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A MÖSSBAUER SPECTROSCOPY STUDY OF AN ANHYDROUS NON-STOICHIOMETRIC EUROPIUM(III) CHLORIDE PHASE

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Summary

Anhydrous europium(III) chloride, when heated under vacuum at temperatures above 570 K, decomposes according to the overall reaction

$EuCl_3(s) \rightarrow EuCl_2(s) + \frac{1}{2}Cl_2(g)$

A non-stoichiometric chlorine-deficient phase with the hexagonal UCl_3-type structure is observed down to at least a europium-to-chlorine ratio of 1:2.84. Samples of composition $EuCl_{>2.8}$ were examined by Mössbauer spectroscopy, X-ray diffraction and electrical conductivity techniques. The temperature-dependent Mössbauer spectra provide, for the first time, evidence for electron exchange between neighbouring europium sites in a non-stoichiometric europium compound. The activation energy E_a for electron mobility above about 200 K is 0.083 ± 0.003 eV for $EuCl_{2.96}$ from electrical conductivity measurements. This value for E_a is in agreement with others derived from the Mössbauer spectra using an electron hopping model according to which a potentially mobile electron is bound at each site for an average time which is a function of temperature. Chemical isomer shifts and ratios of recoil-free fractions (Lamb–Mössbauer factors) for europium(II) to europium(III) are also derived from the spectra. Lattice parameters obtained from X-ray data are discussed in relation to those for the stoichiometric $EuCl_{3.00}$ phase.

1. Introduction

Europium(III) chloride behaves like the chlorides of other electropositive metals and exhibits both high melting and high boiling points. The anhydrous chloride dissolves readily in water to give rise to a clear colourless solution.

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When heated under vacuum at temperatures in excess of 570 K europium(II) chloride is formed according to the reaction

$EuCl_3(s) \rightarrow EuCl_2(s) + \frac{1}{2}Cl_2(g)$

During the initial stages of this reaction a non-stoichiometric chlorine-deficient phase is formed before the hexagonal europium(III) chloride lattice breaks down. This phase has been examined by Mössbauer spectroscopy, a technique well suited to monitor its development as there is a large difference between the chemical isomer shifts associated with europium in these two oxidation states.

The temperature-dependent Mössbauer spectra show, for the first time, evidence for electron exchange between neighbouring europium sites in a non-stoichiometric europium compound. The results appear to be best explained by an electron hopping model similar to that invoked by Berkooz *et al.* [1] in their study of Eu_3S_4. The activation energy associated with the electron mobility is deduced from the time τ the electron is bound to each ion. These activation energies are compared with others derived from electrical conductivity data. Results are discussed in relation to the compositional range of the non-stoichiometric phase and lattice defects.

2. Experimental details

2.1. Preparation of europium chloride samples

The method used to prepare non-stoichiometric samples was similar to that described by Taylor and Carter [2] for the preparation of anhydrous europium(III) chloride. About 300 mg of europium(III) oxide (Rare Earth Products Ltd., Widnes; minimum purity, 99.9%) were dissolved in 6 M hydrochloric acid and ammonium chloride in the approximate molar ratios 1:20:10. The solution was carefully taken to dryness below 420 K and the residue was placed in a silica boat which was then wrapped in platinum foil and inserted into a cylindrical Pyrex reaction tube (13 cm long with an inside diameter of 2.5 cm). The reaction tube was evacuated to better than 10^{-3} Torr and was heated in a tubular furnace initially at 353 K for 1 h and finally at a temperature selected within the range 570–720 K for 6–8 h while still on the vacuum line. Then it was allowed to cool slowly under vacuum. The final temperature and heating time determines the chloride depletion in the product. Stoichiometric anhydrous europium(III) chloride was prepared by heating the product obtained at 570 K according to the above procedure in a stream of dry chlorine gas at 800 K for 5 h and was allowed to cool to ambient temperature under chlorine at 1 atm.

The products were analysed to establish their chemical composition: the total metal ion was determined by ethylenediaminetetraacetic acid titration [3] and the chloride was determined by mercury(II) nitrate titration [4]. Europium(II) was determined by an indirect spectrophotometric method. The weighed sample of europium chloride was added to an excess of acidified iron(III) chloride solution. Europium(II) reacts according to the equation

$Eu^{II} + Fe^{III} \rightarrow Eu^{III} + Fe^{II}$

and the iron(II) thus produced was determined using the orange-coloured complex it forms with 1,10-phenanthroline [5].

