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Long and Short-Range Ordering in $LiTbS_2$

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Electron-microscope studies have been performed on single crystals of $LiTbS_2$. Samples cooled from 1000 °C show diffuse intensity bands in the diffraction patterns, arising from short-range ordering of Li and Tb. After annealing at 500 °C, the ordering range increases and three superstructures are observed. On the basis of the observed diffraction patterns and bright and dark-field images the range and the nature of the ordering is discussed.

Introduction

The ternary rare-earth sulphides of the type $M\mathrm{LnS}_2$, where M is one of the alkaline metals, have been reported to crystallize with an ordered or disordered rock-salt structure (Ballestracci & Bertaut, 1964; Ballestracci, 1965; Bronger, Elter, Maus & Schmitt, 1973; Kabré, Julien-Pouzol & Guittard, 1974).

All the K compounds of this type show an X-ray pattern of the α-$NaFeO_2$ structure, which is a rhombohedral superstructure of NaCl. The structure of $KCeS_2$ has been determined by X-ray single-crystal methods (Plug & Verschoor, 1976). The Na compounds with Ln = Nd–Lu and the Li compounds with Ln = Dy–Lu have the same structure. For the other rare earths, the Na and Li compounds have powder X-ray patterns with only the lines of the NaCl substructure present. In some cases, however, broad and diffuse peaks are observed, suggesting the occurrence of short-range ordering.

A theoretical derivation of all possible superstructures of NaCl for compounds with composition ABX_2, has been given by Brunel, de Bergevin & Gondrand (1972). It assumes Pauling's electro-neutrality rules apply, leading to the occurrence of only two types of anion-centered octahedra in any superstructure.

Both the sizes and the charges of the Li ions and the large rare-earth ions are very different. Therefore, a totally random distribution of the two cation constituents in the 'disordered' compounds $LiLnS_2$ seems to be very unlikely. In order to investigate the nature of the cation distribution in these compounds, we performed electron-microscope experiments on single crystals of $LiTbS_2$.

Experimental

Small crystals of $LiTbS_2$ were prepared by heating a mixture of Tb_2O_3 and an excess of $LiCO_3$ in a stream of H_2S. After cooling from 1000 °C at a rate of 30° h^{-1}, the product was washed with water and acetone, and dried.

The powder X-ray diffractogram shows the lines of the NaCl structure with $a_0 = 5{\cdot}504\ (2)$ Å. A part of the sample thus obtained was additionally annealed in a closed silica tube at 500 °C for one month.

Electron-diffraction studies were performed with a Siemens Elmiskop 102 electron microscope fitted with a tilting stage. Thin crystals were obtained by fragmenting small crystals after cooling them with liquid nitrogen. The fragments were mounted on a 400 mesh grid, covered with a polyethylene holey film. Diffraction patterns as well as bright and dark-field images were recorded.

Results

The diffraction patterns of the sample cooled from 1000 °C show distinctly the spots allowed for the NaCl

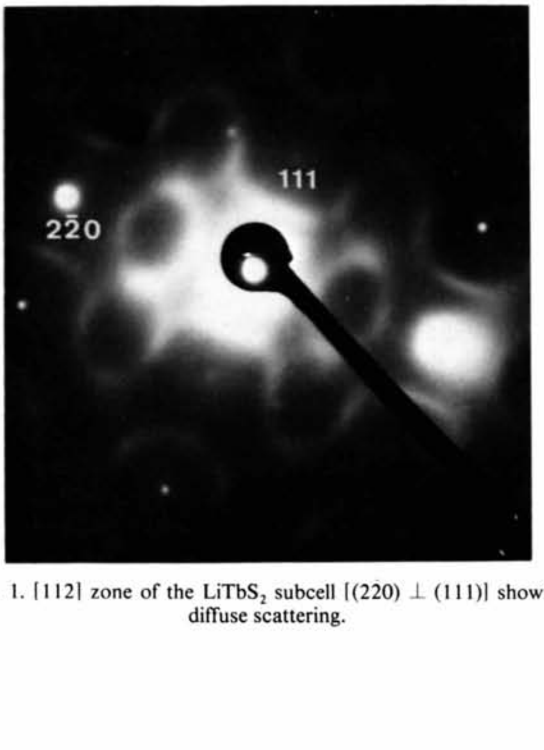

Fig. 1. [112] zone of the $LiTbS_2$ subcell [(2$\bar{2}$0) ⊥ (111)] showing diffuse scattering.

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structure. Between these sharp spots, bands of diffuse intensity are observed (Fig. 1). Close to the points ($h + \frac{1}{2}, k + \frac{1}{2}, l + \frac{1}{2}$) in reciprocal space the diffuse intensity is at a maximum.

