⁺⁺ in both CaF₂ and NaCl-type lattices. The principal distinction between these two lattice types, as regards the 5d states, is that in the CaF₂ structure the states with e_g symmetry have lower energy than the t_{2g} levels, whereas in the NaCl structure the order of these levels is reversed. The magnitude of the splitting, 10 Dq, depends on the amount of covalent mixing of anion wave functions with the 5d orbitals. Also, the t_{2g} orbitals in the NaCl structure are further stabilized by their overlap between adjacent cations.

Two bands are seen in Figure 4 in the absorption curve of EuF₂. This curve was obtained for an evaporated film of EuF₂, but the absorption spectrum is similar

³) The internal magnetic energy (the integrated magnetic specific heat) for a Heisenberg ferromagnet, with nearest neighbor interactions only, is proportional to the nearest neighbor spin correlation function.

to absorption curves for low concentrations of Eu^{++} in CaF_2 . These bands have been commonly interpreted as arising from excitation from the $4f^7$ ground state into the $4f^6 5d$ configuration with t_{2g} and e_g symmetry [27-36]. The invariance of this spectrum to Eu^{++} concentration implies weak interactions between the excited Eu^{++} ion and the other cations in marked contrast to the situation in the chalcogenides, as we shall see. In the e_g band the different multiplet levels of the $4f^6(7F)$ core of the excited ion, with $J = 0$ to 6 can be resolved as separate peaks at low temperatures, whereas those details are obscured in the t_{2g} band by spin-orbit interactions [24].

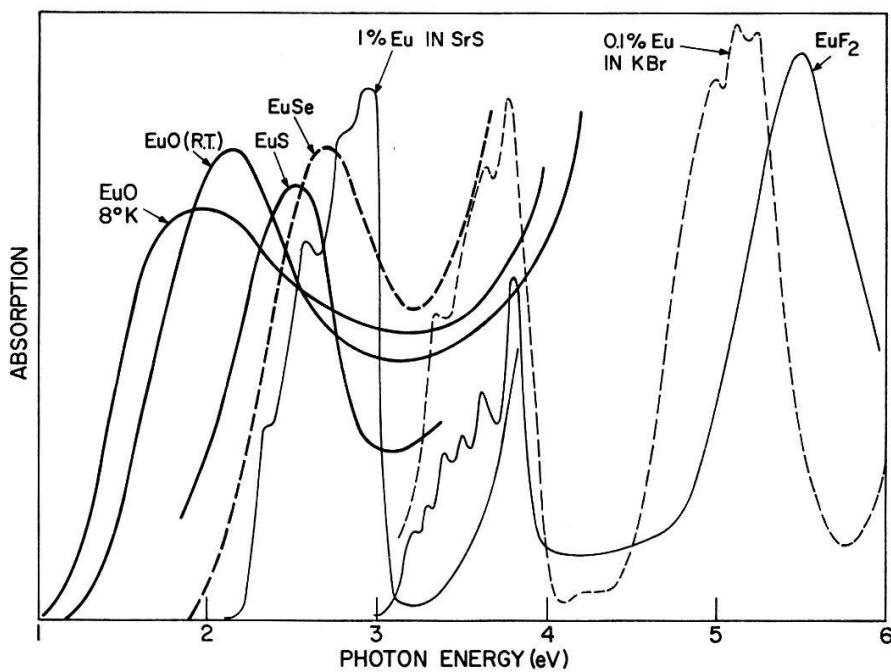


Figure 4

Absorption spectra of several materials containing Eu^{2+} ions. The absorption peaks of the pure Eu-chalcogenides are of the order of 10^5 cm^{-1} . EuO curves at R. T. and 8°K are given to demonstrate the magnetic red shift. The difference between the curves for EuS and 1% Eu in SrS gives the concentration dependence red shift. Data for EuO , EuS , EuSe and EuF_2 were taken on evaporated films and on single crystals for $\text{SrS}:\text{Eu}^{++}$.

