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Electronic structure of the half-metallic ferromagnet KCrSe$_2$

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The electronic structure of the layered compound KCrSe$_2$ in the ferromagnetic spin arrangement is calculated using the augmented-spherical-wave method. For the minority-spin direction the Fermi level lies in a 1.34-eV-wide gap between the bottom of the Cr $3d\downarrow$ band and the Se $4p\downarrow$ band, while for the majority-spin direction the Fermi level crosses the Cr $3d\uparrow$ bands. This means that KCrSe$_2$ is a half-metallic ferromagnet.

A magnetic compound is called a half-metallic (ferro)magnet, when it is metallic for one spin direction, while it is semiconducting for the other spin direction.[1]

Electronic-structure calculations of chromium tellurides and other binary Cr chalcogenides[2] show that none of these compounds are half-metallic ferromagnets. Although the density of states (DOS) at the Fermi level E_F for the minority-spin direction is rather low in these compounds, it is always nonzero. In Cr tellurides the Te $5p\downarrow$ band crosses the Fermi level. In CrSe and CrS the chalcogen p bands for the $\downarrow$ direction all lie below E_F, but the Cr $3d_{z^2}$-Cr $3d_{z^2}$ overlap along the c axis—the direction of the shortest Cr-Cr distances in the NiAs-type structure—leads to a broadening of the Cr $3d$ band, so that the bottom of the Cr $3d\downarrow$ band is situated below E_F.

To achieve a band gap at E_F for the minority-spin direction, the Cr $3d\downarrow$-band width and thus the number of neighboring Cr atoms must be reduced. Introduction of 25% Cr vacancies in CrSe leads to a reduced Cr $3d\downarrow$-band width in Cr$_3$Se$_4$ compared to CrSe, but the Cr $3d\downarrow$ band is not narrow enough that it lies completely above E_F.[2] Cr$_2$Se$_3$ is the next candidate to be a half-metallic ferromagnet, but in this compound the antiferromagnetic exchange interactions largely dominate.[3] Further reduction of the number of Cr atoms and thus also of the number of electrons per Cr atom leads to the disappearance of magnetic moments: Exchange-enhanced Pauli-paramagnetic behavior is found in the layered compound CrSe$_2$.[4] The electronic structure of CrSe$_2$ is calculated by Myron.[5]

Instead of introducing vacancies in every alternate metal layer of hexagonal CrSe in order to diminish the number of Cr—Cr bonds in the c direction, it is also possible to substitute a part of the Cr atoms by nonmagnetic atoms such as alkali-metal atoms. When half of the Cr atoms are replaced by potassium, KCrSe$_2$ is obtained. The structure of this compound (see Fig. 1) can be described in the space group $R\bar{3}m$ (D_{3d}^5, no. 166 in the *International Tables of Crystallography*) with the atoms on the following special positions:[6]

$(0,0,0),(\frac{2}{3},\frac{1}{3},\frac{1}{3}),(\frac{1}{3},\frac{2}{3},\frac{2}{3})+$

3 Cr in (3a): (0,0,0) ,

3 K in (3b): (0,0,$\frac{1}{2}$) ,

6 Se in (6c): (0,0,z),(0,0,$\bar{z}$) with $z=0.275$.

The cell parameters are $a=3.602$ Å and $c=21.15$ Å.[6] This structure can be regarded as an intercalated layer compound: All octahedral sites in the van der Waals gap between the CrSe$_2$ sandwiches are occupied with K atoms. Cr and K both have a trigonally distorted octahedral coordination by six Se. The CrSe$_2$ slabs are shifted over $(\frac{2}{3},\frac{1}{3},\frac{1}{3})$ with respect to each other, so that no short
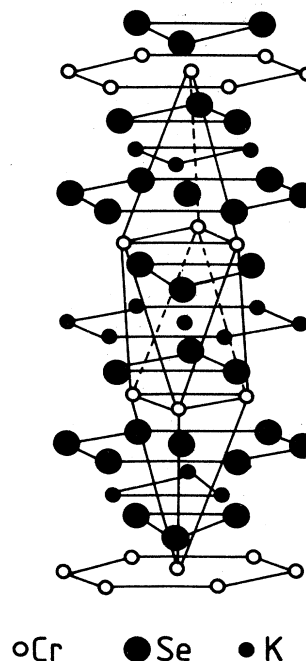

FIG. 1. The crystal structure of KCrSe$_2$.

