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Some new findings in τ-phase organic conductors

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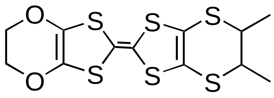
Some new findings concerning the structural, optical, transport, and magnetotransport properties of τ-phase organic conductors, based on the donor molecules ethylenedioxy-*S*,*S*-dimethylethylenedithio-tetrathiafulvalene, ethylenedioxy-*R*,*R*-dimethylethylenedithio-tetrathiafulvalene, pyrazino-*S*,*S*-dimethyl-ethylenedithio-tetrathiafulvalene, pyrazino-*R*,*R*-dimethylethylenedithio-tetrathiafulvalene, pyrazino-*r*-dimethylethylenedithio-tetrathiafulvalene, pyrazino-*S*,*S*-dimethylethyledithio-diselenadithiafulvalene, pyrazino-*r*-methylethylenedithio-tetrathiafulvalene, and pyrazino-*r*-methylethylenediseleno-tetrathiafulvalene are described. Some similarities and differences in their properties are discussed.

Key words: *organic conductors; structure; optical properties; transport properties*

1. Introduction

During the last ten years, a number of τ-phase conductors have been prepared and studied [1–13]. They were based mainly on the following unsymmetrical π-donor molecules:



(EDO-*X*-DMEDT-TTF): *X* = *S*, *S*; *R*, *R*; r (= *S*, *S* + *R*, *R*)

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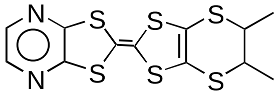
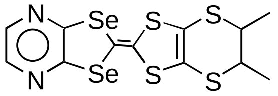
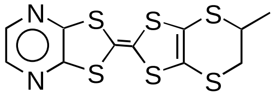
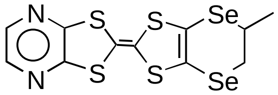

(P-*X*-DMEDT-TTF): *X* = *S*, *S*; *R*, *R*; r (= *S*, *S* + *R*, *R*)


(P-*X*-DMEDT-DSDTF): *X* = *S*, *S*; *R*, *R*


(P-*X*-MEDT-TTF): *X* = r (= *S* + *R*)


(P-*X*-MEDS-TTF): *X* = *r* (= *S* + *R*)

and also on linear anions such as AuI$_2^-$, AuBr$_2^-$ and I$_3^-$. Most of work has been done on τ-(P-*S*,*S*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ and τ-(EDO-*S*,*S*-DMED-TTF)$_2$(AuBr$_2$)$_{1+y}$ ($y \approx 0.75$). Recent investigations of the optical absorption spectra of polycrystalline samples of these two salts in the spectral region from UV to far IR showed some differences in their optical behaviours, attributed to differences in the relative concentrations of the neutral and charged species (i.e., D^0, $D^{\bullet+}$, D^{2+}) in the corresponding salts [1, 2]. Considerable changes in the properties have been observed after heat treatment of the crystals [2, 10]. The changes have a similar origin, since during heat treatment some portion of the anion escapes, leaving the material with various compositions. Also, the redox potentials of the corresponding donor molecules in solution indicate that the preparation and stabilization of (P-*X*-DMEDT-TTF)$^{2+}$ is more difficult than that of (EDO-*X*-DMEDT-TTF)$^{2+}$ [2]. Moreover, it has been found from magnetic measurements that τ-(P-*S*,*S*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ undergoes an antiferromagnetic transition at ca. 11 K, while τ-(EDO-*S*,*S*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ does not exhibit any long-range magnetic order (see [7, 8] and refs. therein). In the last salt, the angular-dependent magnetoresistance oscillations have a peak as the field direction approaches the layers, which indicates interlayer coherency [7, 8]. Also, magnetotransport properties related to the quantum Hall effect and chiral surface states, rather than to other effects [14], have been reported [1].

