



ChemComm

Giant Band Splittings in EuS and EuSe Magnetic Semiconductor Nanocrystals

Journal:	<i>ChemComm</i>
Manuscript ID	CC-COM-02-2020-000994.R1
Article Type:	Communication

SCHOLARONE™
Manuscripts

COMMUNICATION

Giant Band Splittings in EuS and EuSe Magnetic Semiconductor Nanocrystals†

Received 00th January 20xx,
Accepted 00th January 20xx

Dane Romar C. Asuigui,^a Michael C. De Siena,^b Rachel Fainblat,^{b,c} Derak James,^a
Daniel R. Gamelin,^{b,*} and Sarah L. Stoll^{a,*}

DOI: 10.1039/x0xx00000x

Using magnetic circular dichroism (MCD) spectroscopy, we demonstrate giant temperature- and field-dependent conduction-band splittings in colloidal EuS and EuSe nanocrystals.

Spintronic devices can exploit both the spins and the charges of electrons to control the flow of information. As such, spintronics have generated interest for data storage (e.g. tunnel magnetoresistance or magnetoresistive random access memory) and may play an important role in information processing and quantum computing technologies.¹ The development of such devices relies on understanding the creation and manipulation of spin-polarized currents, characterized by the percent spin polarization at the Fermi level.² ‘Spin-filtering’, allowing only one type of spin to cross a magnetic barrier, is an attractive approach to attaining high spin polarization from an unpolarized current. Because spin orientation is conserved in tunnelling, it is possible to use a magnetic tunnel barrier to generate spin-polarized electrons as well as to detect spin.³ The extent of current spin polarization can also be determined using spin-polarized photoemission, but spin-polarized tunneling has the sub-millielectron volt resolution required for device development.⁴

The first demonstration of spin-filter tunneling in the absence of an applied field used EuS as the ferromagnetic spin-filter,⁵ and EuSe provided the first example of fully polarized tunnel current.⁶ Europium selenide is metamagnetic,⁷ antiferromagnetic at low fields and ferromagnetic at high fields, so its spin-filtering efficiency is strongly field-dependent. The origin of spin-filtering by europium chalcogenides can be understood from the density of states diagram shown schematically in Fig. 1. Magnetic exchange interactions couple the half-occupied 4f electrons to the conduction band, comprised primarily of Eu²⁺ 5d orbitals. At T_c , magnetic

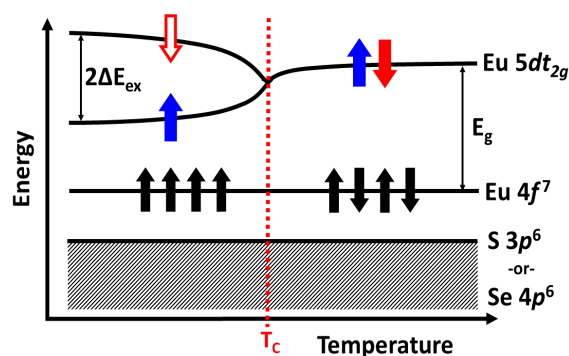


Figure 1. The effect of magnetic ordering on the conduction band. The black arrows indicate the spin of localized 4f electrons and the colored arrows indicate the spins of promoted charge carriers.

ordering of the 4f electrons splits the conduction band into spin-up (lowered by ΔE_{ex}) and spin-down (raised by ΔE_{ex}) levels. Conduction-band splitting leads to a majority of one spin orientation at the Fermi level and highly polarized spin currents.⁸ The extent of spin polarization depends on the magnitude of the splitting ($2\Delta E_{ex}$).⁹

In this work, we report the effect of temperature and magnetic field on the magnetic circular dichroism (MCD) of solution-grown EuS and EuSe nanocrystals. MCD is a differential absorption technique using circularly polarized light, and is a sensitive probe of magnetically dependent electronic transitions. Room-temperature MCD spectra of nanocrystals of EuS have been reported,¹⁰ but we find striking changes in the spectra as a function of temperature and field that indicate a very large conduction-band splitting below T_c . We also report the first MCD study of EuSe nanoparticles, again varying temperature and field. Room-temperature Faraday rotation (FR) spectra of EuSe nanomaterials have been reported;¹¹ but whereas FR is sensitive to long-range order, MCD is sensitive to short-range interactions that are important in this magnetically complex material. Changing temperature and applied field not only aid in sharpening the MCD peaks, but they also provide the opportunity to study changes in the density of states near the ordering temperature to elucidate the effects of magnetic coupling on the optical properties.

