Possible metal-insulator transition in the filled skutterudite CeFe$_4$As$_{12}$

R. Wawryk$^a$, Z. Henkie$^a$, A. Pietraszko$^a$, T. Cichorek$^a$, A. Jezierski$^b$, R.E. Baumbach$^c$, M.B. Maple$^c$

$^a$Institute of Low Temperature and Structure Research, PAS, Wroclaw, Poland
$^b$Institute of Molecular Physics, PAS, Poznan, Poland
$^c$Department of Physics and IPAPS, University of California, San Diego, U.S.A.

Abstract. Single crystals of filled skutterudite CeFe$_4$As$_{12}$ were examined with X-ray diffraction and electrical resistivity measurements. We have found two types of crystals with the same structure which differ in morphology, lattice parameter and, most importantly, in the temperature dependence of the electrical resistivity, $\rho(T)$ below 165 K; $d\rho/dT$ becomes positive or negative, respectively. The band structure calculations point at the low electronic density of states at the Fermi level and an indirect gap at the $\Gamma$ point.

1.  Introduction.
The ternary transition metal pnictides with the formula $MT_4X_{12}$ ($M$ = alkali metal, alkaline earth, lanthanide, actinide; $T$ = Fe, Ru, Os; $X$ = P, As, Sb) crystallize in the body-centered cubic structure (Im$\bar{3}$ space group) that is characteristic of the filled skutterudites. Especially, their 4$f$- and 5$f$-electron counterparts display a wide spectrum of strongly correlated electron phenomena [1−5]. Among these types of behaviour is a metal-insulator transition derived from interactions between the conduction electrons and the localized magnetic moments. This case is of special interest. While only a few Pr-based compounds display a negative sign for the temperature coefficient of the resistivity ($\alpha = 1/\rho \cdot d\rho/dT$) in the low-temperature limit, several Ce-based systems show semiconducting behaviour with an energy gap as large as 0.1 eV. For the Ce-based filled skutterudites, the energy gap can be roughly scaled with the lattice parameter $a$ where smaller lattice parameter is correlated with a larger energy gap [6]. However, CeOs$_8$Sb$_{12}$ and CeOs$_8$As$_{12}$ do not follow this simple picture. Although these compounds have lattice parameters as large as the metallic members of the Ce$T_4X_{12}$ series, their electrical resistivity increases rapidly upon cooling below 50 K. For CeOs$_8$Sb$_{12}$, the low-$T$ electronic specific heat is significantly enhanced ($\gamma \sim 180$ mJ K$^{-2}$ mol$^{-1}$), indicating the existence of heavy-electron carriers. The observed heavy-fermion quasi-particles and pseudogap behaviour are ascribed to a duality of 4$f$/electrons, as concluded from photoemission spectroscopy measurements [7]. CeOs$_8$As$_{12}$ ($\gamma \sim 19$ mJ K$^{-2}$ mol$^{-1}$) is a hybridization gap semiconductor [8], for which an exponential increase of $\rho(T)$ below 2.5 K is depressed by an applied magnetic field, $B$. As a result, $\alpha > 0$ is observed already for $B > 1$ T. Furthermore, the low-temperature $\rho(T, B)$ behaviour was found to be strongly dependent on the magnetic-field orientation with respect to the main crystallographic directions [9]. A semiconducting [10, 6] character of the electrical resistivity was previously reported for a cold-pressed pellet of CeFe$_4$As$_{12}$. We have grown the CeFe$_4$As$_{12}$ single crystals, which display either $\alpha < 0$ [11] or $\alpha > 0$ at $T < 165$ K, for which the behaviour is virtually independent of $B$. 
2. Experimental details.
Single crystals of CeFe$_4$As$_{12}$ were grown from elements with purities > 99.9% using a mineralization process in a molten Cd:As flux at high-temperatures and pressures [12]. The crystals with $\alpha < 0$ and $\alpha > 0$ at $T < 165$ K were selected from the same batch. The crystal structure was determined by X-ray diffraction using a four circle X-ray diffractometer, where the measurements were made at $T = 12$ K and 294 K using a two dimensional CCD detector. The electrical resistivity was measured by a four-point conventional ac method using a PPMS or standard $^3$He cryostat. The electrical contacts were made by electrochemical deposition of copper.

3. Results and discussion.
Displayed in figure 1 are two single crystals of CeFe$_4$As$_{12}$ grown in the same batch. While the majority of selected crystals have an elongated rhombohedron like shape (a) - the minority ones have an isometric shape (b). The X-ray (XRD) diffraction analysis done at $T = 294$ K and 12 K indicate that all the crystals, regardless of the morphology, have the same cubic LaFe$_4$As$_{12}$ structure with two formula units per unit cell. XRD data could be refined to the $\text{Im}\overline{3}$ structure with a final discrepancy factor $R_1/wR_2 < 4/7$ and full occupancy for all constituent atoms at their lattice positions with accuracy better than 1 – 2% (for definitions see ref. [13]). On the other hand, the two types of CeFe$_4$As$_{12}$ crystals have different lattice parameters, as presented in table 1.

