

# Comparison of the electronic structure of a thermoelectric skutterudite before and after adding rattlers: An electron energy loss study

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## Abstract

Skutterudites, with rattler atoms introduced in voids in the crystal unit cell, are promising thermoelectric materials. We modify the binary skutterudite with atomic content  $\text{Co}_8\text{P}_{24}$  in the cubic crystal unit cell by adding La as rattlers in all available voids and replacing Co by Fe to maintain charge balance, resulting in  $\text{La}_2\text{Fe}_8\text{P}_{24}$ . The intention is to leave the electronic structure unaltered while decreasing the thermal conductivity due to the presence of the rattlers. We compare the electronic structure of these two compounds by studying the L-edges of P and of the transition elements Co and Fe using electron energy loss spectroscopy (EELS).

Our studies of the transition metal white lines show that the 3d electron count is similar for Co and Fe in these compounds. As elemental Fe has one electron less than Co, this supports the notion that each La atom donates three electrons. The L-edges of P in these two skutterudites are quite similar, signalling only minor differences in electronic structure. This is in reasonable agreement with density functional theory (DFT) calculations, and with our multiple scattering FEFF calculations of the near edge structure. However, our experimental plasmon energies and dielectric functions deviate considerably from predictions based on DFT calculations.

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## 1. Introduction

For simple crystals of low Z elements the first comparisons of observed electron energy loss near edge structure (ELNES) and calculated density of states were done several decades ago (Egerton and Whelan, 1974; Leapman et al., 1982), see also Egerton (1996). However, in the early days of electronic structure and bonding studies based on electron energy loss spectroscopy (EELS), interpretation of ELNES relied in most studies on empirical rules and fingerprints. Now, with powerful computers combined with density functional theory (DFT) (Kohn, 1999) and multiple scattering ab initio codes (Rehr and Albers, 2000), such as FEEF8 (Ankudinov et al., 1998), the electronic structure can be approached on a general basis.

In this presentation we compare experimental and theoretical EELS spectra of potential thermoelectric materials, two skutterudites with atomic content  $\text{Co}_8\text{P}_{24}$  and  $\text{La}_2\text{Fe}_8\text{P}_{24}$  within the crystal unit cell. For sake of comparison we will throughout this presentation refer to these two skutterudites by the atomic

content of the crystal unit cell rather than the conventional notation of  $\text{CoP}_3$  and  $\text{LaFe}_4\text{P}_{12}$ . Their crystal structures are shown in Fig. 1. While there are two voids in the unit cell of  $\text{Co}_8\text{P}_{24}$  (Fig. 1a), these are filled by La in  $\text{La}_2\text{Fe}_8\text{P}_{24}$  (Fig. 1b).

Skutterudites with the  $\text{CoAs}_3$  structure are promising thermoelectric materials. A good thermoelectric material needs high Seebeck coefficient, high electrical conductivity and low thermal conductivity. Many skutterudites have high Seebeck coefficient and high electrical conductivity. These properties are governed by the electronic structure of the material. However, the thermal conductivity of binary skutterudites is too high for thermoelectric applications. The presence of large the voids in the cubic crystal unit cell of skutterudites, makes it possible to reduce the thermal conductivity by introducing appropriate atoms, rattlers, in the voids Fig. 1 (Sales et al., 1996). This approach of tailoring the thermoelectric properties is based on the concept of a phonon glass/electron crystal (Slack and Tsoukala, 1994). The intention is to leave the electronic structure unaltered while decreasing the lattice contribution to the thermal conductivity due to the presence of the rattlers. In  $\text{La}_2\text{Fe}_8\text{P}_{24}$  the La atoms act as rattlers to reduce the lattice contribution to the thermal conductivity, and Fe has