2.2. *Apparatus*

The Mössbauer spectrometer, variable-temperature cryostat, ^{151}Sm Mössbauer-emitting γ ray source, differential thermal analyser and glove-box facilities used in this work have been described elsewhere [6]. The Mössbauer chemical isomer shifts are reported with respect to monoclinic Eu_2O_3 and the errors quoted are three times the standard deviations.

Electrical conductance measurements were made on pressed discs (1 cm in diameter and 0.2 cm thick) of europium chloride in a conductivity cell of the type described by Bransky *et al.* [7]. Measurements were made between 77 and 300 K.

Powder X-ray data were obtained using a Philips 1008/80 generator and a Debye–Scherrer camera with Cu Kα and Mo Kα radiation.

3. Results and discussion

The exact composition of the non-stoichiometric europium chloride phase is strongly dependent on the temperature and the duration of the final step in its preparation. The relation between the gross chemical composition and the final heating temperature maintained for a fixed period of 8 h is presented in Fig. 1.

In common with all light lanthanide(III) chlorides, the anhydrous europium compound crystallizes with the hexagonal UCl_3-type structure in which the metal ion is surrounded by nine chloride ions, six of which are at approximately 2.7 Å and three at about 3.0 Å distance. The closest approach of the chlorides to each other is 3.3 Å. The structure of the europium(III) chloride is

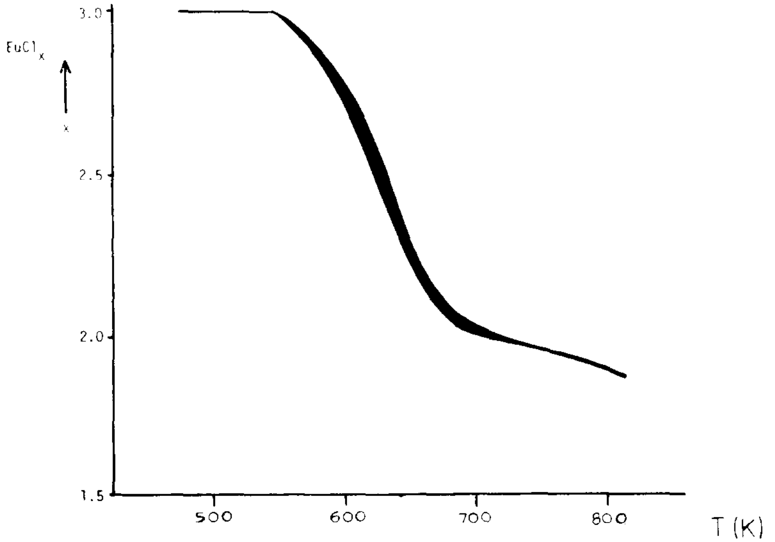


Fig. 1. The effect of varying the final heating temperature, maintained for a fixed time of 8 h duration, on the composition of the europium chloride product.

TABLE 1

Lattice parameters for stoichiometric and non-stoichiometric europium(III) chloride preparations at ambient temperatures

Reference	*Material*	*a* (Å)	*c* (Å)
[10]	$EuCl_3$	7.369 ± 0.004	4.133 ± 0.002
[11]	$EuCl_3$	7.3746 ± 0.0012	4.1323 ± 0.0005
[8]	$EuCl_3$	7.375	4.134
[12]	$EuCl_3$	7.370 ± 0.002	4.137 ± 0.004
This work	$EuCl_{3.00}$	7.278 ± 0.002	4.071 ± 0.003
This work	$EuCl_{2.94}$	7.328 ± 0.002	4.102 ± 0.002
This work	$EuCl_{2.84}$	7.364 ± 0.005	4.116 ± 0.005

quite different from that of any probable impurities such as europium oxychloride [8] or hydrated europium(III) chloride [9], the presence of which should be revealed by X-ray diffraction. The lattice parameters obtained from X-ray measurements for compounds prepared in the course of the present work are compared with published data in Table 1. The non-stoichiometric products all have lattice parameters which are fairly consistent with those of anhydrous europium(III) chloride. The differences that are found between the $EuCl_{3.00}$ parameters reported in this study and those given in the literature could arise from the use of chloride-depleted samples in the earlier work. It was concluded from the X-ray data that the depleted samples share the UCl_3 structure with the stoichiometric compound. This is consistent with Mössbauer spectral data which provide evidence for electron hopping. Such electron movement requires that both europium(II) and europium(III) sites are crystallographically equivalent. The lattice parameters for the non-stoichiometric phases show a small expansion in the unit cell volume; this is consistent with a decrease in the coulombic attractive forces within the crystal lattice owing to the presence of europium(II).