^a Department of Chemistry, Georgetown University, 37th and O Streets NW, Washington, D.C. 20057, United States.

^b Department of Chemistry, University of Washington, Seattle, Washington 98195-1700

^c Werkstoffe der Elektrotechnik and CENIDE, University of Duisburg-Essen, Bismarckstraße 81, 47057 Duisburg, Germany

†Electronic Supplementary Information (ESI) available: Complete experimental details and field-dependent MCD data. See DOI: 10.1039/x0xx00000x

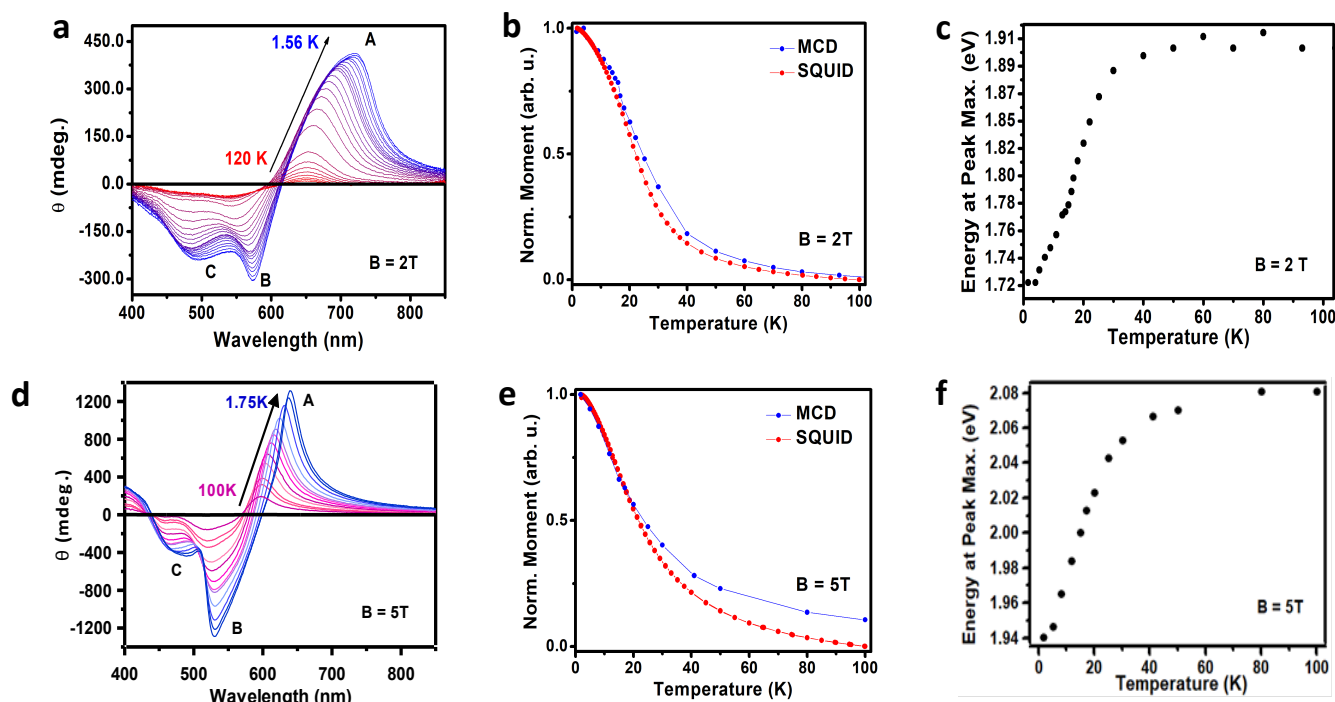


Figure 2. Variable temperature MCD spectra of (a) EuS nanocrystals at 2 T and (d) EuSe nanocrystals at 5 T. Normalized temperature-dependent MCD peak-to-peak amplitudes (blue) and magnetic susceptibilities (red) of (b) EuS nanocrystals measured at 2T and (e) EuSe nanocrystals measured at 5T. The MCD energy of peak A plotted vs temperature for (c) the EuS and (f) the EuSe nanocrystals at 2 and 5 T, respectively.