In this paper, some new findings concerning the properties of the compounds

- τ-(EDO-*S*,*S*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$, τ-(P-*S*,*S*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$,
- τ-(EDO-*R*,*R*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$, τ-(EDO-*R*,*R*-DMEDT-TTF)$_2$(AuI$_2$)$_{1+y}$,
- τ-(P-*R*,*R*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$, τ-(P-*S*,*S*-DMEDT-DSDTF)$_2$(AuBr$_2$)$_{1+y}$,
- τ-(P-*r*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$, τ-(EDO-*S*,*S*-DMEDT-TTF)$_2$[Ag(CN)$_2$]$_{1+y}$,
- τ-(P-*r*-MEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$, and τ-(P-*r*-MEDS-TTF)$_2$(AuBr$_2$)$_{1+y}$

are described. Some similarities and differences in the properties of these compounds are discussed.

2. Results and discussion

The compounds of τ-phase are crystallized in the form of platelets showing several habits. Typical examples of the morphology of crystals and their schematic presentations are shown in Fig. 1. In all cases, the largest surface of each crystal is parallel to the (highly conducting) *ab*-plane, i.e., perpendicular to the *c*-axis.

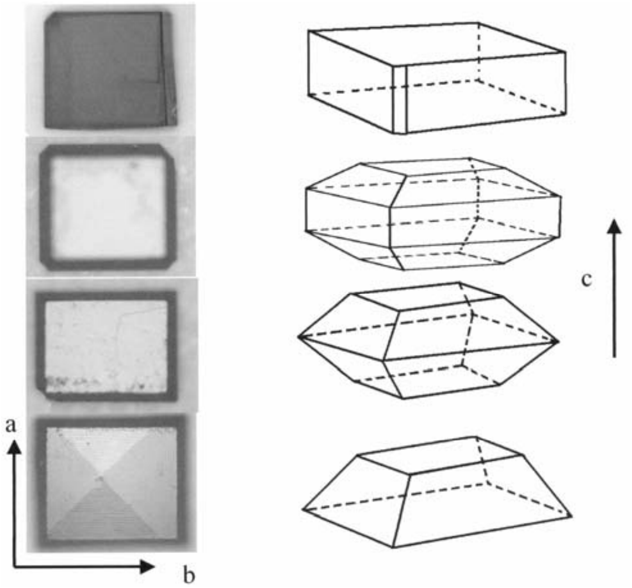


Fig. 1. Morphology of crystals of τ-phase conductors
(four typical habits: A, B, C and D) and corresponding schematic presentations

Room-temperature X-ray diffraction data led to the following results for the crystal structures. The compounds τ-(EDO-*S*,*S*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$, τ-(P-*S*,*S*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$, τ-(P-*R*,*R*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$, and τ-(EDO-*S*,*S*-DMEDT-TTF)$_2$ [Ag(CN)$_2$]$_{1+y}$ are crystallized with the noncentrosymmetric space group $I4_122$ (see [6] and refs. therein). τ-(P-*r*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$, τ-(P-*r*-MEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ and τ-(P-*r*-MEDS-TTF)$_2$(AuBr$_2$)$_{1+y}$ are crystallized with the centrosymmetric space group $I4_1/amd$ [3, 6]. Also, we found that τ-(EDO-*R*,*R*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ and τ-(P-*S*,*S*-DMEDT-DSDTF)$_2$(AuBr$_2$)$_{1+y}$ are crystallized with the centrosymmetric space group $I4_1/amd$. In the last two cases, diffraction data do not provide a clear choice between the centrosymmetric and a noncentrosymmetric space groups (see [3] and ref. [6] cited therein). An uncertainty concerning crystal structures has also been noticed in some other compounds, such as 4,5-dimethylethylenedithio-1,3-dithiole-2-thione (see [3] and ref.[6] cited therein) and (TMET)$_3$(ClO$_4$)$_2$ (see [11] and ref.[4] cited therein). The crystal structure of the compound τ-(EDO-*R*,*R*-DMEDT-TTF)$_2$(AuI$_2$)$_{1+y}$ has not yet been definitely determined. In the compounds τ-(EDO-*S*,*S*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ and τ-(P-*S*,*S*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$, no considerable differences in the crystal structures among the several habits have been found.