In general several conditions must be fulfilled for electron hopping to be observed. First, the europium species involved should occupy crystallographically similar sites otherwise the activation energy barrier to electron transfer becomes prohibitively large. Secondly the temperature range for observation must be well below that required for thermal production of the non-stoichiometric phase. Thirdly the recoil-free fraction in the hopping temperature regime must be large. Fourthly, steric factors will largely determine whether the europium will remain on its lattice site after electron transfer and hence the difference in cation crystal radii should be small to minimize lattice distortion. (The ratio $[Eu^{III}]/[Eu^{II}]$ is 0.95/1.09.) Finally, the compositional range of the non-stoichiometric phase should be such as to enable both species to be observed in the Mössbauer spectra.

A summary of published Mössbauer chemical isomer shifts for the chlorides of europium(II) and europium(III) is presented in Table 2. For present purposes the value of the latter is of direct relevance, while that of the former merely indicates qualitatively the relative difference attributable to a valency

TABLE 2

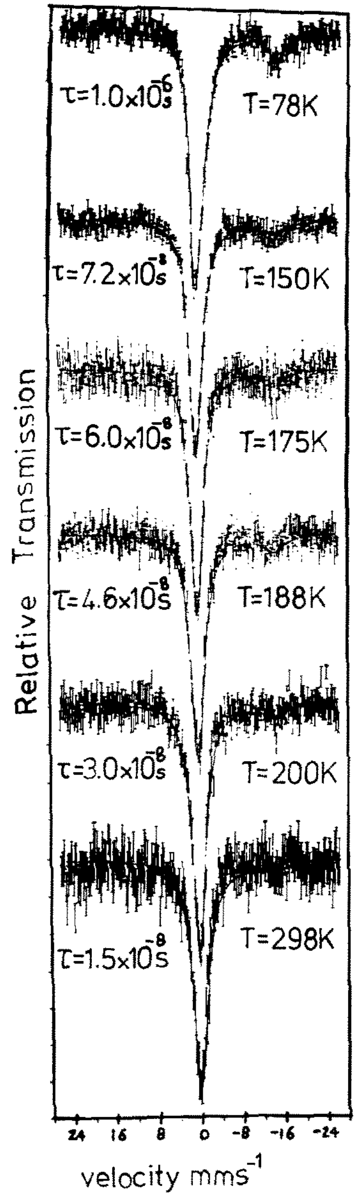
Chemical isomer shift data for europium(II) and europium(III) chlorides

Reference	*Sample*	*Chemical isomer shift* (mm s^{-1})	*Reference material*
[13]	$EuCl_2$	-13.4	Eu_2O_3
[14]	$EuCl_2$	-14.1	Eu_2O_3
[15]	$EuCl_2$	-13.4 ± 0.3	Eu_2O_3
[16]	$EuCl_2$	-14.33 ± 0.08	Eu_2O_3
[17]	$EuCl_2$	-13.40 ± 0.05 (-14.00 ± 0.05)	EuF_3 (relative to Eu_2O_3)
[15]	$EuCl_3$	-0.42 ± 0.04	Eu_2O_3
[16]	$EuCl_3$	-0.29 ± 0.09	Eu_2O_3
This work	$EuCl_3$	-0.34 ± 0.08	Eu_2O_3

All spectra were recorded at room temperature except for the measurement taken from ref. 14 for which the temperature is unclear.

change. Unfortunately there is a substantial difference between the two europium(III) values reported. That resulting from the present work is in reasonable agreement with the value of Gerth *et al.* [16]. The more negative value reported by Deeney *et al.* [15] suggests that their sample may have been chloride deficient as the more negative shift is in the direction of those observed for non-stoichiometric samples studied in the course of the work described here. A more negative chemical isomer shift for the chloride-depleted europium(III) chloride samples is consistent with X-ray data which provide evidence for a lattice expansion on depletion. Such an expansion would reduce the electron density at the europium(III) nucleus and, as $\delta\langle r^2\rangle$ is positive for ^{151}Eu, a more negative isomer shift would result. Unfortunately analytical data relating to the chemical composition of the samples used by Deeney *et al.* [15] have not been published.