EuS and EuSe nanocrystals were synthesized as previously reported¹² and characterized by X-ray powder diffraction and transmission electron microscopy (see ESI†). The nanocrystal diameters were 7 (± 1) nm for EuS and 60 (± 20) nm for EuSe, both with cubic morphology. MCD measurements near the ordering temperature reveal a large conduction-band splitting in the EuS nanocrystals. The MCD data for the EuSe nanocrystals indicate two low-temperature magnetic phases (ferri- and ferromagnetic), and this material also exhibits a large conduction-band splitting.

Figure 2a plots MCD spectra of the EuS nanocrystals collected at various temperatures between 1.5 and 120 K. The EuS nanocrystal MCD spectra are similar to those of EuS thin films in general shape, peak width, and peak positions.¹³ We define three peaks for the spectra in Fig. 2a: A (1.91 eV for the nano and 1.92 eV for thin films), B (2.32 eV -vs- 2.31 eV), and a shoulder C (2.48 eV -vs- 2.62 eV). Although the temperatures and fields are somewhat different, our highest temperature is lower (120K-vs-RT) and our field is also lower (2T-vs-5T),¹³ the expected shifts due to lower temperature and reduced field are in opposite directions and appear to cancel so our values are quite close.

The lowest-energy electronic excited state of EuS has a $4f^65d_{2g}$ configuration, resulting from a $4f-5d$ promotion. At high temperatures, the spin degeneracy of this excited state can be split by an applied magnetic field to generate distinct transition energies for absorption of left and right circularly polarized light according to the selection rule $\Delta M_J = \pm 1$. Transitions to higher J values are dominantly left-circularly

polarized, while transitions to lower and intermediate J states are dominantly right-circularly polarized.^{15,16} Peaks A and B in Figure 2 are transitions to the two components of this spin-split $4f^65d_{2g}$ state. There is some debate in the literature as to the assignment of peak C,¹³ whether it is a $4f-6s$ excitation or a weak spin-forbidden transition to an $S = 5/2$ $4f^65d_{2g}$ state.¹⁷

Several changes are observed in the MCD spectra of the EuS nanocrystals as the temperature is decreased from 120 K down to 1.50 K (Fig. 2a). Because the circular dichroism is proportional to the magnetization,¹⁸ the peak amplitudes increase gradually as the temperature decreases, and then increase more sharply upon reaching the ferromagnetic ordering temperature ($T_C \sim 16.6$ K). Therefore, the temperature dependence of the MCD intensity (Fig. 2b, blue) is quite similar to a plot of χ -vs-T for EuS nanocrystals (Fig. 2b, red).

The evidence for conduction-band splitting in EuS thin films is a red-shift in the absorption edge,¹⁹ but such splittings can also be determined from spin-polarized electron emission measurements¹⁸ as well as by measuring resistance across tunnel junctions as a function of temperature.⁹ Here, a conduction-band splitting in the EuS nanocrystals is evident from the temperature dependence of the energy of peak A, plotted in Fig. 2c. Lowering the temperature from 120 K, the energy of peak A remains relatively constant until ~ 20 K, where it drops sharply to reach a maximum redshift of $\Delta E_{ex} = 0.18$ eV at 1.56 K. The inflection temperature (20 K) is again consistent with the magnetic ordering temperature. In bulk, the redshift is greatest for EuO ($\Delta E_{ex} = 0.23$ eV) and is smaller for EuS ($\Delta E_{ex} = 0.18$ eV).²⁰ The redshift observed in the nanocrystals

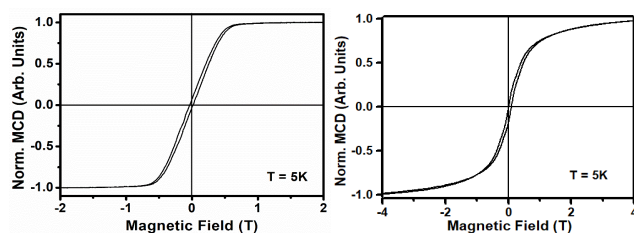


Figure 3. MCD intensity plotted vs magnetic field for the EuS nanocrystals (left, monitored at 700 nm) and the EuSe nanocrystals (right, monitored at 525 nm), at temperatures below T_c .

compares quite well to the shift observed in bulk, and corresponds to a very large conduction band splitting of $2\Delta E_{ex} = 0.36$ eV.

