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Rapid Note

Splitting of the Cr 2p ions states in some ternary sulphides and selenides

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Abstract. X-ray photoelectron spectroscopy was used to investigate ACr_2S_4 (A = Cd, Zn, Mn, Fe, Fe:Cu) and BCr_2Se_4 (B = Cd, Cu, Hg, Hg:Cu) single crystals. Well defined splitting of the Cr 2*p* core level has been found. The local magnetic moments of the Cr ions are responsible for the observed effect.

PACS. 79.60.-i Photoemission and photoelectron spectra – 75.50.Pp Magnetic semiconductors

1 Introduction

Ternary ACr_2X_4 (A = Cd, Hg, Cu, Fe, Mn; X = S, Se) magnetic compounds exhibit a variety of magnetic and electrical properties as there are metallic $CuCr_2X_4$ and semiconducting $Hg(Cd)Cr_2Se_4$ ferromagnets, semiconducting $Fe(Mn)Cr_2S_4$ ferrimagnets and insulating $ZnCr_2S_4$ antiferromagnet. The strong coupling between the 3*d* spins of the magnetic ions and the *sp* electrons results in a number of interesting phenomena, like "giant" red shift of the absorption edge, "colossal" magnetoresistance (CMR), "giant" Faraday rotation, magnetic field induced metal-insulator transition etc. [1–4]. The search for new materials with potential applications taking advantage of the CMR effect renewed the interest in magnetic semiconducting chalcogenides [5]. A complete understanding of the CMR behaviour in the materials exhibiting such effects is of fundamental importance in order to allow the design of new materials with enhanced characteristics. The thiospinels, for example, are therefore particularly interesting, since the mechanism for CMR behaviour seems to be different from that of the widely studied perovskite manganese oxides, where the Zener double exchange and the strong electron-lattice interaction are possible [6–8].

This paper presents the results of X-ray photoelectron spectroscopic investigations of the Cr 2*p* core levels in some ternary magnetic sulphides ACr_2S_4 (A = Cd, Zn, Mn, Fe, Fe:Cu) and selenides BCr_2Se_4 (B = Cd, Cu, Hg, Hg:Cu) crystals in order to investigate the local magnetic properties of these interesting materials.

2 Experimental details

The ACr_2S_4 (A = Cd, Mn, Fe, Fe:Cu) and BCr_2Se_4 (B = Cd, Cu, Hg, Hg:Cu) single crystals were grown by chemical transport reactions using chlorine or iodine as transport agents. The $ZnCr_2S_4$ polycrystals were prepared by solid state reaction. X-ray diffractometry revealed the single phase spinel structure of the samples with the lattice parameters close to those reported in literature [1,4]. The XPS measurements were performed with a PHI 5600ci ESCA-spectrometer. Using monochromated Al Kα-radiation an overall resolution of 0.3 eV was achieved. The angle between the incident light and the outgoing electrons was 90° for all measurements. The base pressure in our ultrahigh-vacuum chamber was controlled to be less than 3×10^{-9} mbar. In order to minimize contamination, the samples were cleaved *in situ*. Furthermore, we checked possible contamination by analysing the O 1*s* and C 1*s* XPS signals during the measurements. No important enhancement, except for the $Fe_{0.5}Cu_{0.5}Cr_2S_4$ crystal, was found.

3 Results and discussion

Figure 1 shows the XPS spectra of the Cr 2*p* levels for the ACr_2S_4 (A = Cd, Mn, Fe, Fe:Cu) sulphides. The spectra are normalized to their maximum. The binding energy of the Cr $2p_{3/2}$ level (middle position) is around 575 eV. For $MnCr_2S_4$ and $ZnCr_2S_4$ charging effects occur due to their more insulating character in comparison with the other studied compounds. Using a low energy electron flood gun, charging effects could be avoided by neutralization, thus the spectra shown in Figures 1 and 2 contain no charging

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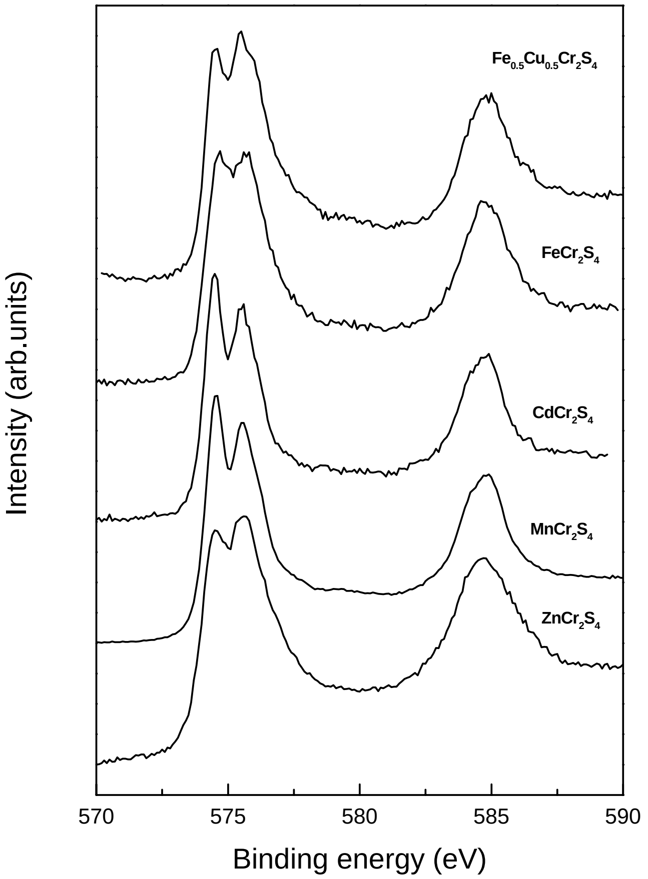