Temperature-dependent Mössbauer spectra are presented in Figs. 2 and 3 for samples of composition $EuCl_{2.85}$ and $EuCl_{2.95}$ respectively; they can be interpreted in terms of an electron hopping model similar to the treatment [1] accorded to Eu_3S_4. The spectra in Fig. 3 are included to demonstrate that the effect is still evident close to stoichiometry. At 78 K the spectra consist of two well-resolved components. At higher temperatures the spectral envelopes widen and ultimately coalesce with a maximum at the "centre of gravity" of the two low temperature components. According to the model, the electron is bound at each europium site for an average time τ. This characteristic time decreases rapidly as the temperature increases. For sufficiently low temperatures (*e.g.* 78 K) the characteristic time is greater than the time required for a Mössbauer event and hence the spectrum consists of independent components associated with nuclear absorption by europium(II) and europium(III) sites. However, at sufficiently high temperatures several hopping events occur within the lifetime of a Mössbauer event and this results in the europium sites experiencing an averaged environment. A single Mössbauer absorption envelope is thus obtained as at 298 K for the samples quoted above.



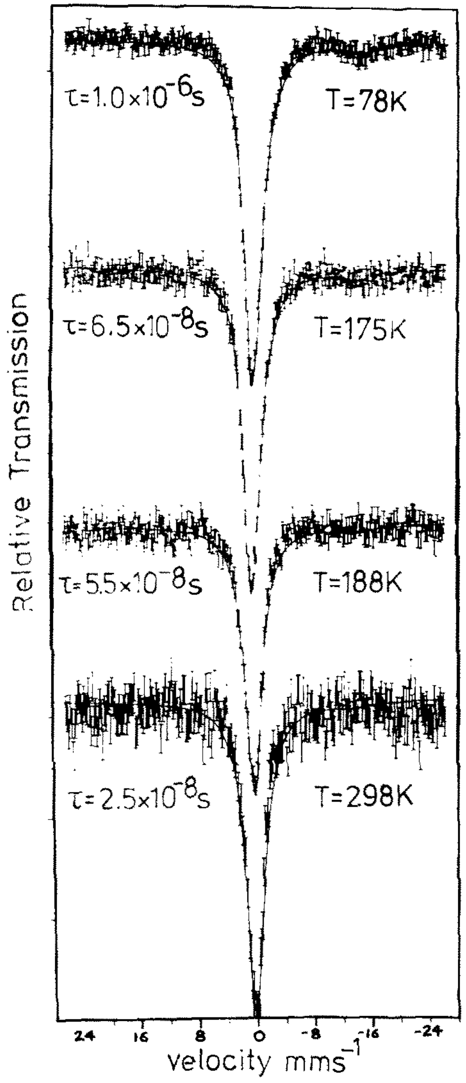


Fig. 2. Mössbauer spectra of $EuCl_{2.85}$ between 78 and 298 K.

Fig. 3. Mössbauer spectra of $EuCl_{2.95}$ between 78 and 298 K.

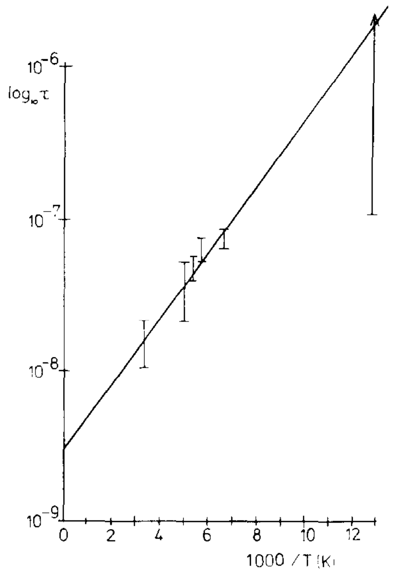
The error bars for each series of spectra (Figs. 2 and 3) are derived from experimental data points. The full curves are the best theoretical fit to the data obtained using Wickman's general relaxation equations [18, 19]. The relaxation times τ for each spectrum were calculated from these equations using the resonant frequencies ω_A and ω_B taken from the chemical isomer shifts obtained from a lorentzian profile least-squares fitting of the spectra at 78 K. The ratio of the populations of the two europium species was obtained in a similar manner, for at this temperature the line shapes can be considered to be lorentzian to a very good approximation. A greater degree of precision for these parameters is not available by considering other factors that may modify the lorentzian line shape, such as quadrupole and hyperfine effects, because of the limitations imposed by the quality of the best available data. The best fit of the theoretically generated curves to the experimental data was found by a reiterative process using difference values of τ in the relaxation equations.