The pattern of the bands is very similar to that observed for some transition-metal carbides (Billingham, Bell & Lewis, 1972), for which theoretical analysis has been given (Sauvage & Parthé, 1972).

The diffuse intensity indicates the presence of short-range ordering in the sample of $LiTbS_2$. Bright-field images and dark-field images from diffuse intensity contain contrast that is mottled on a scale of 40 Å (Fig. 7). Hence, the short-range ordering presumably extends over that distance.

In the electron-diffraction patterns of sample 2, which has been annealed at 500 °C, the diffuse bands

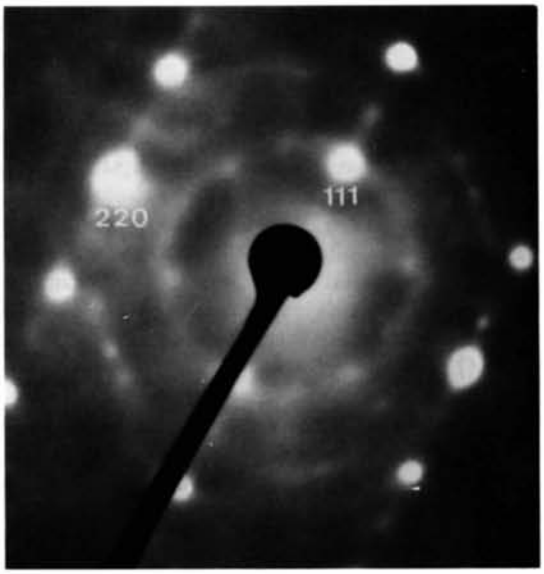

Fig. 2. [112] zone of the $LiTbS_2$ subcell, after one month of annealing at 500 °C. The diffuse scattering is stronger where the rhombohedral supercell spots will appear.

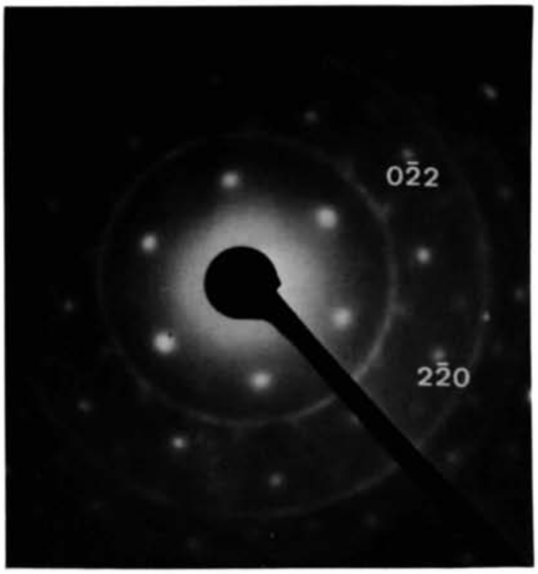

Fig. 4. [111] zone of the $LiTbS_2$ subcell, after one month of annealing at 500 °C. The superspots correspond to an overlapping of the rhombohedral – $(0\bar{2}2) \rightarrow (11.0)_H$; $(2\bar{2}0) \rightarrow (1\bar{2}.0)_H$ – and the $2a_{NaCl}$ cubic – $(0\bar{2}2) \rightarrow (0\bar{4}4)_C$; $(2\bar{2}0) \rightarrow (4\bar{4}0)_C$ – structures.

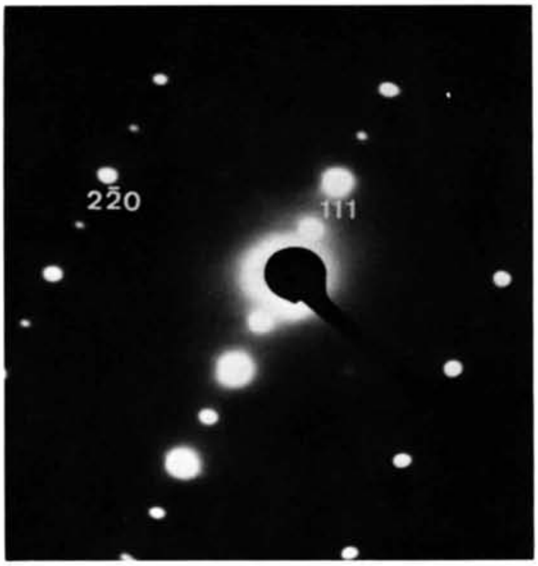

Fig. 3. The same as under Fig. 2, but a different area. Two overlapping sets of superspots are observed, which both fit with the rhombohedral supercell: $(2\bar{2}0) \rightarrow (11.0)_H$; $(111) \rightarrow (00.6)_H$ and $(2\bar{2}0) \rightarrow (11.0)_H$; $(111) \rightarrow (\bar{1}1.2)_H$.