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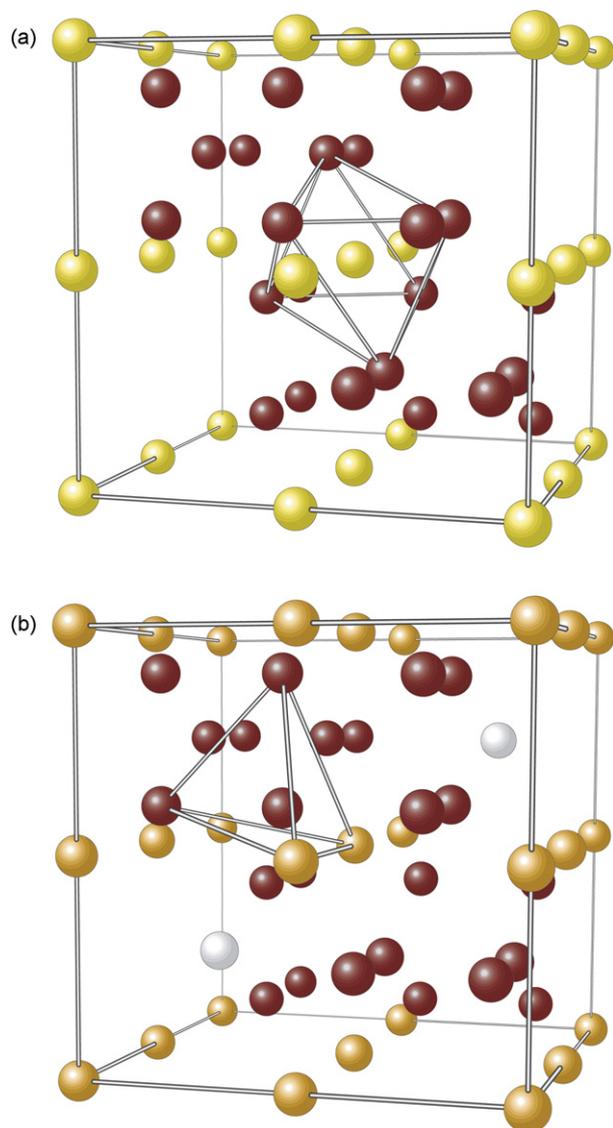


Fig. 1. The skutterudite unit cell. (a)  $\text{Co}_8\text{P}_{24}$  with the octahedral environment of Co emphasised. (b)  $\text{La}_2\text{Fe}_8\text{P}_{24}$  where La atoms fill the voids, here the tetrahedral coordination of P is indicated.

replaced Co to compensate for the electrons donated by the rattler atoms (Uher, 2001).

The accepted picture of the electronic structure of skutterudites comes from general chemical considerations and electronic structure calculations, while experimental studies are scarce. In this paper we present a résumé of our previously published EELS studies of skutterudites (Prytz et al., 2006, 2007). For further details we refer to these papers. In addition, we supplement the previous studies with our recent study of the L edges of phosphorous in these two compounds. We will use the results from our different EELS studies in discussing the electronic structure of these skutterudites.

The purpose of this study is twofold: To test for significant changes in the electronic structure of these compounds, which are thought to be isoelectronic, and to scrutinize state of the art calculation methods used to extract information about the electronic structure from near edge fine structure and low energy loss spectra.

## 2. Specimens

The samples of  $\text{Co}_8\text{P}_{24}$  and  $\text{La}_2\text{Fe}_8\text{P}_{24}$  were synthesized using the tin-flux method (Diplas et al., 2007). The composition was confirmed, within the experimental accuracy, by detecting the electron induced X-ray emission, EDS. The lattice parameters were measured from powder X-ray data, and were found to be in excellent agreement with previous studies reporting 7.711 and 7.831 Å (Jeitschko et al., 2000; Jeitschko and Braun, 1977). Thin areas for EELS studies in transmission electron microscopes were obtained by crushing in ethanol.

## 3. Observed and calculated EELS

The  $L_{2,3}$  edges of transition metals are dominated by the 2p to 3d transitions, and their intensity gives information about the number of empty 3d states. Through appropriate normalization and correction for the transition matrix element, the 3d occupancy can be determined (Pearson et al., 1993). The  $L_{2,3}$  edges of Co and Fe were obtained using a Philips EM 430 TEM at 200 keV (Prytz et al., 2007). The EELS spectrometer was a Gatan 666 parallel-detection electron energy loss spectrometer with an energy resolution of 1.5–2.0 eV. For comparison we also recorded spectra from pure Co and pure Fe in addition to the spectra from the two compounds. Fig. 2 shows experimental spectra after background subtraction and deconvolution. Furthermore, the spectra were normalized using a 50 eV window located 50 eV beyond the edge onset. In  $\text{Co}_8\text{P}_{24}$  the edge intensity is increased relative to what is observed in elemental Co. On the other hand the Fe edges are reduced in intensity in  $\text{La}_2\text{Fe}_8\text{P}_{24}$  compared to the metal. However, due to the complications associated with the occupancy of the 4s states in free atoms, elemental metals and compounds of transition elements, we compare the intensities of the white lines of Co and Fe in the two skutterudites to arrive at the valency of Fe (see Prytz et al., 2007).