Fig. 1. Cr $2p$–XPS spectra of the $\mathrm{ACr_2S_4}$ (A = Cd, Mn, Fe, $\mathrm{Fe_{0.5}Cu_{0.5}}$) single crystals and ZnCr2S4 polycrystal.

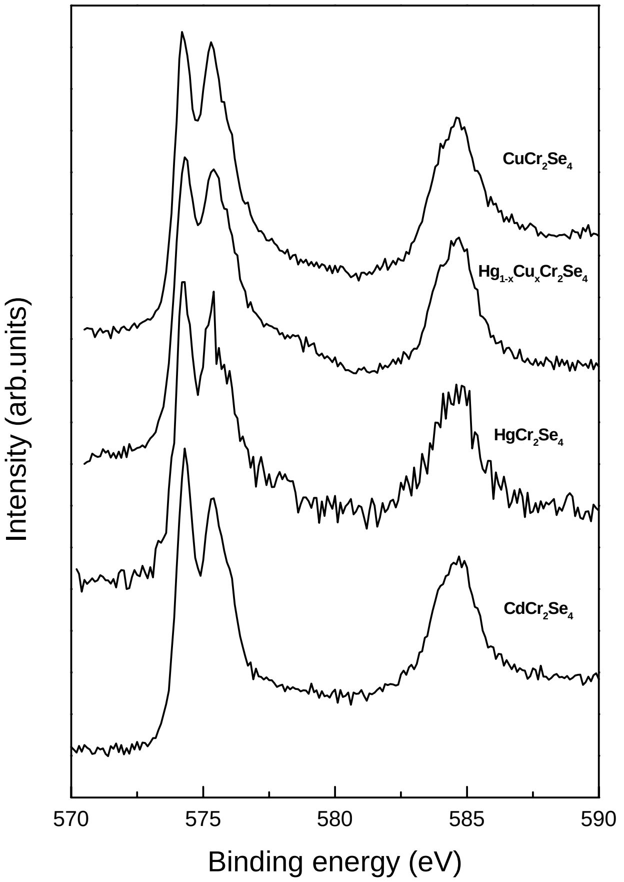

Fig. 2. Cr $2p$–XPS spectra of the $\mathrm{BCr_2Se_4}$ (B = Cd, Cu, Hg, $\mathrm{Hg_{0.96}Cu_{0.04}}$) single crystals.

effects. In all compounds a clear splitting of the Cr $2p_{3/2}$ line is seen. This splitting is for all samples about 1.0 ± 0.1 eV.

The splitting of the core levels of the magnetic ions is generally attributed to the existence of spin polarisation of the $3d$ states. It is necessary to note that recently, a similar splitting of the Mn $2p$ core level in some half-metallic ferromagnetic Heusler alloys has been found and was considered as a result of the well defined local $3d$ states of the Mn ions [9]. In accordance with these experimental and theoretical results, we attribute the observed effect to the magnetic exchange splitting due to the local magnetic moment of the Cr ion. Theoretical calculations of this splitting predicted this effect to be angle dependent [10]. Experiments on the MnO single crystals revealed this behaviour [11]. Our studies of the Cu- and Hg-based compounds have not shown any substantial angular dependence of the splitting or redistribution of the intensities of the splitted peaks. Eventually this is a result of the highly magnetic isotropic behaviour of these compounds.

Neutron diffraction measurements have shown a magnetic moment of $2.9\,\mu_\mathrm{B}$ on the Cr-site for $\mathrm{FeCr_2S_4}$ at 4.2 K [12] and for $\mathrm{Fe_{0.5}Cu_{0.5}Cr_2S_4}$ at 10 K [8]. The value of $3\,\mu_\mathrm{B}$ for the Cr ions in $\mathrm{MnCr_2S_4}$ [13] and $\mathrm{CdCr_2S_4}$ [14] was also found. In order to estimate the magnetic moment on the Cr-site, we compared the observed Cr $2p$ splitting with the Mn $2p$ splitting, which was found to be proportional to the local magnetic moment [10]. For $\mathrm{Co_2MnAl}$ a local magnetic moment of $3.0\,\mu_\mathrm{B}$ for the Mn ions was obtained by neutron scattering [15]. A Mn $2p$ core level splitting of 1.0 eV was measured for the same compound [9]. The local magnetic moment of $2.9-3.0\,\mu_\mathrm{B}$ for the Cr ions in our compounds would lead to a splitting of 0.95–1.0 eV, which is in good agreement with the observed value of the splitting.

