



Synthesis and characterisation of a novel europium-based graphite intercalation compound

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ABSTRACT

In the lithium–europium–graphite system, a novel ternary compound was synthesised by direct immersion of a pyrolytic graphite platelet in a molten lithium-based alloy with a well chosen Li/Eu ratio at 400 °C. The ternary compound exhibits poly-layered intercalated sheets mainly constituted of two europium planes. Its chemical formula can be written Li_xEuC_4 , since the amount of lithium is still not determined. The ¹⁵¹Eu Mössbauer spectra clearly indicate a +II valence for europium. The magnetic susceptibility and the magnetisation versus temperature reveal a complex behaviour which is qualitatively described thanks to structural hypothesis and analogies with the magnetic properties of the binary EuC_6 compound. A first ferromagnetic transition occurring at 225 K is attributed to interactions between both intercalated europium planes. The lower temperature susceptibility behaviour can be interpreted by antiferromagnetic interactions between in-plane neighbours and ferromagnetic interactions along the *c*-axis.

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1. Introduction

Lithium metal is a good intercalation vector for a few elements such as calcium, barium and europium [1]. Indeed, immersion of pyrolytic graphite platelets in lithium-based liquid alloys recently appears as an efficient method for the sample preparation of MC_6 graphite intercalation compounds (with $M = \text{Ba}, \text{Ca}$ and Eu). Indeed, contrary to the well-known vapour phase reaction [2,3], the two steps mechanism involved in the correlated intercalation process allows the preparation of pure bulk sample. In this case, lithium intercalates first and the alloyed metal progressively eliminates and substitutes lithium leading to a binary compound. As it was already shown in the mercurio-graphitides [4], depending on the reactions conditions, lithium and its alloyed metal can both remain in the graphite galleries leading then to a ternary compound such as $\text{Li}_3\text{Ca}_2\text{C}_6$ or $\text{Li}_{0.5}\text{Ca}_3\text{C}_6$ in the lithium–calcium–graphite system [5,6]. Taking into account the wide analogy between calcium and europium, Hérold et al. [7] have started the study of the lithium–europium–graphite system, in order to prepare novel ternary graphite intercalation compounds. Indeed, ionic radii and electronegativities of calcium and europium are very similar. Moreover, europium, as calcium, can stabilise a +II

valence. These metals are able to intercalate into graphite in vapour phase but this reaction remains mainly incomplete and leads to a superficial intercalation [2,3]. On the other hand, Eu^{2+} ions holding a magnetic moment give interesting magnetic properties to the EuC_6 binary compound that were studied during the 1980s [8–10]. A review of the physical properties of GICs is given in [11]. According to the Monte-Carlo simulation of Chen et al. [10], the magnetic behaviour below the Néel temperature ($T_N = 40 \text{ K}$) can be mainly described by in-plane antiferromagnetic and out-of-plane ferromagnetic interactions with in addition, higher-order exchange interactions.

In their preliminary studies, Hérold et al. [7] have reported the existence of two ternary graphite intercalation compounds containing lithium and europium. In the present work, a first description of the synthesis conditions, the crystal chemistry and the magnetic properties of one of them are given.

2. Synthesis

The synthesis procedure is similar to that used in the lithium–calcium–graphite system [5,6]. The first step is to weigh precisely pieces of lithium and europium in a glove box filled with a very pure argon atmosphere. Both metals are successively placed in a stainless steel reactor and heated until the formation of a well-homogenised liquid. A pyrolytic graphite platelet is then

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immersed in the reactive alloy and then the reactor is tightly closed. Outside of the glove box, the reactor is arranged in a vertical furnace and heated for several days in order to reach the thermodynamical equilibrium. At the end of the reaction, the reactor is opened in a glove box, the alloy is heated to extract the sample(s) from the liquid. The sample is then cleaved and differently conditioned for each kind of characterisation. For X-ray diffraction, the sample is placed in a capillary tube sealed under argon atmosphere. For Mössbauer measurements, several pieces of sample are deposited on a mylar film, a second mylar film is then sealed on the first one in the glove box so that the sample is protected from atmosphere in an air-tight sample holder. For magnetic measurements, the sample is introduced in a silica tube sealed after introduction of a low pressure of helium.

Due to a lack of knowledge concerning the lithium–europium phase diagram, the melting point of each alloy was first approximately determined. The reaction temperature was limited to a maximum of 420 °C to avoid carbide formation. Consequently, the Li/Eu ratio of the reactive alloy needs to be higher than 1.2 to be sure that the alloy is entirely liquid. The above-mentioned ternary compound was observed in a wide range of reactive alloy compositions, since the Li/Eu ratio has to be included between 1.2 and 3. However, the best results were obtained for reactions carried out at 400 °C for 10 days with a lithium–europium alloy containing 75at% of lithium. All the following characterisations were done on samples synthesised using these conditions.