The L edges of P and low loss spectra were acquired at an energy resolution of 1–1.5 eV with 197 keV incident electrons using a Gatan imaging filter attached to a JEOL 2010F TEM. The experimental spectra are shown in Fig. 3 together with spectra calculated using the FEFF8.5 code (Ankudinov et al., 1998; Moreno et al., 2007).

The calculations were performed using the Hedin–Lundquist self energies and self consistent field clusters with 46 and 45 atoms for  $\text{Co}_8\text{P}_{24}$  and  $\text{La}_2\text{Fe}_8\text{P}_{24}$ . The full multiple scattering calculations were performed with clusters of 150 and 157 atoms, and no additional broadening was applied to the spectra. The calculations were performed with and without core hole included. In the case of  $\text{La}_2\text{Fe}_8\text{P}_{24}$ , background subtraction in the experimental spectra was complicated by the intense La  $N_{4,5}$  edge located at approximately 100 eV. Thus, the experimental spectrum should be considered qualitative at this stage. It is interesting though, that the calculated spectrum with core hole is fairly similar to the experimental one up to some 15 eV above onset, apart from the splitting of the first peak in the filled skutterudite that we did not resolve in the experiment.

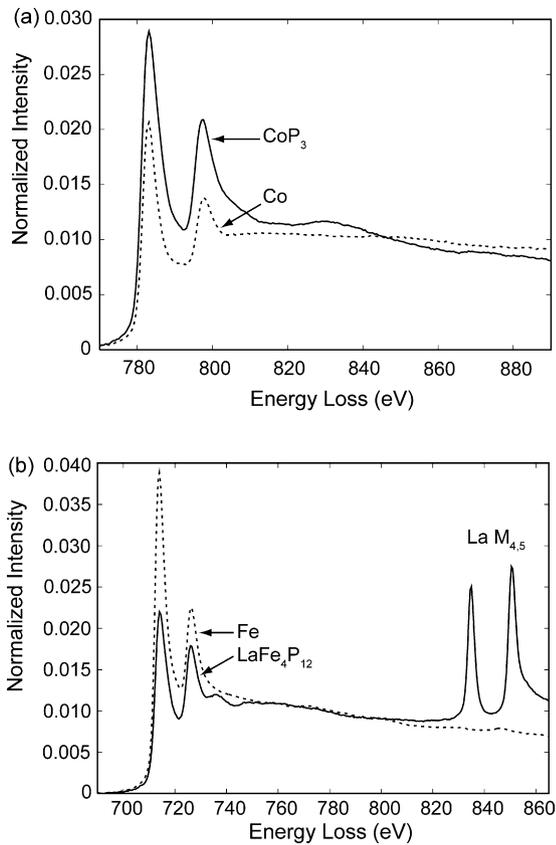


Fig. 2. The  $L_{2,3}$  edges: (a) Co in elemental Co and in  $Co_8P_{24}$ . (b) Fe in elemental Fe and  $La_2Fe_8P_{24}$ .

Fig. 4 shows low energy loss spectra of  $Co_8P_{24}$  and  $La_2Fe_8P_{24}$  with multiple plasmon losses. The plasmon energy of  $Co_8P_{24}$  was previously found to be  $21.67 \pm 0.08$  eV (Prytz et al., 2006), and for  $La_2Fe_8P_{24}$  we find  $22.32 \pm 0.09$  eV.