A pronounced splitting of the Cr $2p$ levels was also observed in ternary selenides $\mathrm{BCr_2Se_4}$ (B = Cd, Hg, Cu), as shown in Figure 2. The value of the Cr $2p$ splitting in the selenides was found be similar to those of the sulphides.

The similar values of the splitting of the Cr $2p$ levels for all investigated samples may indicate a similar value of the local magnetic moment of the chromium ions in $3d^3$ configuration, although they exhibit completely different macroscopic magnetic properties. It is necessary to mention that in [16] using neutron diffraction it has been concluded that the Cr ions exhibit a mixed valence and a reduced magnetic moment ($2.64\,\mu_\mathrm{B}$). From our results on Cu-based compounds one could expect the divalent copper ions. However, our XPS investigation of the $2p$ core level of Cu [17] did not reveal the features typical for $\mathrm{Cu^{2+}}$ ions, as it was observed, for example, in oxides [18].

Furthermore, we have found recently that the XPS spectra of our $Fe_{0.5}Cu_{0.5}Cr_2S_4$ crystals show no splitting of the Cu 3*s* level, in accordance with the diamagnetic $3d^{10}$ configuration of the Cu^+ ion [19]. The similar results we have obtained for the $CuCr_2Se_4$ crystals.

To summarise, we have observed the splitting of the Cr 2*p* core levels in a number of ternary ACr_2X_4 (A = Cd, Hg, Cu, Fe, Mn; X = S, Se) magnetic compounds, which indicates the localised character of the magnetic moments for Cr in a $3d^3$ configuration for all investigated materials.

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References

1. S. Methfessel, D.C. Mattis, *Magnetic semiconductors*, Handbuch der Physik, Bd.XVIII/1 (Springer-Verlag, 1968).
2. *New Developments in Semiconductors* (North-Holland Publishing Company, Leyden, 1973).
3. E.L. Nagaev, *Physics of Magnetic Semiconductors* (Moskow, Science, 1979).
4. R.P. Van Stapele, in *Ferromagnetic Materials*, edited by E.P. Wohlfarth (Elsevier Sciences Publisher B.V., Netherlands, 1982), Vol. 3, p. 603.
5. A.P. Ramirez, R.J. Cava, J. Krajewski, Nature **386**, 156 (1997).
6. C. Zener, Phys. Rev. **82**, 403 (1951).
7. A. P.Ramirez, J. Phys. Cond. Matter **9**, 8171 (1997).
8. H.M. Palmer, C. Greaves, J. Mater. Chem. **9**, 637, (1999).
9. Yu.M. Yarmoshenko, M.I. Katsnelson, E.I. Shreder, E.Z. Kurmaev, A. Slebarski, S. Plogmann, T. Schlatholter, J. Braun, M. Neumann, Eur. Phys. J. B **2**, 1 (1998).
10. S. Plogmann, T. Schlatholter, J. Braun, M. Neumann, Yu.M. Yarmoshenko, M.V. Yablonskikh, E.I. Shreder, E.Z. Kurmaev, A. Wrona, A. Slebarski, Phys. Rev. B **60**, 6428 (1999).
11. St. Uhlenbrock. Ph.D. thesis (Osnabrueck, 1994).
12. G. Shirane, D.E. Cox, S.J. Pickart, J. Appl. Phys. **35**, 954 (1964).
13. N. Menyuk, K. Dwight, A. Wold, J. Appl. Phys. **36**, 1088 (1965).
14. S. Pouget, M. Alba, N. Fanjat, M. Nogues, Physica B **180 & 181**, 244 (1992).
15. P.J. Webster, J. Phys. Chem. Solids **32**, 1221 (1971).
16. O. Yamashita, Y. Yamaguchi, I.Nakatani, H. Watanabe, K. Masumoto, J. Phys. Soc. Jpn **46**, 1145 (1979).
17. E.Z. Kurmaev, A.V. Postnikov, H.M. Palmer, C. Greaves, St. Bartkowski, V. Tsurkan, M. Demeter, D. Hartmann, M. Neumann, D.A. Zatsepin, V.R. Galakhov, S.N. Shamin, V. Trofimova (to be published).
18. K.S. Kim, J. Electron Spectr. **3**, 217 (1974).
19. V. Tsurkan, M. Demeter, B. Schneider, D. Hartmann, M. Neumann, Solid State Comm. **114**, 149 (2000).