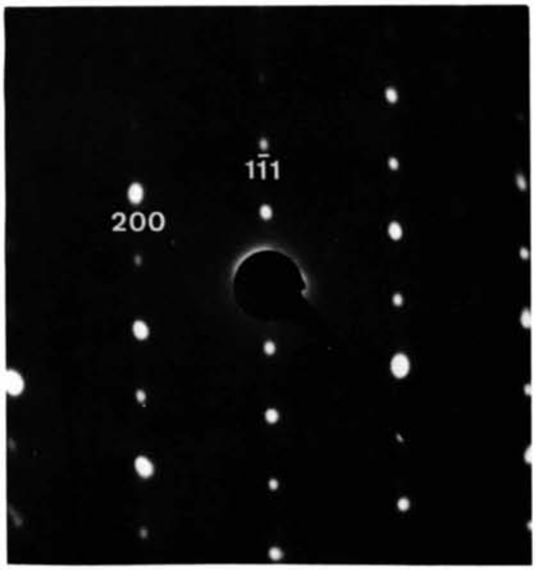

Fig. 5. [011] zone of the $LiTbS_2$ subcell; two sets of superspots are visible, one stronger and one weaker. Both correspond to the rhombohedral supercell: $(1\bar{1}1) \rightarrow (10.2)_H$ and $(1\bar{1}1) \rightarrow (00.6)_H$.

have in most cases disappeared (Figs. 3–6). Instead, sharp superspots are observed between the NaCl reflections. In some of the patterns both superspots and diffuse bands appear (Fig. 2).

The superspots can be indexed with two superstructures assumed to be present, both characterized by the reciprocal-lattice vector $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$. We identify these structures as the α-$NaFeO_2$ structure ($a_{\text{hex}} = \frac{1}{2}\sqrt{2}\, a_{\text{NaCl}}$, $c_{\text{hex}} = 2\sqrt{3}\, a_{\text{NaCl}}$) and a cubic structure with $a = 2a_{\text{NaCl}}$, described by Brunel *et al.* (1972). In one case (Fig. 6) superspots corresponding to a tetragonal supercell ($a_{\text{tetr}} = a_{\text{NaCl}}$, $c_{\text{tetr}} = 2a_{\text{NaCl}}$) are also observed.

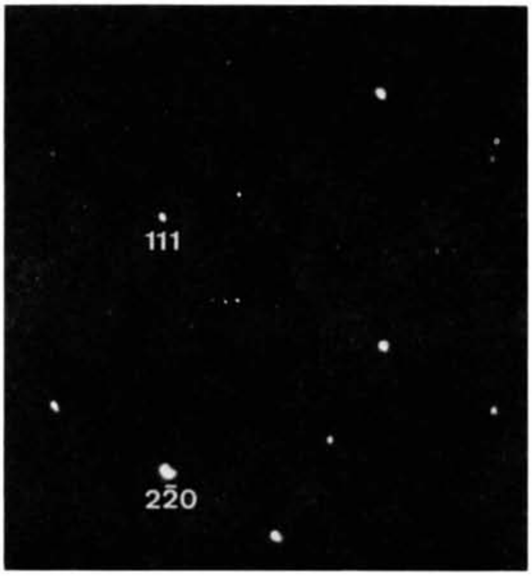

Fig. 6. $[11\bar{2}]$ zone of the $LiTbS_2$ subcell, showing superspots of the tetragonal supercell: $(111) \rightarrow (112)_T$; $(2\bar{2}0) \rightarrow (2\bar{2}0)_T$.

Bright and dark-field images, with the NaCl spots as well as the superspots reveal the existence of distinct domains which are about 1000 Å in diameter. When only one beam has been left through the objective aperture, in some regions equally spaced lines are observed (Fig. 8). We attribute these to plate-like microdomains, oriented in the direction of the beam.

Discussion

The features observed in the electron-diffraction patterns and the micrographs of $LiTbS_2$ may be explained in terms of a structure containing domains of two ordered superstructures. In the sample that was cooled from 1000 °C, these domains are about 40 Å in diameter, giving rise to diffuse intensity bands in the diffraction patterns. The diffuse bands form a surface in reciprocal space, the shape of which is very similar to that of the theoretical Fermi surface of a monovalent primitive cubic metal, as has been indicated by Sauvage & Parthé (1972).

After annealing short-range-ordered $LiTbS_2$ at 500 °C, the size of the domains increases and the diffraction patterns show long-range ordering.