○ Cr ● Se ● K

metal-metal distances along the c axis exist.

The same structure, which is a superstructure of the NaCl lattice, is found in $NaCrS_2$, $KCrS_2$, and $NaCrSe_2$.[7-9] For the smaller alkali-metal ion Li the CrS_2 slabs are stacked right on top of each other and an ordered NiAs-type structure results for $LiCrS_2$.[10]

The anisotropic structure of these compounds is reflected in their magnetic structures. In $KCrSe_2$, $NaCrSe_2$, and $KCrS_2$ the Cr magnetic moments form ferromagnetic sheets perpendicular to the c axis, which are antiferromagnetically coupled to adjacent layers. The antiferromagnetic coupling between different planes is much weaker than the in-plane ferromagnetic coupling, leading to metamagnetic behavior. Applied magnetic fields H_{c2} of a few T are enough to overcome the small antiferromagnetic interaction and to order neighboring planes ferromagnetically.[6] The predominantly ferromagnetic character of the exchange interactions in these compounds is also reflected in their positive asymptotic Curie temperatures Θ.

For the band-structure calculation in the ferromagnetic spin structure we have chosen the compound which is closest to overall ferromagnetism, $KCrSe_2$. It has the highest Θ (250 K), the lowest H_{c2} (1.3 T), and the smallest ratio $|J_2/J_1|$ (3×10^{-3}), where J_1 is the strong intralayer ferromagnetic exchange and J_2 the weaker antiferromagnetic interlayer exchange.[6] The saturation magnetization of $KCrSe_2$ amounts to $2.6\mu_B$ per Cr, while the spin-only moment from a Curie-Weiss analysis of the high-temperature susceptibility is $3.0\mu_B$.[6]

Band-structure calculations of ferromagnetic $KCrSe_2$ were performed, using the augmented-spherical-wave (ASW) method.[11] Exchange and correlation are treated in the local-density approximation. In these self-consistent calculations scalar-relativistic effects are included. In the ASW method the crystal is divided into so-called Wigner-Seitz spheres, in which the potentials are taken spherically symmetric. Wigner-Seitz sphere radii $r_{Cr} = 1.081$ Å and $r_K = r_{Se} = 1.904$ Å were used. For Cr the $3d$, $4s$, and $4p$ functions were used as a basis, for K, $4s$ and $4p$ functions, and for Se, $4s$, $4p$, and $4d$ functions.