The 5 K MCD intensity of the EuS nanocrystals saturates at low magnetic fields and shows a hysteresis in field-sweep measurements (Fig. 3, left, and Fig. S3, ESI†). The coercive field from these data is 310 Oe (0.031 T). Increasing the field also increases the red shift of peak A, but the magnetization saturates at low applied fields (<0.5 T) which means the conduction band splitting won't change significantly above this field. Interestingly, EuS thin films used as tunnel barriers exhibit 90% spin polarization at zero field, and this spin polarization, like the conduction band splitting, is largely independent of applied field.⁵

We also used variable-temperature and variable-field MCD to probe the EuSe nanocrystals. Figure 2d plots the MCD spectra of the EuSe nanocrystals as a function of temperature. These data appear qualitatively similar to those of the EuS nanocrystals, and the optical transitions have the same assignments. The EuSe nanocrystal MCD spectra are similar to MCD spectra reported for EuSe thin films (variable T, $H = 5T$);¹⁴ however, peak positions were not reported in previous studies. The EuSe nanocrystals exhibit peaks: A (2.08 eV), B (2.38 eV), and at low temperatures C (2.71 eV), as well as a fourth peak D (~3.12 eV) not seen in EuS. As expected from the literature values of E_g for both materials (EuSe > EuS), peak A is higher in energy in the EuSe nanocrystals (2.08 eV) than in the EuS nanocrystals (1.91 eV). In addition, band A is narrower for EuSe than EuS. The width of the 4f band has been determined to be ~0.62 eV and unaffected by the anion;²¹ however, the crystal-field splitting of the 5d orbitals is greater in EuS (Δ_{Oct} estimated at 2.2 eV) than in EuSe (Δ_{Oct} estimated at 1.7 eV),²¹ consistent with the assignment of this peak.

The temperature dependence of the EuSe nanocrystal MCD must be interpreted differently from that of the EuS nanocrystals, because EuSe does not have a defined Curie temperature. EuSe has a more complex magnetic phase diagram than EuS because of its nearly equivalent magnitudes of ferromagnetic ($J_1/k(K) = +0.1$) and antiferromagnetic ($J_2/k(K) = -0.09$) exchange-coupling strengths.²² As a result, EuSe is metamagnetic. Measurements at low temperatures and fields ($H < 250$ mT, $T < 4$ K) have found evidence of type II antiferromagnetic ordering ($\uparrow\downarrow\uparrow\downarrow$), ferrimagnetic ordering ($\uparrow\uparrow\downarrow$), and type I antiferromagnetic ordering ($\uparrow\uparrow\downarrow\downarrow$) in bulk EuSe.²³ The field dependence of these transitions provides insight into the strength of the magnetic coupling.

Figure 2e plots the EuSe nanocrystal MCD intensity as a function of temperature, in comparison with magnetic susceptibility data collected on the same sample. The temperature dependence for EuSe is broadened relative to the EuS nanocrystal data (Fig. 2b). Both the MCD and the magnetic susceptibility reflect the ferromagnetic coupling at 5 T, but the magnetization appears at higher temperatures. The spontaneous magnetization at high temperatures that causes this increase in intensity is not long-range order—there is a noticeable deviation between the MCD intensity, which is still appreciable above 80K, and the magnetic susceptibility, which is diminished by this temperature. The interpretation of MCD spectra of thin films of EuSe, which are quite similar, is that domains form locally at temperatures ~30K, as described by a near-neighbor spin correlation function.²⁴

Large conduction-band splitting is also observed in the EuSe nanocrystals by MCD. Relative to the EuS nanocrystals, the splitting energy is smaller yet it persists at higher temperatures. The conduction-band splitting energy depends on the coupling of the 4f and 5d electrons and can be estimated as proportional to J_1S ($S = 7/2$), and J_1 is smaller for EuSe.²⁵ Consistent with this expectation, we have measured a redshift of $\Delta E_{ex} = 0.14$ eV (at 5T) in the EuSe nanocrystals, which is smaller than the redshift observed in the EuS nanocrystals (0.18 eV). The measured redshift compares well with the literature value for bulk EuSe, $\Delta E_{ex} = 0.15$ eV ($H = 1.5$ T).¹⁹ Our data lead to a conduction band splitting value of $2\Delta E_{ex} = 0.28$ eV. In thin films of EuSe, the gradual red-shift with decreasing temperature exhibits a kink at the anti-ferromagnetic ordering temperature of 4 K (T_N);¹⁸ a comparable kink is difficult to

