Diffuse electron scattering of a region in the system Li$_2$SnO$_3$-CoO

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Abstract

The occurrence of short range order in a region of the system Li$_2$SnO$_3$-CoO was identified via electron diffraction experiments. In the region studied, the resultant products have a NaCl-type structure in which oxygen anions and the Li^{1+}, Co^{2+}, and Sn^{4+} cations form a distorted close packed network. Two types of electron diffraction patterns were obtained, one of them belongs to an ordered superstructure of rock salt type and the other one exhibits diffuse scattering intensity. Short-range order arises due to occurrence of a particular spatial cation distribution at microscopic level. These microscopic regions are responsible for the diffuse scattering in the electron diffraction patterns, which exhibit striking geometrical forms depending on crystallographic orientation. We describe the most probable cation distribution of the cationic species Li^{1+}, Co^{2+}, and Sn^{4+}, on octahedral clusters to give rise to the observed diffuse scattering.
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1. Introduction

As is known, short range order produces in the reciprocal space a three-dimensional distribution of diffuse scattering when electron diffraction experiments are carried out. So, depending on crystal lattice characteristics, diffraction patterns can exhibit a variety of sharp intensity contours for different crystalline orientations.

There are a variety of compounds where diffuse scattering intensity in their electron diffraction patterns have been observed: Au-Cu alloys [1], Au-Pd alloys [2], ternary W-Nb oxides [3], Cu$_x$NbS$_2$ and Cu$_x$TaS$_2$ [4], and others with NaCl type structure. Using identical polyhedra of ions regularly arranged in space, then we can describe appropriately crystal structures. Although within the polyhedra ionic disorder may exist, Pauling's electrostatic valence rule states that it is required that

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within each of the polyhedra the composition should be the same as the overall composition of the crystal.

Sauvage and Parthé [5] have generalised the last rule to give an ordering principle for derivative structures, which requires that the smallest building blocks of the structure have, as far as possible, an identical composition with the overall composition of the compound; giving rise to relations amongst short-range order parameters. This involves the overall probability for an A atom to have a B atom as mth-nearest neighbour in a $(A_{xA}B_{xB})C_{YC}$ compound. Their analysis leads to the conclusion that even if we cannot build the whole crystal, it can still be described as an association of N polyhedra. Such polyhedra could have different occupation ratios among, say for example A, B, and C atoms on the corners of the corresponding polyhedra. Authors also found the exact form in which short-range order parameters are related to the intensity scattered in between the reflections of the base structure, which can occur as diffuse intensity, as happens in NaCl-derivative structures. In this case, the diffuse intensity lies on a surface given by $\cos\pi h_1 + \cos\pi h_2 + \cos\pi h_3 = 0$, where h_1, h_2, h_3 are continuous variables in a reciprocal space.

In the present study we have synthesised and selected some compounds from the system Li_2SnO_3-CoO [6], whose general formula is $Li_{2(1-x)}Sn_{(1-x)}Co_xO_3$. The prepared samples lie in the interval $0.07 \leq x \leq 0.20$, in which region coexist the oxide $Li_8CoSn_4O_{13}$ (PDF 48–69), and a solid solution of cobaltous oxide. The aim is to show their electron diffraction characteristics. The products belong to the NaCl type structure, and their electron diffraction patterns correspond to two different types. One of them corresponds to an ordered superstructure of rock salt type and the other one exhibits diffuse scattering intensity. These compounds are part of a set of new synthesised ceramic oxides, which belong to the system Li_2SnO_3-MO, where M^{2+} = Mn, Mg, Co, Cu, Ni, and Zn [6,7]. Two of them, M^{2+} = Mg and Cu, also exhibit diffuse scattering in their electron diffraction patterns [6,7]. In principle, we can visualise the compounds as the result of introducing M^{2+} atoms into the long-range-ordered Li_2SnO_3 structure, as it happens in another set of compounds closely related

with the system Li_3XO_4-2MO, X = Nb, Ta, Sb: $Li_3Ni_2XO_6$; X = Nb, Ta, Sb [8], and $Li_3Zn_2XO_6$; X = Sb, Bi [9], which exhibit rock salt superstructures, and in which certain types of preferential cation order occur. For these last compounds an orthorhombic unit cell has been determined, as well as their space group, which is Fddd [10].

2. Experimental

Syntheses was performed by solid state reaction of the precursor Li_2SnO_3 with the oxide CoO, using materials of analar grade. Mixed materials were dried and fired in Pt crucibles in a laboratory atmosphere in high temperature furnaces. Final firing was at 1100°C for 2 days, then cooled in air. X-ray experiments were systematically carried out to facilitate the control of the reaction. Electron microscope samples were prepared by dropping a suspension of the microcrystalline products in alcohol on a Cu grid covered with carbon film. These specimens were observed in a Jeol 1200EX electron microscope.