The occurrence of two superstructures in short-range-ordered $LiTbS_2$ may be understood by looking at these structures in more detail. The structure of α-$NaFeO_2$ is obtained by occupying parallel $\{111\}$ cation planes in NaCl alternately with Li and Tb ions. In the $2a$ cubic structure, the ordering of Li and Tb is in the four equivalent $\{111\}_{\text{NaCl}}$ planes, *viz* (111), $(\bar{1}11)$, $(1\bar{1}1)$ and $(11\bar{1})$. It is not possible to have all four of these

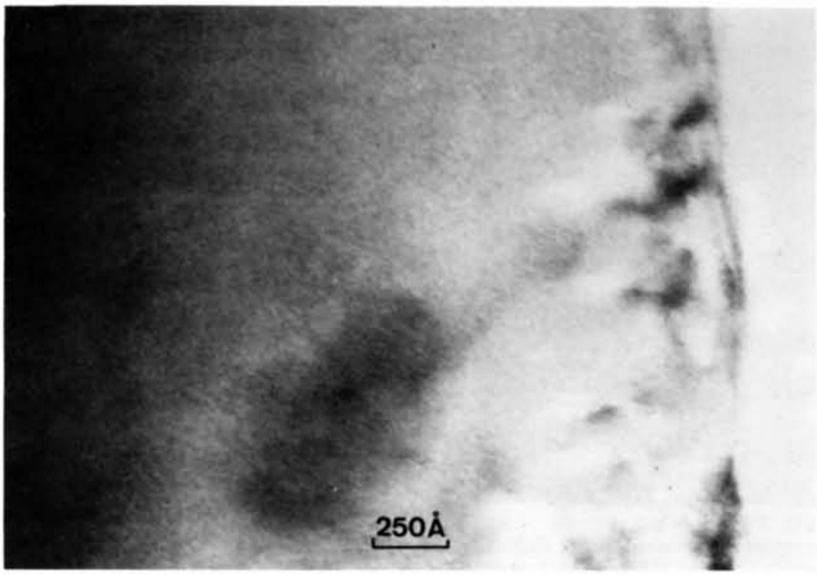

Fig. 7. Bright-field micrograph (only the central beam), corresponding to the diffraction pattern of Fig. 1 (times 4×10^5).

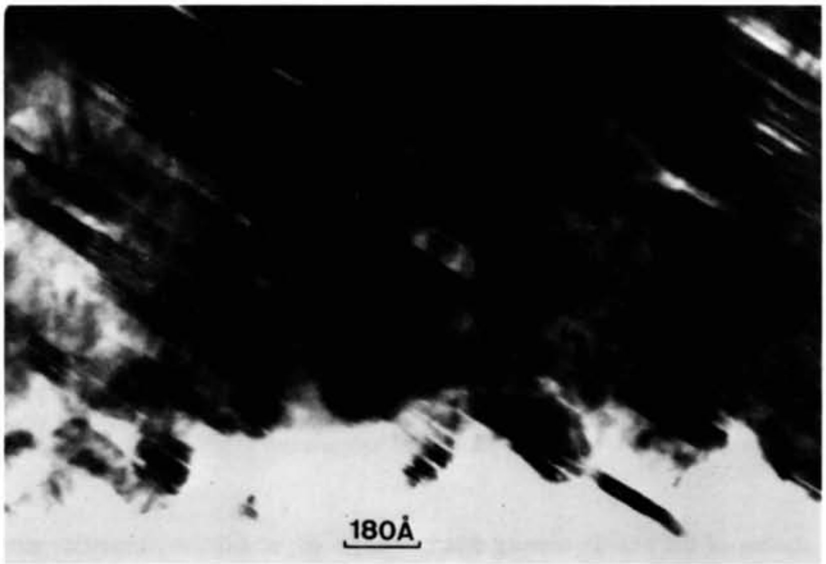

Fig. 8. Bright-field micrograph (only the central beam), corresponding to the diffraction pattern of Fig. 3 (times $5 \cdot 5 \times 10^5$).

planes occupied with only one type of cation: the result is an alternate 1 to 3 and 3 to 1 ordering of Li and Tb in all {111} cation planes. This ordering yields a pattern of corner-connected hexagons, known as a 'kagome pattern' (Iida, 1957). In both structures the anion-centered octahedra are of the same type.

With the short-range-ordered domains assumed to consist mainly of this type of anion-centered octahedra, as is indicated by the intensity distribution in the diffuse bands, all four orientations of ordered {111} planes may be equally present in the NaCl matrix. By annealing the short-range-ordered sample, the domains will grow and from each domain a larger domain with the α-$NaFeO_2$ structure will arise. These domains being oriented in four directions, intermediate domains of the cubic $2a$ structure may be formed in the regions where different α-$NaFeO_2$ domains grow into each other.

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