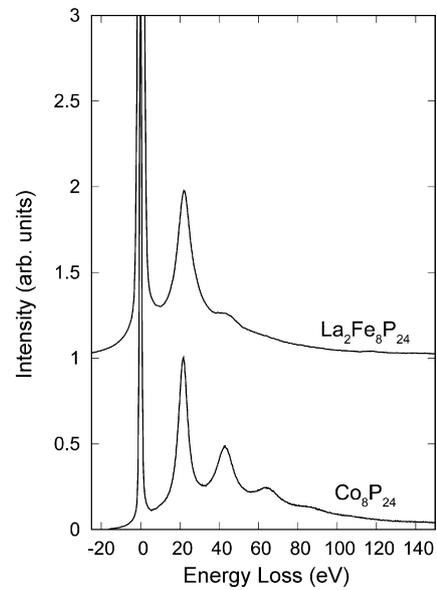


Fig. 4. Plasmon spectra of  $Co_8P_{24}$  and  $La_2Fe_8P_{24}$ .

According to the free electron model, the plasmon energy scales as  $E_p \propto \sqrt{n}$  where  $n$  is the density of valence electrons.  $Co_8P_{24}$  and  $La_2Fe_8P_{24}$  have similar plasmon energies, indicating that the valence electron density is similar and signalling that the idea of charge compensation is valid.

Apart from the plasmons, the low energy loss region of the EELS spectra has contributions from interband transitions close to the Fermi-level. These transitions are central in determining the dielectric response of the material and can be expected to be particularly sensitive to bonding effects. Experimental and DFT calculated low energy loss spectra and dielectric function of  $Co_8P_{24}$  are shown in Fig. 5. The experimental dielectric function was retrieved from the low loss spectra by Kramers–Kronig analysis, while the theoretical spectra were obtained using the

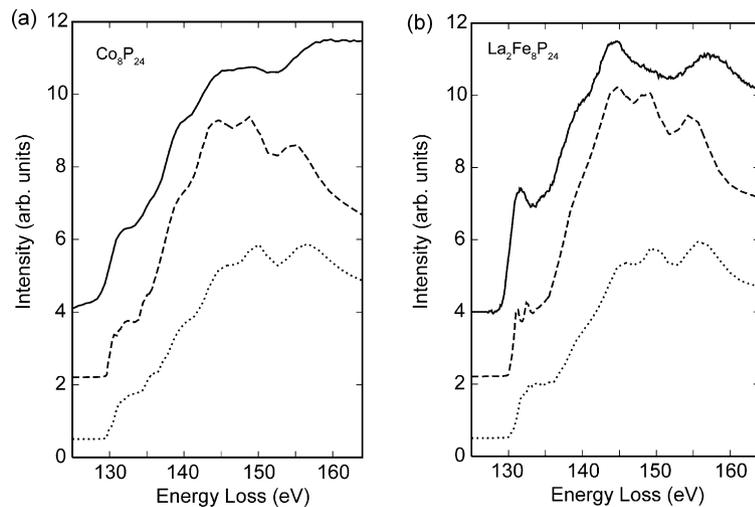


Fig. 3. (a)  $L_{2,3}$  edge of P in  $Co_8P_{24}$ . From top: deconvoluted experimental spectrum with subtracted background, FEFF calculated spectrum with core hole, and without core hole. (b)  $L_{2,3}$  edge of P in  $La_2Fe_8P_{24}$ . From top: deconvoluted experimental spectrum with subtracted background, FEFF calculated spectrum with core hole, and without core hole.