The reflectance spectra, with the wave vector of light parallel to the conducting plane, and optical absorption spectra of τ-phase crystals exhibit a broad band at ca. 5500 cm^{-1}. Figure 2. shows the observed [4, 9] and calculated spectra, based on the mean-field Hubbard model, assuming anti-ferromagnetic order [7, 9, 15]. One can see that there is a good agreement between experiment and theory.

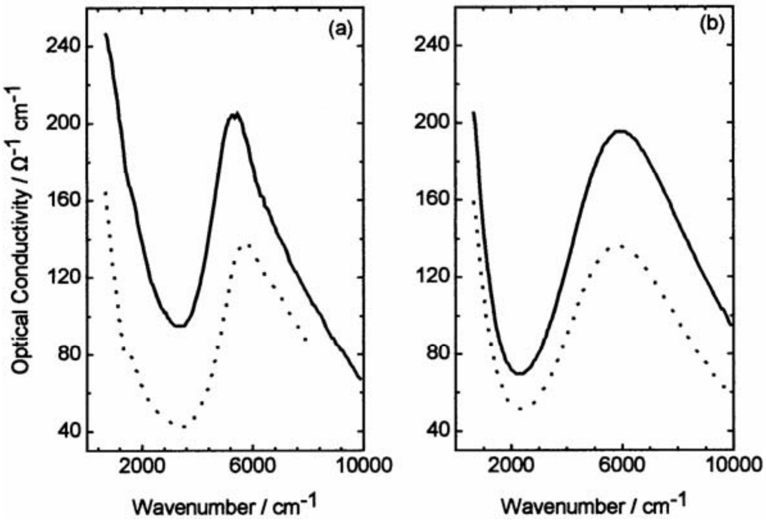


Fig. 2. Observed (a) and calculated (b) optical conductivity spectra of τ-(EDO-*S*,*S*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ (solid lines) and τ-(P-*S*,*S*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ (dotted lines), using transfer integral values of t_1 = 0.184 and 0.138 eV, respectively, t_2 = 16 meV, a filling factor of ρ = 0.9375, and Δ = 0.31 eV

The in-plane resistivity (ρ_{ab}) of τ-(P-*S*,*S*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ shows a metallic temperature dependence down to low temperatures, with an upturn at ca. 10 K and a weak crossover at ca. 120 K. The out-of-plane resistivity (ρ_c) shows a semiconducting behaviour down to low temperatures, a crossover at ca. 20 K, and an upturn in resistivity at ca. 5 K. The resistivity anisotropy ρ_c/ρ_{ab} is of the order 10^3 at room temperature and much higher at low temperatures (see [5, 7, 8] and refs. therein). The compounds τ-(P-*R*,*R*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ and τ-(P-*r*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ exhibit similar behaviour [6]. The resistivity anisotropy for these compounds was found to be 310–1250 at room temperature. The in-plane resistivity of τ-(EDO-*S*,*S* -DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ shows a metallic temperature dependence, with an upturn at 30–50 K. The out-of-plane resistivity varies from crystal to crystal. Some crystals exhibit weak metallic behaviour down to very low temperatures (ca. 0.4 K), while other crystals exhibit an upturn in resistivity at ca. 30–40 K. The resistivity anisotropy is of the order 10^3–10^4 (see [1, 7, 8, 10] and refs. therein). Interlayer transport is coherent in τ-(EDO-*S*,*S*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ and incoherent in τ-(P-*S*,*S*-DMEDT