We have calculated the band structure of $KCrSe_2$ only for the ferromagnetic spin structure, using experimental cell axes, because we are mainly interested in half-metallic ferromagnetism. Minimization of the total energy by variation of the spin structure, cell axes, or z parameters is out of the scope of this study. Figure 2 shows the calculated energy bands along high-symmetry directions in the hexagonal Brillouin zone. Most bands have little dispersion in the ΓA direction due to the strongly two-dimensional structure of this compound. Therefore only the dispersion in the central plane of the Brillouin zone is shown. The total and partial DOS are plotted in Fig. 3. Around 13-eV binding energy the Se $4s$ band is found, while the Se $4p$ bands range from a binding energy of -5.5 eV up to E_F. Covalent mixing between the Cr $3d$ and Se $4p$ states is observed. The Cr $3d$ derived bands show an exchange splitting of 2.3 eV between the $\uparrow$ and $\downarrow$ directions. The Cr $3d$ bands in $KCrSe_2$ are rather narrow, comparable in width with antiferromagnetic CrSe, while the Cr $3d$ bands in ferromagnetic CrSe are much wider.[2] The strong Cr $3d$ band-broadening effect in ferromagnetic CrSe was shown to be due to Cr $3d_{z^2}$-$3d_{z^2}$ overlap between neighboring Cr atoms with parallel magnetic moments along the c axis.[2] Cr $3d$ bands are rather narrow for cases in which there are no short Cr-Cr distances along the c axis ($KCrSe_2$) or when neighboring Cr atoms are antiferromagnetically coupled (antiferromagnetic CrSe).
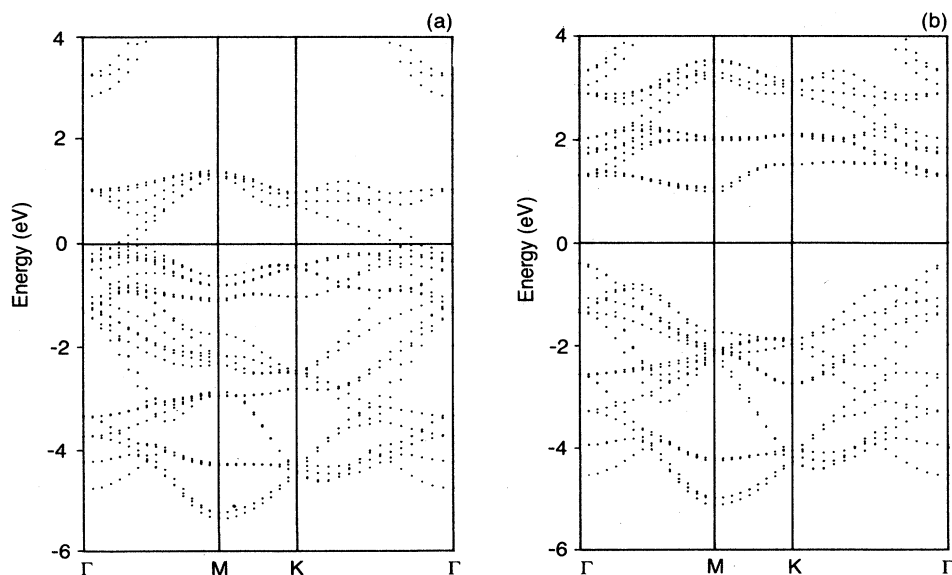

FIG. 2. The energy bands along the high-symmetry directions of $KCrSe_2$ in the basal plane of the hexagonal Brillouin zone for the (a) majority- and the (b) minority-spin direction.
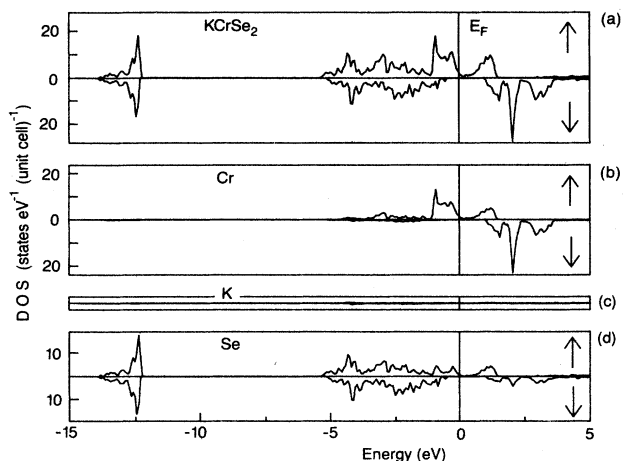
FIG. 3. The DOS of ferromagnetic $KCrSe_2$. (a) Total DOS; (b) partial Cr DOS; (c) partial K DOS; (d) partial Se DOS. Units: states/(eV unit cell).

The absence of K partial DOS in the valence-band regions shows that the role of K in this compound is restricted to donating one electron to the $CrSe_2$ host band structure and keeping the $CrSe_2$ sandwiches apart. The K $4s$ band lies far above E_F. Of course the K ion cores do give a contribution to the Madelung energy, which is the determining factor for the stacking of the slabs.