3. Results and discussion

Typical X-ray diffraction patterns of the oxides in the region $0.07 \leq x \leq 0.20$ are shown in Fig. 1.
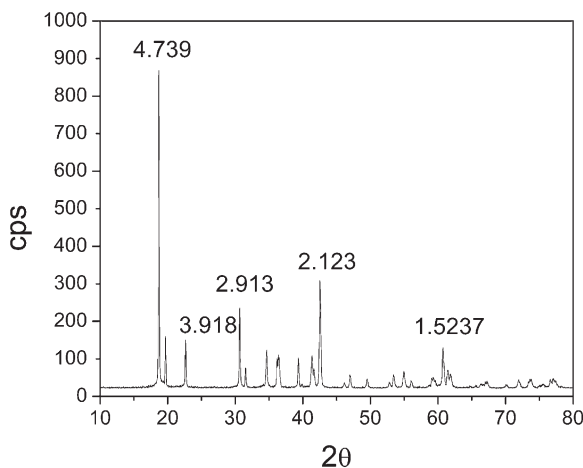

Fig. 1. Typical powder X-ray diffraction pattern of the studied oxides, given by $Li_{2(1-x)}Sn_{(1-x)}Co_xO_3$; $0.07 \leq x \leq 0.20$.

Due to differences in the ionic radii, $Li^{1+}>Co^{2+}>Sn^{4+}$, displacements of atoms relative to their average position in the periodic structure, may be a probable source for the diffuse scattering present in the electron diffraction patterns. On the other hand, the substitution mechanism may not be achieved homogeneously throughout the compound. In that event, numerous small regions in which special arrangements of atoms would exist, giving rise to the possibility of short-range order occurrence in the structure. We propose that the last possibility is a much more probable source of diffuse scattering in the studied compounds.

Formally, complex oxides with a rock salt derivative structure can have a variety of cation ordering arrangements, depending on the number and nature of cations. On the other hand, there are two types of coordination for the oxygen atoms in $R_2^{1+}M^{4+}O_3$ compounds with NaCl structure [11]. In Fig. 2, we show that corresponding to Li_2SnO_3. Furthermore, according to this, in Fig. 3 we show a probable spatial cation distribution, where one of the sub-lattices for the NaCl structure is occupied by Li^{1+}, Co^{2+}, and Sn^{4+} ions.

As pointed out before, Li_2SnO_3 has a NaCl-type structure in which the oxygen anions and the cations form a distorted close packed network [12].

The authors in this last reference claim that the structure of Li_2SnO_3 include two types of layers the first one with lithium occupied octahedra only, and the second with lithium and tin occupied octahedra. In this last case Li^+ and Sn^{4+} would be in the ratio 1:2. Layers would be stacked alternately along the perpendicular to the monoclinic a–b plane developed in the NaCl-type structure. Hodeau and co-workers [12] consider the possibility of substitution of some Li^+ by Sn^{2+}, rather than Sn^{4+}, with the consequent formation of cationic vacancies and structural distortion of the lattice.

We believe that the compounds of $Li_{2(1-x)}Sn_{(1-x)}Co_xO_3$ can be structurally considered as related to Li_2SnO_3, where the cations occupy all octahedral sites. Furthermore, we also consider that the most probable substitution mechanism is $2Li^{1+} + Sn^{4+} \Leftrightarrow 3Co^{2+}$. Therefore, the only question is which type of occupancy ratio is actually taking place in the structure. It is, of course, too difficult to determine, nevertheless what we hope is that nonrandom site occupancies occur through long distances in the crystal. Schematically, we show in Fig. 4 the second layer of Li_2SnO_3, in which are hexagonal rings of SnO_6 (white), and LiO_6 octahedra. Here we included the probable
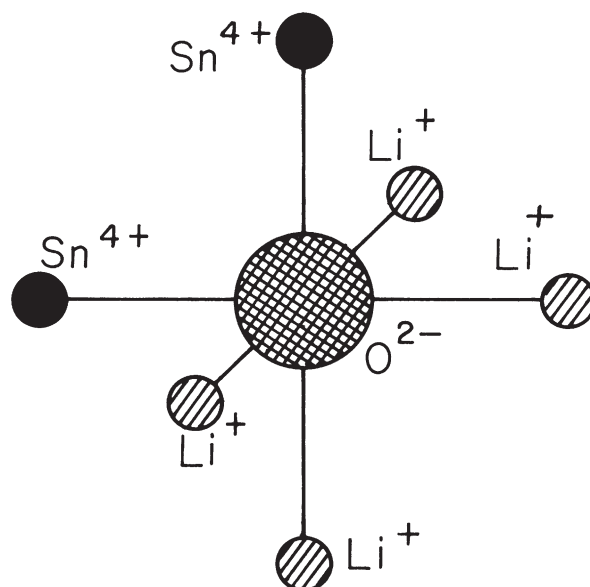