Next we consider Eu^{++} dilute in KBr , a halide having the rock salt structure [37]. Here the t_{2g} levels lie below the e_g levels. Then the halogens are replaced by the chalcogens. The similarity of the curve for Eu^{++} diluted in SrS to the curve for Eu^{++} in KBr is evident and the oscillator strengths are similar. The transitions of Eu^{++} in SrS occur at lower energy than in KBr , since sulfur is less electronegative than bromine. The e_g band cannot be seen in SrS because it lies at higher energy than the intrinsic absorption due to transitions from the valence band.

The stabilization of the t_{2g} orbitals in the NaCl structure by overlap between adjacent Eu^{++} ions is made clear in Figure 5, which shows the displacement of the peak towards lower energies with increasing Eu^{++} concentration in the Sr -chalcogenides. The data were obtained at R. T. from single crystals in the low concentration range and from evaporated thin films. The decrease in concentration dependence from oxide to telluride may be related to the increase in cation-cation distance with anion size. The fact that the ferromagnetic transition temperature decreases in the

same order supports the assumption that the ferromagnetic exchange in Eu-chalcogenides is connected with the overlap of $5d$ wave functions at neighboring cations [12, 38, 39]. (Superexchange coupling would *increase* with covalency from oxide to telluride.) In this context, the paramagnetism and concentration independence of the spectrum in EuF_2 can be explained by the smaller effective radius of $5d$ orbitals in this material because of lower covalency, which is reflected also in the dielectric constants (the refractive indices [40] are 1.55 and 2.3 for EuF_2 and EuS , respectively).

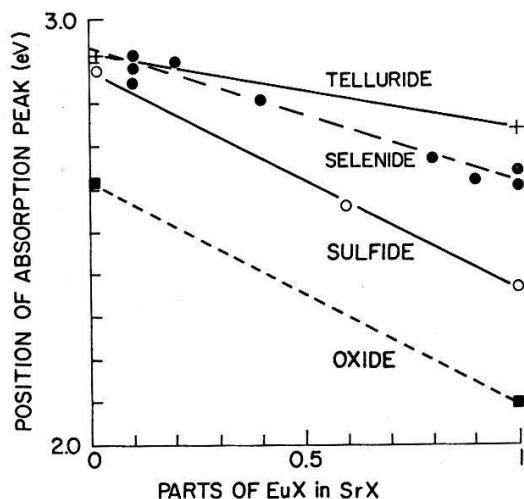


Figure 5

Shift of the absorption peak of the $4f-5d$ transition of Eu^{2+} with Eu-concentration in Sr-chalcogenides.

These considerations support the assumption that the localized $4f$ levels lie above the valence band, within the forbidden gap. The interpretation of the optical data as due to $4f \rightarrow 5d$ transitions, and the evidence for the delocalization of excited t_{2g} states in the NaCl structure through overlap between adjacent Eu^{++} ions provides an account of the magnetic red shift in terms of the 'magnetic-exciton' model. These excitonic states can be related to the occurrence of ferromagnetism in the Eu-chalcogenides.

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References

- [1] G. BUSCH, P. JUNOD and P. WACHTER, Phys. Lett. 12, 11 (1964).
- [2] G. BUSCH and P. WACHTER, Phys. Cond. Matter 52, 32 (1966).
- [3] G. BUSCH, J. appl. Phys. 38, 1386 (1967).
- [4] B. E. ARGYLE, J. C. SUITS and M. J. FREISER, Phys. Rev. Lett. 15, 882 (1965).
- [5] J. C. SUITS, B. E. ARGYLE and M. J. FREISER, J. appl. Phys. 37, 1391 (1967).
- [6] S. METHFESSEL, M. J. FREISER, G. D. PETTIT and J. C. SUITS, J. appl. Phys. 38, 1500 (1967).
- [7] Review articles by S. SUGANO and Y. TANABE and by K. A. WICKERSHEIM, *Magnetism I*, Editor G. T. RADO and H. SUHL (Academic Press, New York 1963), p. 243 and p. 269.
- [8] S. METHFESSEL and D. C. MATTIS, *Handbook of Physics* (Springer Verlag, Heidelberg 1968), vol. 18A, in publication.
- [9] F. RYS, J. HELMAN and W. BALTENSPERGER, Helv. phys. Acta 39, 197 (1966); Phys. Kond. Materie 6, 105 (1967).