The most conspicious aspect of this band structure is its half-metallic ferromagnetic nature. While E_F falls in a band gap of 1.34 eV for the minority-spin direction, it crosses some majority-spin bands. The conduction electrons are thus fully spin polarized. This phenomenon was discovered and given its name half-metallic magnetism by de Groot et al.[1] in the Heusler alloy NiMnSb. Later other half-metallic materials were found: various Heusler alloys,[12] CrO_2,[13] and Fe_3O_4.[14] The ferromagnetic sulfospinel $CuCr_2S_4$ is also a half-metallic ferromagnet.[15] Very few experimental techniques can undoubtly give an answer to the question of whether a compound is a half-metallic ferromagnet or not. Spin-polarized photoemission experiments did not show the 100% spin polarization at the Fermi level for NiMnSb (Ref. 16) and CrO_2,[17] which one would expect for a half-metallic material. However, photoelectron spectra are, especially in the case of $3d$ transition metals, partly determined by final-state effects, which make it very hard to draw definite conclusions about ground-state properties. Recently, the results of spin-polarized positron-annihilation measurements of NiMnSb could only satisfactorily be explained by a half-metallic ferromagnetic band structure.[18]

The bands crossing E_F mainly have Cr $3d$ character, although an appreciable amount of Se $4p$ is mixed in. The structure of the $3d$ bands is usually explained in terms of the octahedral ligand field around the $3d$ atom, giving a t_{2g}-e_g splitting. Band formation and covalency broaden both subbands and a closing of the gap between the t_{2g} and e_g subbands is not uncommon.[19] In $KCrSe_2$ there is no gap around E_F for the majority-spin electrons,

so that $KCrSe_2$ has not the band structure of a semiconductor, but of a half-metallic ferromagnet. The bands crossing E_F are rather dispersive, and the density of states at the Fermi level is 0.9 states per eV per formula unit.

The presence of a band gap at E_F for the $\downarrow$ electrons implies an integer value of the magnetization per unit cell, which was calculated to be $9.00\mu_B$ (3.00 μ_B per formula unit $KCrSe_2$): 2.980, +0.014, and $-0.008\mu_B$ within the Cr, Se, and K Wigner-Seitz spheres, respectively. The observed saturation magnetization of $KCrSe_2$ at 4.2 K is $2.6\mu_B$, while the number of unpaired spins, calculated from the high-temperature paramagnetic susceptibility is 3.0.[6] No other physical measurements on $KCrSe_2$ have been reported. For $K_{0.6}CrSe_2$ a semiconductorlike conductivity is reported,[20] but disorder effects may be of importance in this partly intercalated compound.

One can ask the question whether $KCrSe_2$ should be classified as a magnetic Mott-Hubbard insulator.[21] The Mott-Hubbard model states that the charge fluctuations $d^n + d^n \rightarrow d^{n+1} + d^{n-1}$, which are necessary for electronic conduction in narrow d bands, are strongly suppressed by d-electron correlation effects. This is the case when the effective electron-electron correlation energy U_{eff} is larger than the d-band width. Compounds of early $3d$ transition metals as Cr are borderline cases: For instance, according to Zaanen et al.[22] Cr_2O_3 is a Mott-Hubbard insulator, CrO_2 is a d-band metal, while the chromium tellurides[2] are p-type metals, with holes in the anion p band.

The optical properties of $NaCrS_2$, which is isoelectronic with $KCrSe_2$, have been interpreted in terms of a qualitative band model with discrete, localized Cr $3d$ levels,[23,24] suggesting that $NaCrS_2$ should be classified as a Mott-Hubbard insulator. The relative positions of the energy bands derived from Cr $3d$, Cr $4s$, and S $3p$ orbitals in the model proposed by Khumalo[23,24] are very different from the energy-band positions calculated with the ASW method for $KCrSe_2$. Further, the bands crossing E_F in $KCrSe_2$ are rather dispersive. In our opinion a revised assignment of the optical spectra of $NaCrS_2$ based on a reliable band-structure calculation is required.

Transport and magneto-optical measurements are necessary to discern whether $KCrSe_2$ really is a half-metallic ferromagnet or whether d-electron correlation effects are so dominant that this compound is a Mott-Hubbard insulator.

It is to be expected that one or more of the isoelectronic alkali-metal Cr chalcogenides with the same or a very related crystal structure are also half-metallic ferromagnetic when the Cr moments are ferromagnetically aligned.

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