-TTF)$_2$(AuBr$_2$)$_{1+y}$ [7, 8]. The results are similar in τ-(EDO-*R*,*R*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$, as shown in Fig. 3. In the crystal (#0209), the temperature dependence of in-plane resistivity shows a metallic behaviour down to low temperatures, while the temperature dependence of the out-of-plane resistivity shows weak metallic behaviour and an upturn at ca. 50 K. There is no crossover in ρ_c at high temperatures. Also, as in other compounds, resistivity anisotropy is large. Similar results have been obtained for τ-(P-*S*,*S*-DMEDT-DSDTF)$_2$(AuBr$_2$)$_{1+y}$, except that ρ_c shows a weak crossover at ca. 270 K [3]. The behaviour of ρ_{ab} and ρ_c for one crystal (#0302) of this compound is similar to that observed in [3] for two other separate crystals. Also, another crystal of τ-(EDO-*R*,*R*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ (#0213) exhibited metallic behaviour in ρ_{ab}, and weak metallic behaviour in ρ_c down to ca. 5 K (Fig. 3). Details will be reported elsewhere [12]. The results are much different in τ-(EDO-*R*,*R*-DMEDT-TTF)$_2$(AuI$_2$)$_{1+y}$, as shown in Fig. 4. This compound exhibits metallic behaviour in both directions, with resistivity anisotropy of the order 10^3. A weak crossover is observed in ρ_c at ca. 250 K. At 7K, a sudden drop in ρ_{ab} was observed, which is not associated with superconductivity. As in the case of other τ-phase compounds, several significant features are observed in the temperature dependence of resistivity at low temperatures (e.g., a weak upturn in resistivity is observed at ca. 5 K). These are more pronounced under pressure, as shown in Fig. 5. One can see that when the pressure is increased from 0 to 1.23 GPa, the compound becomes more metallic. As the pressure increases above 1.65 and 2.02 GPa, however, the compound becomes semiconducting, showing upturns in resistivity at ca. 18.3–20.5 and 24.8–26.5 K, respectively. The results are similar to those observed for τ-(EDT-*S*,*S*-DMEDT-TTF)$_2$(AuI$_2$)$_{1+y}$ [2, 11], where EDT-*S*,*S*-DMEDT-TTF is ethylenedi-

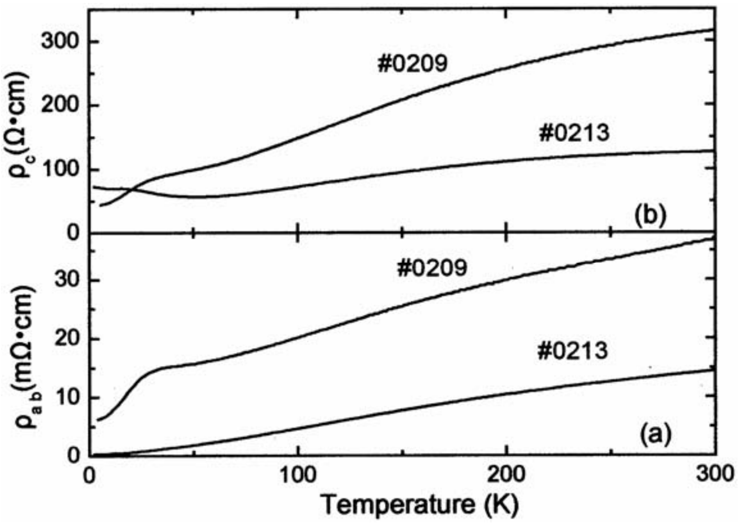


Fig. 3. Temperature dependences of the in-plane resistivity (a) and out-of-plane resistivity (b) for two crystals of τ-(EDO-*R*,*R*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$

thio-*S*,*S*-dimethylethylenedithio-tetrathiafulvalene, abbreviated as *S*,*S*-DMBEDT-TTF in [11]. The behaviour is different in τ-(EDO-*S*,*S*-DMEDT-TTF)$_2$[Ag(CN)$_2$]$_{1+y}$, τ-(P-r-MEDT-TTF)2(AuBr2)$_{1+y}$, and τ-(P-r-MEDS-TTF)$_2$(AuBr$_2$)$_{1+y}$.