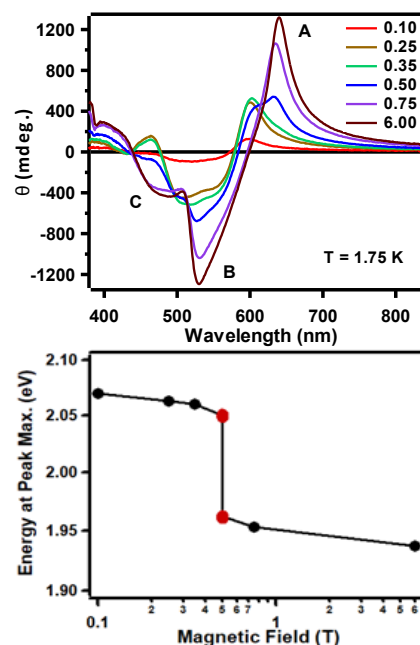


Figure 4. (top) Field-dependent MCD spectra of EuSe nanocrystals collected at 1.75 K. At 0.5 T, blue spectrum, both phases are observable. (bottom) The energy of peak A as a function of magnetic field strength, from the data in the top panel. The red dots show the energies of the two peaks observable in the 0.5 T spectrum.

discern in the MCD data here because of the higher field used.

The MCD field dependence adds information to the complex magnetic ordering in the EuSe nanocrystals. In Figure 3, the field dependence of the EuSe 5 K MCD intensity at peak B (525 nm) is similar to the hysteresis curve measured for EuS nanocrystals. Based on this data the coercive field for the EuSe nanocrystals is 850 Oe (0.085 T). However, the field dependence of the EuSe nanocrystal spectra collected at lower temperature (1.75 K, Fig. 4, top) are more revealing. These data show one spectrum at $H < 0.5$ T (exemplified by $H = 0.25$ T, 0.35 T) but a different spectrum at $H > 0.5$ T (exemplified by $H = 0.75$ and 6 T). Both spectra coexist at 0.5 T. The high-field peaks are distinctly red-shifted, as seen in a plot of the peak A energy vs field (Fig. 4, bottom). The abrupt step-like change in peak energy seen here corresponds to a red shift of $\Delta = 0.10$ eV between 0.35–0.5 T. A similar effect has been observed in the optical absorption of EuSe epilayers and ascribed to a magnetic phase transition, where at a critical field the magnetism changes from ferrimagnetic ($\uparrow\uparrow\downarrow$) to ferromagnetic ($\uparrow\uparrow\uparrow$).⁷ The μ_{eff} in the ferrimagnetic phase is $\sim 2/3$ of that in the ferromagnetic phase, and therefore the redshift is $\sim 2/3$ of the high-field MCD redshift (0.14 eV). The critical field for the EuSe nanocrystals here is slightly larger (>0.35 T) than that reported for thin films (0.3 T), but it is closer in agreement to that determined from EuSe films used as tunnel junctions, where a change in electron-spin polarization due to magnetic ordering was observed at applied fields greater than ~ 0.5 T.⁶ This comparison suggests that the critical field increases as the EuSe dimensions decrease. Such a size effect could conceivably relate to the presence of uncompensated spins at the surfaces of the nanocrystals, or to small changes in unit cell volume with greater surface-to-volume ratios, but the origins of this effect require further investigation.

In conclusion, the temperature dependence of the MCD of both EuS and EuSe nanocrystals reveal large conduction-band splittings in these materials, which is a key attribute for spin-filtering. The conduction-band splitting is greater in the EuS nanocrystals ($2\Delta E_{\text{ex}} = 0.36$ eV vs $2\Delta E_{\text{ex}} = 0.28$ eV) and less sensitive to applied field than it is in the EuSe nanocrystals. In addition, the field-dependence of the EuSe nanocrystal MCD spectra show evidence of a critical field at which the nanocrystals convert from ferrimagnetic to ferromagnetic ordering. We are interested in investigating why the critical field is greater in nanocrystals than in the bulk and, in future work, will use small angle neutron scattering to determine whether this trend is due to surface effects.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements.

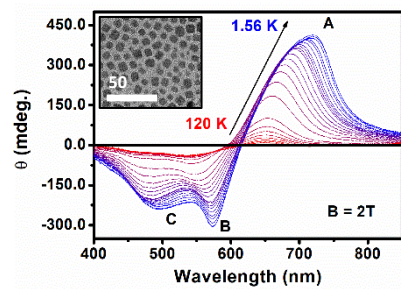
This research was partially supported by the US National Science Foundation (NSF) through project DMR-1807394 (to

DRG), and CHE-1607905, and CHE-1904616 (SLS). Additional support through the UW Molecular Engineering Materials Center (NSF MRSEC DMR-1719797) is gratefully acknowledged.