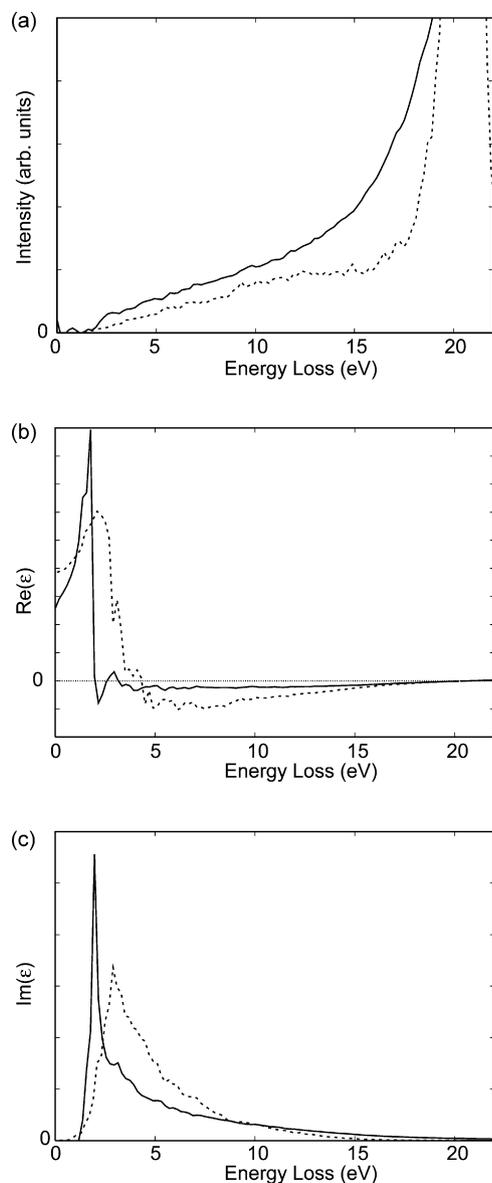


Fig. 5. Experiments (fully drawn line) and DFT calculations (dashed) on  $\text{Co}_8\text{P}_{24}$ . (a) Low energy loss spectrum. (b) Real part of the dielectric function. (c) Imaginary part of the dielectric function.

generalized gradient approximation (GGA) in the DFT calculations. To arrive at the calculated dielectric function, the Optic package of the Wien2K code was used (Prytz et al., 2006).

#### 4. Discussions

In  $\text{Co}_8\text{P}_{24}$ , each P atom is located near the center of a tetrahedron with two P atoms and two Co atoms as nearest neighbors at the four corners of the tetrahedron as shown in Fig. 1b. Each P atom has five valence electrons (valency 5+ in this context). Thus the four P atoms in Fig. 6 are surrounded by the 20 electrons shown as small black circles. The Co is considered trivalent (valency 3+) and surrounded by six P atoms, Fig. 1a. Thus, the Co atoms may contribute with half an electron to each Co–P bond, or alternatively with one electron

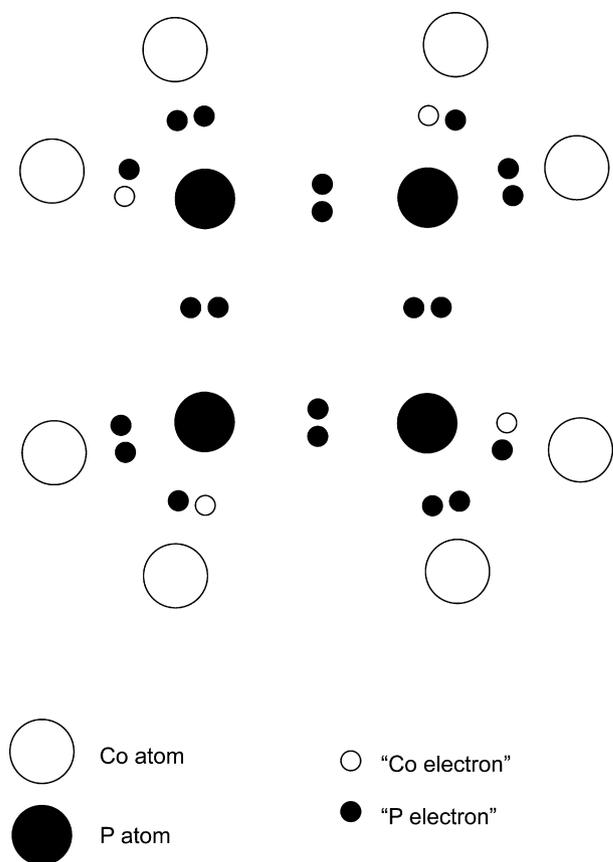


Fig. 6. Lewis diagram of bonding. This is a schematic drawing. In the real three-dimensional crystal the four atoms (two P atoms and two Co atoms) surrounding each P atom form a tetrahedron.

(small open circles) to every second Co–P bond as indicated in Fig. 6.

Based on the white lines, Fig. 2, the 3d occupancy of the transition elements was calculated by the procedure of Pearson et al. (1993). We find that the number of d electrons in occupied states is  $7.53 \pm 0.05$  for Co in  $\text{Co}_8\text{P}_{24}$  and  $7.66 \pm 0.11$  for Fe in  $\text{La}_2\text{Fe}_8\text{P}_{24}$ . Thus, our studies of the transition metal white lines indicate that the number of 3d electrons is similar for Co and Fe in these compounds. As elemental Fe has one electron less than Co, this observation fits reasonably well with the notion that each La atom donates three electrons to compensate for the shortage of electrons from Fe (valency 2+) compared to Co (valency 3+), although 4 electrons, rather than 3, would be needed for full compensation.