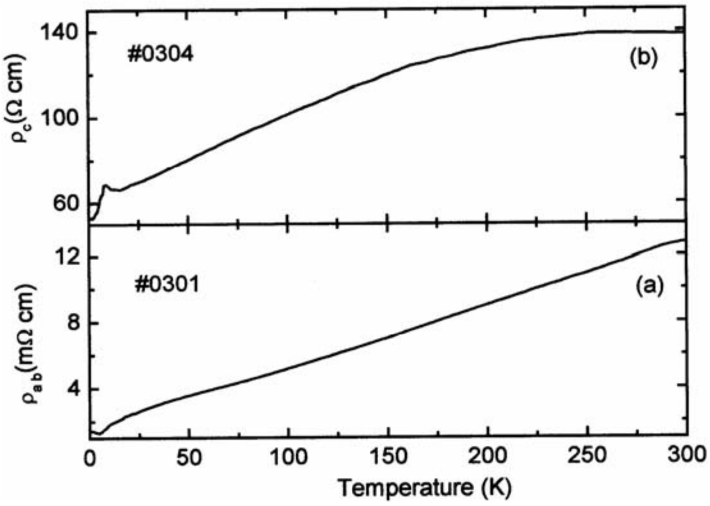


Fig. 4. Temperature dependences of in-plane (a) and out-of-plane (b) resistivity for τ-(EDO-*R*,*R*-DMEDT-TTF)$_2$(AuI$_2$)$_{1+y}$ (under ambient pressure)

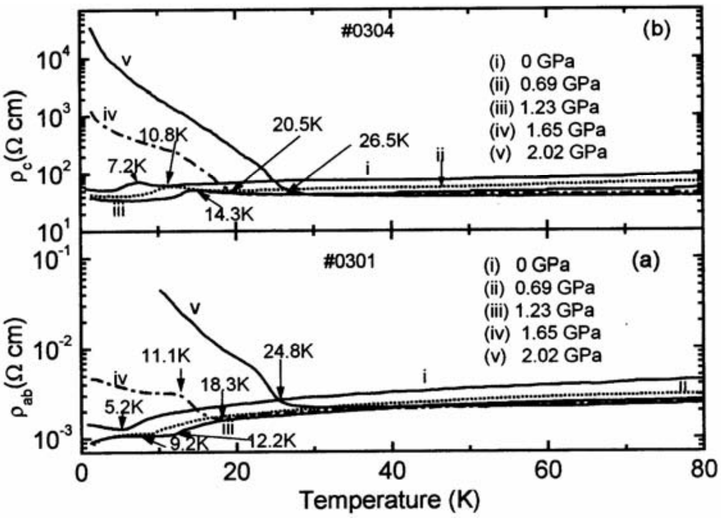


Fig. 5. Temperature dependences of in-plane (a) and out-of-plane (b) resistivity for τ-(EDO-*R*,*R*-DMEDT-TTF)$_2$(AuI$_2$)$_{1+y}$ under ambient and high pressure

In these compounds, both ρ_{ab} and ρ_c exhibit a semiconducting behaviour from room temperature down to very low temperatures. The anisotropy ρ_c/ρ_{ab} for the first compound is c.a. 10^3, while for the latter two it is small, i.e., 27 and 3–15, respectively.

Some similarities and differences concerning magnetotransport properties of τ-(EDO-*S*,*S*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ and τ-(P-*S*,*S*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ have been reported in [1, 6, 7]. Crystals of τ-(P-*S*,*S*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$, τ-(P-*R*,*R*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$, and τ-(P-*r*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ exhibit a negative magnetoresistance at low fields and fast Shubnikov–de Haas (SdH) oscillations at higher fields (see also [5–8]), with frequencies close to those of τ-(EDO-*S*,*S* -DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$, as well as weak slow oscillations of frequency ca. 180 T [7, 8]. The compounds exhibit an upturn in magnetoresistance near ca. 35 T. Semiconducting and metallic crystals of τ-(EDO-*R*,*R*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ exhibit two kinds of SdH oscillations at high fields, with frequencies of 42.1–44.5 T and 487–500 T. In other words, the Fermi surface area shows some dependence on the sample. The details of SdH oscillations in metallic and semiconducting crystals of this compound will be reported elsewhere [12]. Also, the compound τ-(EDO-*R*,*R*-DMEDT-TTF)$_2$(AuI$_2$)$_{1+y}$ exhibits negative magnetoresistance at low fields. At high fields, the compound exhibits SdH oscillations with frequencies << 40 T and ca. 586 T [13].