Notes and references

- Hirohata, A.; Yamada, K.; Nakatani, Y.; Prejbeanu, L.; Dieny, B.; Pirro, P.; Hillebrands, B. *Journal of Magnetism and Magnetic Materials* 2020, in press, 10.1016/j.jmmm.2020.16671.
- Hirohata, A.; Takanashi, K. *J. Phys. D: Appl. Phys.* 2014, **47**, 193001–193040
- Miao, G.; Moodera, J. Spin Manipulation with Magnetic Semiconductor Barriers, *Phys. Chem. Phys.*, 2015, **17**, 751–761.
- Joshi, V. K. *Engineering Science and Technology, an International Journal* 2016, **19**, 1503–1513.
- Moodera, J.; Hao, X.; Gibson, G. A.; Meservey, R. *Phys. Rev. Lett.*, 1988, **61**, 637–640.
- Moodera, J.; Meservey, R.; Hao, X. *Phys. Rev. Lett.*, 1993, **70**, 853–856.
- Kirchschlager, R.; Heiss, W.; Lechner, R. T.; Bauer, G.; Springholz, G. *Appl. Phys. Lett.*, 2004, **85**, 67–69.
- Moodera, J. S.; Santos, T. S.; Nagahama, T. *J. Phys.: Condens. Matter.*, 2007, **19**, 165202–165224.
- Santos, T. S.; Moodera, J. S.; Raman, K. V.; Negusse, E.; Holroyd, J.; Dvorak, J.; Liberati, M.; Idzerda, Y. U.; Arenholz, E. *Phys. Rev. Lett.*, 2008, **101**, 147201–147204.
- Tsukahara, Y.; Kataoka, T.; Hasegawa, Y.; Kaizaki, S.; Wada, Y. *J. Alloys Compd.*, 2006, **408–412**, 203–206.
- Hasegawa, Y.; Adachi, T.-A.; Tanaka, A.; Afzaal, M.; O'Brien, P.; Doi, T.; Hinatsu, Y.; Fujita, K.; Tanaka, K.; Kawai, T. *J. Am. Chem. Soc.*, 2008, **130**, 5710–5715.
- Dalafu, H. A.; Rosa, N.; James, D.; Asuigui, D. R. C.; McNamara, M.; Kawashima, A.; Omagari, S.; Nakanishi, T.; Hasegawa, Y.; Stoll, S. L. *Chem. Mater.*, 2018, **30**, 2954–2964.
- Ferre, J.; Briat, B.; Paparoditis, C.; Pokrzywnicki, S.; Suryanarayanan, R. *Solid State Commun.*, 1972, **11**, 1173–1177.
- Ferre, J.; Billardon, M.; Badoz, J.; Suryanarayanan, R.; Paparoditis, C.; *J. Phys., Colloq.*, 1971, **32**(2-3), 930–931.
- Feinleib, J.; Scouler, W.; Dimmock, J.; Hanus, J.; Reed, T.; Pidgeon, C. *Phys. Rev. Lett.*, 1969, **22**, 1385–1388.
- Dimmock, J. O., *IBM J. Res. Develop.*, 1970, **14**, 301–308.
- Schoenes, J. Z. *Physik B*, 1975, **20**, 345–368.
- Mauger, A.; Godart, C. *Phys. Rep.*, 1986, **141**, 51–176.
- Wachter, P., *Crit. Rev. in Solid State Sci.*, 1972, **3**(2), 189–241.
- Busch, G.; Wachter, P. *Phys. Kondens. Mater.*, 1966, **5**, 232–242.
- Güntherodt, G.; Wachter, P.; Imboden, D. *Phys. Kondens. Mater.*, 1971, **12**, 292–310.
- Zinn, W. *J. Magn. Magn. Mater.*, 1976, **3**, 23–36.
- Díaz, B.; Granado, E.; Abramof, E.; Torres, L.; Lechner, R. T.; Springholz, G.; Bauer, G. *Phys. Rev. B*, 2010, **81**, 621–626.
- Callen, H.; Callen, E. *Phys. Rev.*, 1964, **136**(6A), 1675–1683.
- Wachter, P., *Handbook on Physics and Chemistry of Rare Earths*, ed. Gschneidner, North-Holland Publishing Company, 1979, **Volume 2**, Ch.19, p. 507–572.

TOC abstract and graphic



Giant band-splitting observed in EuS and EuSe nanocrystals by magnetic circular dichroism.