Although the transition metal  $L_{2,3}$  edges are useful for extracting 3d occupancies, the comparison of 3d occupancies between elements is not trivial. However, the element P is present in both  $\text{Co}_8\text{P}_{24}$  and  $\text{La}_2\text{Fe}_8\text{P}_{24}$ , and the compounds may be more directly compared by investigating the  $L_{2,3}$  edges of P. An interesting observation is that the  $L_{2,3}$  edges of P are fairly similar in these two compounds, see Fig. 3. We consider this observation to be an indication of similar nature of the bonding because the P atoms having bonds both to other P atoms and to T atoms (T = transition element), and the resemblance between the two spectra is suggestive of similar P–P and P–T bonds in the two compounds. The obvious differences in the fine details

will be discussed in a forthcoming paper (Sæterli et al., in preparation). We note also the good agreement between the experimental spectra and the FEFF calculations up to 15 eV above the threshold, in particular when a core hole is considered in the calculations. As expected from the Lewis diagram of Fig. 6, the  $L_{2,3}$  edges in these two compounds exhibit features very similar to the  $L_{2,3}$  edge of crystalline Si, but quite different from the  $L_{2,3}$  of Si in  $\text{SiO}_2$  (Ahn and Krivanek, 1983). In these skutterudites each P atom can be looked upon as a core of 10 electrons surrounded by eight shared valence electrons as shown in Fig. 6, and the same applies to elemental Si. This model is in agreement with the notion of predominant covalent bonding in binary as well as filled skutterudites. Also, the observed plasmon energies are similar for the two compounds. This is expected because the one valence electron less supplied by the Fe atom than the Co atom is nearly compensated by the additional three electrons from La. Our observations support previous DFT calculations showing that there are only minor changes in the band structure by introducing rattlers in skutterudites if Co is replaced by Fe to maintain charge balance (Løvvik and Prytz, 2004; Mangersnes et al., submitted for publication).

In Fig. 5, we notice the poor agreement between the experimental and DFT calculated dielectric function. This may, at least partly, be attributed to inaccuracies in the experimental data and data processing. Our experimentally determined plasmon energy for  $\text{Co}_8\text{P}_{24}$  is  $21.67 \pm 0.08$  eV, while the DFT calculated value is 20.9 eV (Prytz et al., 2006). The DFT calculated plasmon energies are only marginally better than those calculated using the free electron model. The discrepancy between the experimental and theoretical plasmon energy signals a significant limitation in the DFT calculations of low loss spectra. This suggests that core-hole effects need to be included in the DFT calculations of low loss spectra. Considering the accuracy and robustness of the plasmon energy measurements, EELS may provide valuable inputs in efforts to improve DFT calculations, and may become especially useful in studies of nanomaterials.

## 5. Summary

In agreement with DFT calculations (Fornari and Sing, 1999; Mangersnes et al., submitted for publication) of the electronic structure of  $\text{Co}_8\text{P}_{24}$  and  $\text{La}_2\text{Fe}_8\text{P}_{24}$ , our EELS measurements suggest that these two compounds are isoelectronic. However, only property measurements of the Seebeck coefficient and the electrical conductivity will eventually tell whether the small changes have a decisive influence on these attributes. For many skutterudites it has been shown that introducing rattlers with concomitant charge compensation by transition element substitution, has resulted in the intended response: maintaining the electronic properties while reducing the thermal conductivity, and thus achieving a better thermoelectric material (Slack and Tsoukala, 1994).