![Figure 1. Various single crystals of the filled skutterudite CeFe$_4$As$_{12}$ showing a rhombohedral (a) and an isometric (b) shape.](image)

The lattice constants are very similar to the value $a = 8.2959$ Å, as reported previously for polycrystalline CeFe$_4$As$_{12}$ [10] in which case semiconducting ($\alpha < 0$) behaviour is observed in $\rho(T)$ data. Our preliminary results suggest a correlation between the lattice parameter and the semiconducting properties for the single crystal specimens. Crystals with $a \geq 8.2946$ Å show a transition to a low-$T$ semiconducting state and presumably their composition is more precisely close to the stoichiometric composition than those with $a \leq 8.289(2)$ Å, which do not become semiconducting at low-$T$ ($\alpha > 0$). Upon cooling the crystals down to 12 K, the lattice constants are reduced and the structure type remains unchanged (Table 1). It is interesting to note that the decrease in lattice constant is more pronounced for the specimens that show semiconducting behaviour.

| No. | Shape      | $a [\text{Å}]$ at $T = 294$ K | $a [\text{Å}]$ at $T = 12$ K | $\alpha$ at $T = 12$ K |
|-----|------------|-------------------------------|-------------------------------|------------------------|
| 2   | elongated  | 8.3108(3)                     | negative below 165 K          |                        |
| 3   | elongated  | 8.2946(5)                     | 8.2741(8)                     | negative below 165 K   |
| 4   | isometric  | 8.289(2)                      | positive                      |                        |
| 6   | isometric  | 8.2759(2)                     | 8.2596(12)                    | positive               |

Shown in figure 2 are electrical resistivity data for 0.4 K < $T < 300$ K for various CeFe$_4$As$_{12}$ single-crystal specimens, normalized to the room temperature value $\rho_{300}$ K. The absolute value of $\rho_{300}$ K was found to be 380 ± 40 µΩ cm, within the limit of uncertainty due to the geometrical factor. Note that this value is only slightly higher than the corresponding value for LaFe$_4$As$_{12}$ ($\rho_{300}$ K = 290 µΩ cm) [14]. The resistivity for all six specimens shows the same temperature dependence down to 225 K, where the semiconducting specimens (curves 1, 2, 3) deviate from the nonsemiconducting ones (curves 4, 5, 6), and reaches a minimum value of $(\rho/\rho_{300\text{K}}) = 0.65$ at $T_{\text{min}} = 165$ K (figure 2). Below $T_{\text{min}}$, there are
two temperature ranges where the strength of the increase in resistivity with decreasing \( T \) changes significantly: (1) strong increase and weak sample dependence of the resistivity down to about 50 K and (2) weak increase or saturation with decreasing \( T \) as well as strong sample dependence of the resistivity down to the lowest-T measured.

For the nonsemiconducting specimens, we observe nearly temperature independent resistivity over two \( T \) ranges: (1) 160 K - 75 K, and (2) below 25 K. These two regions presumably correspond to the two temperature regions noted for the semiconducting specimens.

We note that for \( T < 165 \) K, \( \rho(T) \) of CeFe\(_{4}\)As\(_{12}\) deviates somewhat from a Bloch-Grüneissen relation. Similar behaviour was found for CeFe\(_{3}\)Sb\(_{12}\) [15].

Finally, the low-\( T \) \( \rho(T) \) data for specimens 1 - 3 do not follow an Arrhenius equation, which would be appropriate for a simple single-gap semiconductor. Instead, these data are described by a two-gap expression (the solid lines in the inset to figure 2) [16, 17, 8]:

\[
1/\rho = \sum_i A_i \exp(-A_i/k_B T),
\]

where \( A_1 \) and \( A_2 \) are equal to 2.5 and 4.6 m\( \Omega \) cm\(^{-1}\) cm\(^{-1}\), respectively. The activation energies \( A_1/k_B \) and \( A_2/k_B \) are equal to 0.005 and 139 K, respectively for specimen 1. The values with subscript 1 refer to the lowest temperature range, while those for subscript 2 cover the temperatures from about 40 K to 160 K. The large \( A_1 \) gap can be considered as an opening of the energy gap due to 4f-conduction electron hybridization. The low value for \( A_1 \) may indicate that it describes the energy for the activation of hopping of electrons between localized states in an impurity band. It could also represent the tail of an intrinsic or impurity band, or it even might describe the activation of carriers over a mobility edge [16, 17].

Longitudinal magnetoresistivity, \( |\Delta \rho/\rho| \) is less than 0.1 % in field \( B = 9 \) T and at \( T = 2 \) K for both the semiconducting and nonsemiconducting CeFe\(_{4}\)As\(_{12}\) crystals. This behaviour is different from that found in the hybridization gap semiconductor CeOs\(_{4}\)As\(_{12}\) where \( B \geq 3 \) T closes the smallest energy gap [8]. Therefore a lack of the longitudinal magnetoresistivity for CeFe\(_{4}\)As\(_{12}\) suggests that the 4f electron states are not involved in the electron activation processes.