3. Crystal chemistry

The first step of the characterisation of this new graphite intercalation compound is the study of its 001 X-ray diffraction pattern registered using a X-ray diffraction equipment with a reflection configuration. This diagram contains one family of 001 reflections clearly indicating the presence of only one intercalated phase in the sample. From this diagram, its *c*-axis repeat distance was evaluated at 803 pm (Fig. 1). Very small amount of EuC_6 and metallic europium inclusions are observed in the sample. The *c*-axis electronic density profile was determined from the intensities of the 001 reflections and compared to a *c*-axis

stacking model which takes into account the amount of carbon and europium in the sample. Experimental and theoretical intensities and structure factors are listed in Table 1.

In this preliminary study, the amount of lithium that is not precisely known was not introduced in the model. Its very small atomic number justifies this approximation. The best agreement (residual factor: $R_F = 14\%$) was obtained for a 2 layers stacking according to the Li_xEuC_4 composition (Fig. 2). Each europium plane is distant of 244 pm from the nearest graphene sheet.

In order to determine the amount of lithium and its distribution in the graphitic framework, a nuclear microprobe experiment is required and will be done in the future. The stoichiometry of each element can be determined simultaneously [12]. Moreover, if there are some heterogeneities, they can also be put into evidence (especially that of lithium, as it was shown in [12,13]).

The $hk0$ diffraction pattern does not show any reflection. This phenomenon can be attributed either to a particular structure leading to an absence of reflection (see for example the structure of KC_8 for which the rotating crystal pattern shows only the $hk0$ reflections from graphite, [14]) or to a too large absorption of the sample. Indeed, the important atomic number of europium conducts to high X-ray absorption, not favourable to an analysis using an X-ray diffraction equipment with a transmission configuration.

Table 1

Experimental and calculated intensities and structure factors of the 001 Li_xEuC_4 reflexions used in the electronic density profile calculations

Reflexion (l_c)	θ (°, Mo $K\alpha_1$)	D_{001} (pm)	F_{001}^{exp}	F_{001}^{calc}	I_{001}^{exp}	I_{001}^{calc}
1	2.53	803	0	−9.76	0	2.93
2	5.07	401.50	−19.47	−26.80	5.77	10.93
3	7.61	267.67	100	100	100	100
4	10.17	200.75	40.70	55.68	12.18	22.80
5	12.76	160.60	−83.89	−71.37	40.38	29.23
6	15.37	133.83	52.52	57.40	12.80	15.29
7	18.01	114.71	57.72	59.53	12.80	13.61
8	20.69	100.38	−44.48	−42.41	6.40	5.81
9	23.42	89.22	0	6.81	0	0.13
10	26.21	80.30	46.40	65.79	5.12	10.29

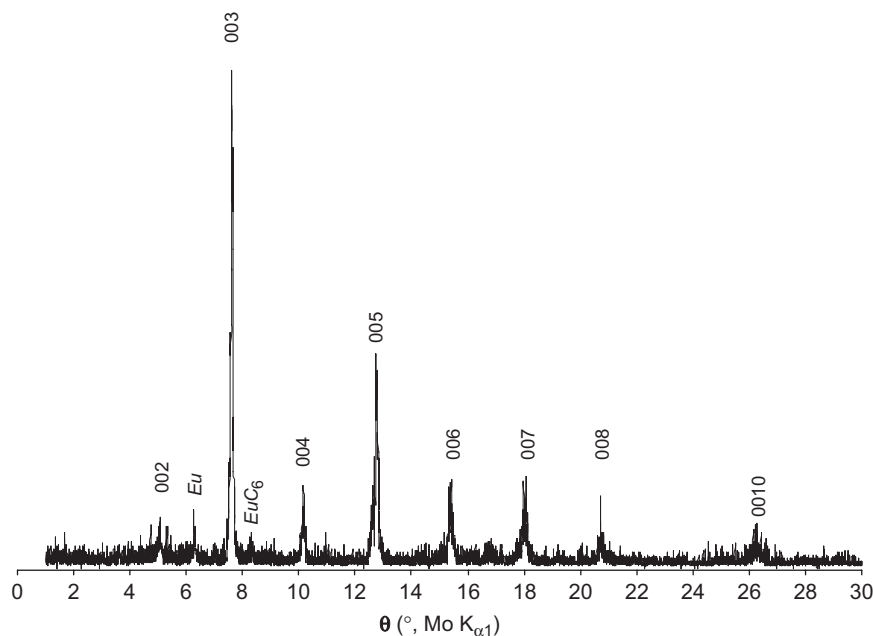


Fig. 1. 001 X-ray diffraction pattern of Li_xEuC_4 .

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