As stated earlier, for the electron to hop to an adjacent europium site an activation energy barrier E_a must be overcome. The characteristic time for this transfer is related exponentially to E_a in the same way as the electrical conductivity so that

$$\tau = \tau_0 \exp\left(-\frac{E_a}{kT}\right)$$

where k is the Boltzmann constant and T is the temperature. Hence an estimate of E_a can be obtained graphically by using values of τ derived from the spectra taken at different temperatures. Figure 4, which is a plot of $\log_{10} \tau$ against $1/T$ for $EuCl_{2.85}$, provides an example of this treatment. It is seen that the quality of the data is rather limited; E_a is estimated to be 0.04 ± 0.03 eV for $EuCl_{2.85}$ and 0.07 ± 0.03 eV for $EuCl_{2.95}$.

A typical plot of relative conductivity against $10^3/T$ is presented in Fig. 5 for $EuCl_{2.96}$. This and other such plots of data from samples from the non-stoichiometric compositional range consist of curves resolvable into two linear



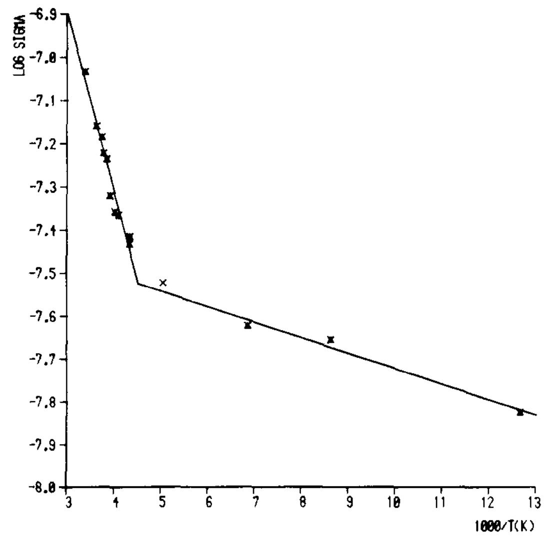


Fig. 4. $\log_{10} \tau$ as an inverse function of temperature for $EuCl_{2.85}$.

Fig. 5. Electrical conductivity of $EuCl_{2.96}$ plotted as an inverse function of temperature.

components. Comparable results have been reported for Eu_3S_4 [20] and Sm_3S_4 [21], and the former study was supplemented by differential scanning calorimetry from which it was concluded that the transition associated with the change in mechanism of electronic conductivity was the effect of charge ordering as postulated by Carter [22]. It was deduced from the conductivity measurements on $EuCl_{2.96}$ and $EuCl_{2.99}$ that the transition from the high temperature to the low temperature region occurred at 221 K and 197 K respectively. The differential thermal analysis profile of $EuCl_{2.99}$ exhibits a small endothermic feature at 190 K. These observations, together with the conductivity data and the absence of magnetically induced structure in the Mössbauer spectra above or below temperatures in this region (200 ± 30 K), support the occurrence of a charge ordering phenomenon. Activation energies in the high temperature region are 0.083 ± 0.003 eV and 0.071 ± 0.003 eV and in the low temperature region are 0.007 ± 0.003 eV and 0.009 ± 0.003 eV for the $EuCl_{2.96}$ and $EuCl_{2.99}$ specimens mentioned previously. A small difference between the high temperature activation energies of the two components is to be expected for it was shown empirically at room temperature that the lattice expands with increasing chloride depletion. This results in an increased electron hop distance from one europium site to another, thus changing the activation energy. The higher temperature region corresponds to that for which τ is obtained from the Mössbauer spectra and the activation energies derived from conductivity measurements are in good agreement with those deduced from τ as a function of temperature. Paucity of data and large uncertainties in τ prevent the revelation of a low temperature component in $\log \tau$ plotted as a function of $10^3/T$ from Mössbauer spectral data. As in the case of Eu_3S_4 it is concluded that only the electrons converting europium(III) into europium(II) sites participate in hopping, for at ambient temperatures the Mössbauer spectra retain virtually no evidence of the discrete europium(II) isomer shift observable at 78 K. Thus the carrier concentration is taken to be constant and the intrinsic conductivity to result from a variation in electron mobility.