Finally, the magnetoresistance was measured for virgin and heated samples from the same crystal of τ-(EDO-*S*,*S*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ at 0.5 K and up to 45 T. Both samples showed two series of SdH oscillations corresponding to the smaller and larger Fermi surfaces. It was found that the SdH frequency corresponding to the smaller Fermi surface decreases by about 20% after heating the sample up to 400 K, while the faster frequency remains unchanged. No difference was found with X-ray studies in the crystal structures of another sample before and after heating up to 420 K. This means that band filling can be controlled by simply heating the crystal in vacuum.

In conclusion, we found that the properties of τ-phase compounds exhibit small differences from crystal to crystal of the same compound, and large differences from compound to compound, the origin of which being not understood yet. Also, external conditions play an important role in the properties of these materials. Under ambient pressure, EDO-containing conductors exhibit similar transport properties (see Figs. 3, 4 and refs. [1, 5, 12]). It is expected that these compounds will also exhibit quantum Hall plateaus and chiral surface effects in their magnetotransport properties, as in the case of τ-(EDO-*S*,*S*-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ [1].

Acknowledgements

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References

[1] Papavassiliou G.C., Mousdis G.A., Anyfantis G.C., Murata K., Li L., Yoshino H., Tajima H., Konoike T., Brooks J.S., Graf D., Choi E.S., Z. Naturforsch. A., 59a (2004), 952.

[2] Papavassiliou G.C., *Tetrachalcogenafulvalenes with Four Additional Heteroatoms*, [in:] J. Yamada and T. Sugimoto (Eds.), *TTF Chemistry*, Kodansha and Springer, Tokyo, 2004, p.35.

[3] PAPAVASSILIOU G.C., MOUSDIS G.A., TERZIS A., MURATA K., LI L., YOSHINO H., J. Phys. IV France, 114 (2004), 569.

[4] LAPINSKI A., GRAJA A., PAPAVASSILIOU G.C., MOUSDIS G.A., Synth. Metals,139 (2003), 405.

[5] GRAF D., CHOI E.S., BROOKS J.S., HARRISON N., MURATA K. KONOIKE T., MOUSDIS G.A., PAPAVASSILIOU G.C., Phys. Rev. B, in press.

[6] PAPAVASSILIOU G.C., MOUSDIS G.A., TERZIS A., RAPTOPOULOU C., MURATA K., KONOIKE T., YOSHINO H., GRAJA A., LAPINSKI A., Synth. Metals, 135–136 (2003), 651.

[7] KONOIKE T., PhD Thesis, Osaka State Univ. (2003).

[8] KONOIKE T., IWASHITA K., YOSHINO H., MURATA K., SASAKI T., PAPAVASSILIOU G.C., Phys. Rev., B 66 (2002), 245308.

[9] OLEJNICZAK I., MUSFELDT J.L., PAPAVASSILIOU G.C., MOUSDIS G.A., Phys. Rev., B 62 (2000), 15634; H. TAJIMA, private communication.

[10] MURATA K., SHIRAKAWA N., YOSHINO H., TSUBAKI Y., PAPAVASSILIOU G.C., TERZIS A., ZAMBOUNIS J.S., Synth. Met., 86 (1997), 2021; YOSHINO H., [in:] Proc. ICSM ‘04, Wollongong, Australia (2004).

[11] ZAMBOUNIS J.S., MAYER C.W., HAUENSTEIN K., HILTI B., HOFHERR W., PFEIFFER J., BURKLE M., RIHS G., Mat. Res. Soc. Symp. Proc., 247 (1992), 509.

[12] NAKANISHI T., [in:] Proc. ICSM 2004, Wollongong, Australia (2004).

[13] LI L., [in:] Proc. ICSM ‘04, Wollongong, Australia (2004).

[14] CHAMPEL T., MINEEV V.P., Physica, B 346-347 (2004), 392 and refs. therein.

[15] DING Y., TAJIMA H., Phys. Rev., B 69 (2004), 115121 and refs. therein.

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