The sample dependence properties, lattice parameters, and resistivities originate presumably from small differences in composition but not exceeding inaccuracy of occupancy factor determination for the examined CeFe\(_{4}\)As\(_{12}\) crystals. However, the variation does not seem to be uniformly monotonic. For instance, there is only a small difference in the lattice parameter between specimen 3 (\( a = 8.2946(5) \) Å, \( \alpha < 0 \)) and specimen 4 (\( a = 8.289(2) \) Å, \( \alpha > 0 \)) i.e., much smaller than what is observed for various specimens displaying the same sign for \( \alpha \). On the other hand, differences of resistivity behaviour between that observed for specimens from the same group - semiconducting or nonsemiconducting - are much smaller than corresponding differences between any representatives of these groups. Thus, we speculate that the deviation of different constituent atoms composition from perfect stoichiometry may have different affects on the unit cell dimension and the energy gap formation. Indeed, preliminary results from band structure calculations, using the Full-Potential Local-Orbital (FPLO) method [18, 19] (figure 3), highlight an extraordinary sensitivity of the ground state of
Figure 3. Calculated band structure of CeFe₄As₁₂. The Fermi level is at zero energy.

CeFe₄As₁₂ to the position of the Fermi level, as determined by the degree of filling. The exchange correlation potential was used in the form of [19]. The self-consistent calculations were carried out on a $k$ mesh of 663 $k$ points in the irreducible Brillouin zone. The density of states at the Fermi level, $N(E_F) = 0.26$ states/eV f.u. and indirect gap at $\Gamma$ point, $\Delta E = 0.1475$ eV were determined.

On the basis of above results we conclude that it is possible that a continuous metal-insulator (semiconductor) transition in the CeFe₄As₁₂ is controlled by variation in atomic distances.

Acknowledgements

Research at ILTSR, PAS Wroclaw was supported by the Polish Ministry of Science and Higher Education (Grant No. NN 202 4129 33). Research at UCSD was supported by the U.S. Department of Energy (Grant No. DE-FG02-04ER46105).

References

[1] Maple M B, Bauer E D, Frederick N A, Ho P –C, Yuhasz W M, and Zapf V S 2003 Physica B 328 29
[2] Aoki Y, Sugawara H, Harima H and Sato H 2005 J. Phys. Soc. Jpn. 74 209
[3] Maple M B, Henkie Z, Baumbach R E, Sayles T A, Butch N P, Ho P –C, Yanagisawa T, Yuhasz W M, Wawryk R, Cichorek T and Pietraszko A 2008 J. Phys. Soc. Jpn. 77 Suppl. A 7
[4] Sato H, Kikuchi D, Tanaka K, Ueda M, Aoki H, Ikeno T, Tatsuoka S, Kuwahara K, Aoki Y, Kohgi M, Sugawara H, Iwasa K and Harima H 2008 J. Phys. Soc. Jpn. 77 Suppl. A 1
[5] Sekine C, Uchiumi T, Shirotani I and Yagi T 1997 Phys. Rev. Lett. 79 3218
[6] Sugawara H, Osaki S, Kobayashi M, Namiki T, Saha S R, Aoki Y and Sato H 2005 Phys. Rev. B 71 125127
[7] Matsunami M, Eguchi R, Kiss T, Horiba K, Chainani A, Taguchi M, Yamamoto K, Tagoshi T, Watanabe S, Wang X –Y, Chen C –T, Senba Y, Ohashi H, Sugawara H, Sato H, Harima H and Shin S 2009 Phys. Rev. Lett. 102 036403
[8] Baumbach R E, Ho P –C, Sayles T A, Maple M B, Wawryk R, Cichorek T, Pietraszko A and Henkie Z 2008 PNAS 105 17307
[9] Cichorek T et al. in preparation
[10] Grandjean F, Gérard A, Braun D J, and Jeitschko W 1984 J. Phys. Chem. Solids 45 877
[11] Baumbach R E 2009 Doctoral Dissertation (University of California, San Diego)
[12] Henkie Z, Maple M B, Pietraszko A, Wawryk R, Cichorek T, Baumbach R E, Yuhasz W M and Ho P –C 2008 J. Phys. Soc. Jpn. 77 Suppl. A 128
[13] Sheldrick G M 2008 Acta Cryst. A 64 112
[14] Tatsuoka S, Sato H, Tanaka K, Ueda M, Kikuchi D, Aoki H, Ikeno T, Kuwahara K, Aoki Y, Sugawara H and Harima H 2008 J. Phys. Soc. Jpn. 77 033701
[15] Maple M B, Dilley N R, Gajewski D A, Bauer E D, Freeman E J, Chau R, Mandrus D, Sales B C 1999 Physica B 259-261 8
[16] Mott N F and Twose W D 1961 Adv. Phys. 10 107
[17] Markowski P J, Henkie Z and Wojakowski A 1979 Solid State Commun. 32 1119
[18] Koepernik K and Eschrig H 1999 Phys. Rev. B 59 1743
[19] Perdew J P and Wang Y 1992 Phys. Rev. B 45 13244