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## References

- Ahn, C.C., Krivanek, O.L., 1983. EELS Atlas. Gatan Inc., Warrendale.
- Ankudinov, A.L., Ravel, B., Rehr, J.J., Conradson, S.D., 1998. Real-space multiple scattering calculation and interpretation of X-ray-absorption near-edge structure. *Phys. Rev. B* 58, 7565–7576.
- Diplas, S., Prytz, Ø., Karlsen, O.B., Watts, J.F., Taftø, J., 2007. A quantitative study of valence electron transfer in the skutterudite compound  $\text{CoP}_3$  by combining X-ray induced Auger and photoelectron spectroscopy. *J. Phys. Cond. Matter* 19, 246216.
- Egerton, R.F., Whelan, M.J., 1974. The electron energy-loss spectrum and band structure of diamond. *Phil. Mag.* 30, 739–749.
- Egerton, R.F., 1996. *Electron Energy-Loss Spectroscopy in the Electron Microscope*, 2nd ed. Plenum Press, New York.
- Fornari, M., Sing, D.J., 1999. Electronic structure and thermoelectric prospects of phosphide skutterudites. *Phys. Rev. B* 59, 9722–9724.
- Jeitschko, W., Braun, D., 1977.  $\text{LaFe}_4\text{P}_{12}$  with filled  $\text{CoAs}_3$ -type structure and isotypic lanthanoid-transition metal polyphosphides. *Acta Cryst. B* 33, 3401–3406.
- Jeitschko, W., Foecker, A.J., Paschke, D., Dewalsky, M.V., Evers, C.B.H., Kuennen, B., Lang, A., Kotzyba, G., Rodenwald, U.C., Moeller, M.H., 2000. Crystal structure and properties of some filled and unfilled skutterudites:  $\text{GdFe}_4\text{P}_{12}$ ,  $\text{SmFe}_4\text{P}_{12}$ ,  $\text{NdFe}_4\text{As}_{12}$ ,  $\text{Eu}_{0.54}\text{Co}_4\text{Sb}_{12}$ ,  $\text{Fe}_{0.5}\text{Ni}_{0.5}\text{P}_3$ ,  $\text{CoP}_3$  and  $\text{NiP}_3$ . *Z. Anorg. Allg. Chem.* 626, 1112–1120.
- Kohn, W., 1999. Nobel lecture: electronic structure of matter-wave functions and density functionals. *Rev. Mod. Phys.* 71, 1253–1266.
- Leapman, R.D., Grunes, L.A., Fejes, P.L., 1982. Study of the  $L_{23}$  edges in 3d transition metal oxides by electron-energy-loss spectroscopy with comparisons to theory. *Phys. Rev. B* 26, 614–635.
- Løvvik, O.M., Prytz, Ø., 2004. Density-functional band-structure calculations for La-, Y-, and Sc-filled  $\text{CoP}_3$ -based skutterudite structures. *Phys. Rev. B* 70, 195119.
- Mangersnes, K., Løvvik O.M., Prytz, Ø., submitted for publication. Optimization of P-based skutterudites for thermoelectricity from first principles calculations. *Phys. Rev. B*.
- Moreno, M.S., Jorissen, K., Rehr, J.J., 2007. Practical aspects of electron energy-loss spectroscopy (EELS) calculations using FEFF8. *Micron* 38, 1–11.
- Pearson, D.H., Ahn, C.C., Fulz, B., 1993. White lines and d-electron occupancies for the 3d and 4d transition metals. *Phys. Rev. B* 47, 8471–8478.
- Prytz, Ø., Løvvik, O.M., Taftø, J., 2006. Comparison of theoretical and experimental dielectric functions: Electron energy-loss spectroscopy and density-functional calculations on skutterudites. *Phys. Rev. B* 74, 245109.
- Prytz, Ø., Taftø, J., Ahn, C.C., Fulz, B., 2007. Transition metal d-band occupancy in skutterudites studied by electron energy-loss spectroscopy. *Phys. Rev. B* 75, 125109.
- Rehr, J.J., Albers, R.C., 2000. Theoretical approaches to X-ray absorption fine structure. *Rev. Mod. Phys.* 72, 621–654.
- Sales, B.C., Mandrus, D., Williams, R.K., 1996. Filled skutterudite antimonides: a new class of thermoelectric materials. *Science* 272, 1325–1328.
- Slack, G.A., Tsoukala, V.G., 1994. Some properties of semiconducting  $\text{IrSb}_3$ . *J. Appl. Phys.* 76, 1665.
- Sæterli, R., Prytz, Ø., Holmestad, R., Marthinsen, K., Taftø, J., in preparation. Electronic structure of phosphorus-based skutterudites studied by electron energy-loss spectroscopy.
- Uher, C., 2001. Skutterudites: prospective novel thermoelectrics. *Semiconduct. Semimetals* 69, 139–253.