- [10] S. J. CHO, Phys. Rev. 157, 632 (1967).
- [11] J. C. SLATER, J. appl. Phys. 39, 761 (1968).
- [12] S. METHFESSEL, Z. angew. Phys. 18, 414 (1965).
- [13] J. C. SUITS and B. E. ARGYLE, J. appl. Phys. 36, 1251 (1965).
- [14] J. C. SUITS, B. E. ARGYLE and M. J. FREISER, J. appl. Phys. 37, 1391 (1966).
- [15] S. METHFESSEL, F. HOLTZBERG and T. R. McGuire, IEEE Trans. Mag. 2, 305 (1966).
- [16] S. METHFESSEL, J. J. FREISER, G. D. PETTIT and J. C. SUITS, J. appl. Phys. 38, 1500 (1967).
- [17] F. HOLTZBERG, T. R. McGuire and S. METHFESSEL, J. appl. Phys. 37, 976 (1966).
- [18] F. C. JOHODA, Phys. Rev. 107, 1261 (1957).
- [19] R. J. ZOLLWEG, Phys. Rev. 111, 113 (1958).
- [20] G. A. SAUM and E. B. HENSLEY, Phys. Rev. 113, 1019 (1959).
- [21] A. YANASE and T. KASUYA, J. appl. Phys. 39, 430 (1968).
- [22] A. YANASE and T. KASUYA, J. Phys. Soc. Japan (to be published).
- [23] R. O. KNOX, *Theory of Excitons* (Academic Press, New York 1963), p. 152 et seq.
- [24] M. J. FREISER, S. METHFESSEL and F. HOLTZBERG, J. appl. Phys. 39, 900 (1968).
- [25] J. C. SUITS, J. appl. Phys. 38, 1498 (1967).
- [26] B. E. ARGYLE, M. MIYATA and T. D. SCHULTZ, Phys. Rev. 160, 413 (1967).
- [27] S. FREED and S. KATCOFF, Physica 14, 17 (1948).
- [28] F. D. S. BUTEMENT, Trans. Faraday Soc. 44, 617 (1948).
- [29] P. P. FEOFILOV, Opt. Spect. 1, 992 (1956).
- [30] W. LOW, Nuovo Cim. 17, 607 (1960).
- [31] W. KAISER, C. G. B. GARETT and D. L. WOOD, Phys. Rev. 123, 766 (1961).
- [32] A. KAPLYANSKII and P. FEOFILOV, Opt. Spect. 12, 272 (1962); 13, 129 (1962).
- [33] P. P. SOROKIN, M. J. STEVENSON, J. R. LANKARD and G. D. PETTIT, Phys. Rev. 127, 503 (1962).
- [34] R. REISFELD and A. GLASNER, J. opt. Soc. Am. 54, 331 (1964).
- [35] D. L. WOOD and W. KAISER, Phys. Rev. 126, 2079 (1962).
- [36] Z. KISS, Phys. Rev. 127, 718 (1962).
- [37] R. REISFELD and A. GLASNER, J. opt. Soc. Am. 54, 331 (1964).
- [38] G. B. GOODENOUGH, *Magnetism and the Chemical Bond* (J. Wiley, New York 1963).
- [39] J. SMIT, J. appl. Phys. 37, 1455 (1966).
- [40] J. D. AXE and G. D. PETTIT, J. chem. Phys. Solids 27, 261 (1966); and private communication.

Localized Versus Band Model of Electrons in Solids

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(29. IV. 68)

The sixtieth birthday of Georg Busch is a welcome opportunity for discussing certain electronic properties which in the current theoretical literature are frequently treated wrongly. I refer to the so-called 'small' polaron – an electron in a polar lattice in which its interaction with the lattice displacements is so large that its properties are very different from those of an electron in a substance in which the band model holds. Conditions for such possibilities were first mentioned by myself [1] in 1957; reference to some of the frequently occurring mistakes are found in Reference [2].

Under the circumstances in question, an electron is best described as localized around an ion with a certain chance of jumping to a neighbour. Such a state is de-