The hopping model as applied above to the extraction of a value for E_a from the Mössbauer spectra does not take account of possible differences between the recoil-free fractions of europium(II) and europium(III) in the lattice. If the recoil-free fractions of the europium species are different then the relative ratio of the areas under the peaks in the spectra will vary with temperature. However, this would not explain the observed changes in chemical isomer shifts with temperature and so, with the assumption of negligible second-order Doppler shift, the electron hopping process is considered dominant. For the small concentrations of europium(II) in the host lattice in the non-stoichiometric samples, quantitative measurements of relative recoil-free fractions are difficult to make owing to large errors in the determination of the peak area due to europium(II). This measurement would be further complicated as the line shapes are temperature dependent. However, it is reasonable to assume that the europium(II) ions are less rigidly held in the lattice than their europium(III) counterparts as the latter are in an energetically more favourable environment. Hence, the ratio $f(\mathrm{Eu^{II}}, T)/f(\mathrm{Eu^{III}}, T)$ of the Lamb–Mössbauer factors will be less than unity. These ratios have been calculated at 78 K, with the assumption of lorentzian line shapes, from the relation

$$\frac{\text{Eu}^{\text{II}}\text{ peak area}}{\text{Eu}^{\text{III}}\text{ peak area}}\,\frac{f(\text{Eu}^{\text{III}}, T)}{f(\text{Eu}^{\text{II}}, T)}=\frac{\text{no. of moles of Eu}^{\text{II}}}{\text{no. of moles of Eu}^{\text{III}}}$$

The results are presented in Table 3. The ratios, which are shown in the fifth column, are all less than unity in accordance with the qualitative reasoning above. The more reliable ratios suggest that the differences between the recoil-free fractions are of the order of 5%–10%. It is interesting to note that the mole ratios of chlorine to europium derived from the spectra are in good agreement with those deduced from chemical analysis.

TABLE 3

Ratio of Lamb–Mössbauer factors of europium(II) to europium(III) ions in some depleted europium(III) chlorides

Mole ratio of chlorine to europium from chemical analysis	*Percentage Eu^{II} from chemical analysis*	*Percentage Eu^{II} calculated from spectra at 78 K*	*Mole ratio of chlorine to europium from spectra*	*Ratio of Lamb–Mössbauer factors of Eu^{II} to Eu^{III}*[a]
2.95:1.00	5.0	3.7	2.96:1.00	0.73(±22.9%):1.00
2.85:1.00	15.4	13.4	2.87:1.00	0.85(±15.0%):1.00
2.94:1.00	6.10	5.84	2.94:1.00	0.95(±16.5%):1.00
2.80:1.00	19.7	18.4	2.82:1.00	0.91(±11.5%):1.00

The measurements were recorded at 78 K.

[a] Errors deduced from Mössbauer peak areas and in the chemical determinations.

Finally, it is possible to estimate the compositional range of the non-stoichiometric europium(III) chloride phase from the X-ray and Mössbauer data accumulated in the course of this work. The electron hopping phenomenon was observed in the UCl_3-type lattice down to chloride-to-europium ratios of 2.84:1. However, Mössbauer data from samples with grosser deviations from stoichiometry show the phase to be less extensive than that in the europium(III) fluoride system. For example, the room temperature Mössbauer spectra of samples of empirical formulae $EuCl_{2.26}$ and $EuCl_{2.47}$ exhibit persistent europium(II) and europium(III) absorption peaks rather than the single peak characteristic of the initial stages of the thermal decomposition of stoichiometric europium(III) chloride. X-ray evidence supports the existence of at least two phases in such samples.

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