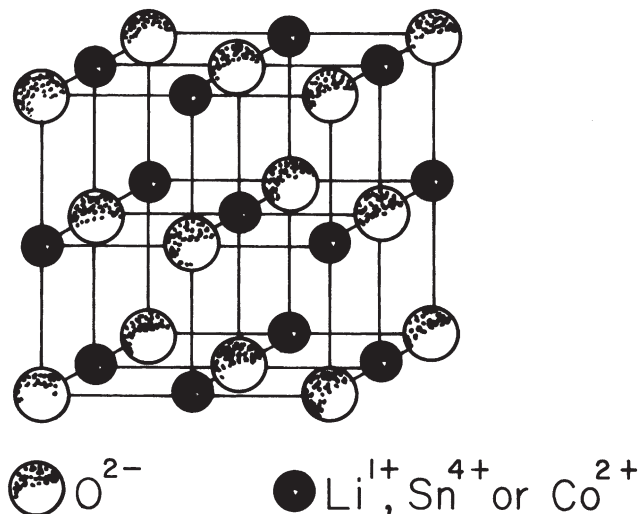Fig. 2.   Probable cation ordering arrangement of Li and Sn atoms around oxygen.

Fig. 3.   Outline of the NaCl type structure where the ions participating are; Li^{1+}, Co^{2+}, Sn^{4+}, and O^{2-}.
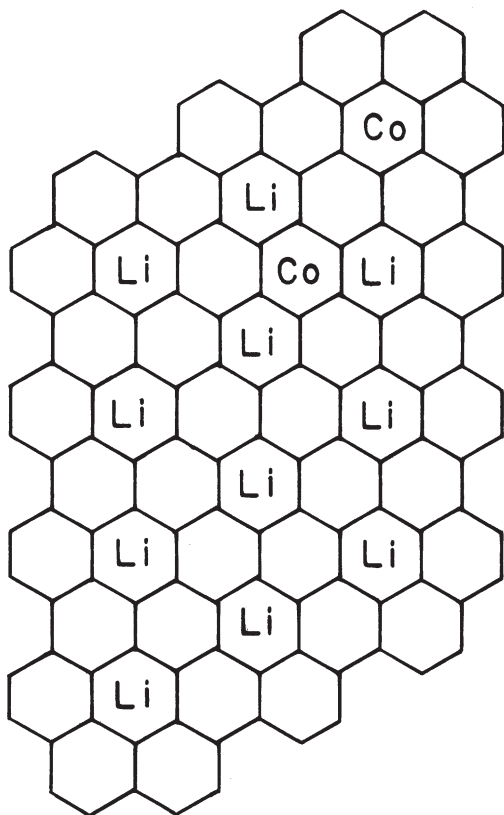

Fig. 4.   Ideal mixed layer of the Li_2SnO_3 structure with Li^+ and Sn^{4+} in the ratio 1:2. This also illustrates two probable positions for Co^{2+} ions.

presence of Co^{2+} ions in either of both positions. This mixed layer offers only two possible positions for Co^{2+} substitution, since every tin position is equivalent. So, the possibility of occurrence of microscopic short-range order in the structure is open. A similar argument was used by de Ridder and co-workers [13] to explain short-range order in the NaCl type structure lithium ferrate.

In Fig. 5a–d, we show electron diffraction patterns for various orientations and different compositions.

When Co^{2+} ions replace some Sn^{4+} in the host lattice, the cation distribution is modified in the layers, as well as their spatial location due to small additional distortion introduced by the difference in their ionic size radii, and nominal charge. As a consequence, diffuse intensity is located on a geometric locus in the diffraction patterns. This effect can be described by the cluster model [5,14], in which case an octahedral cluster or a set of them should not only have an appropriate combination of Li^{1+}, Co^{2+} and Sn^{4+} ions to exhibit the macroscopic composition, but also to give rise to the observed short-range order as discussed above. This assertion is reinforced by the close similarity in shape observed between the diffraction patterns obtained from compounds of $Li_{2(1-x)}Sn_{(1-x)}Co_xO_3$ and those in Ref. [13].

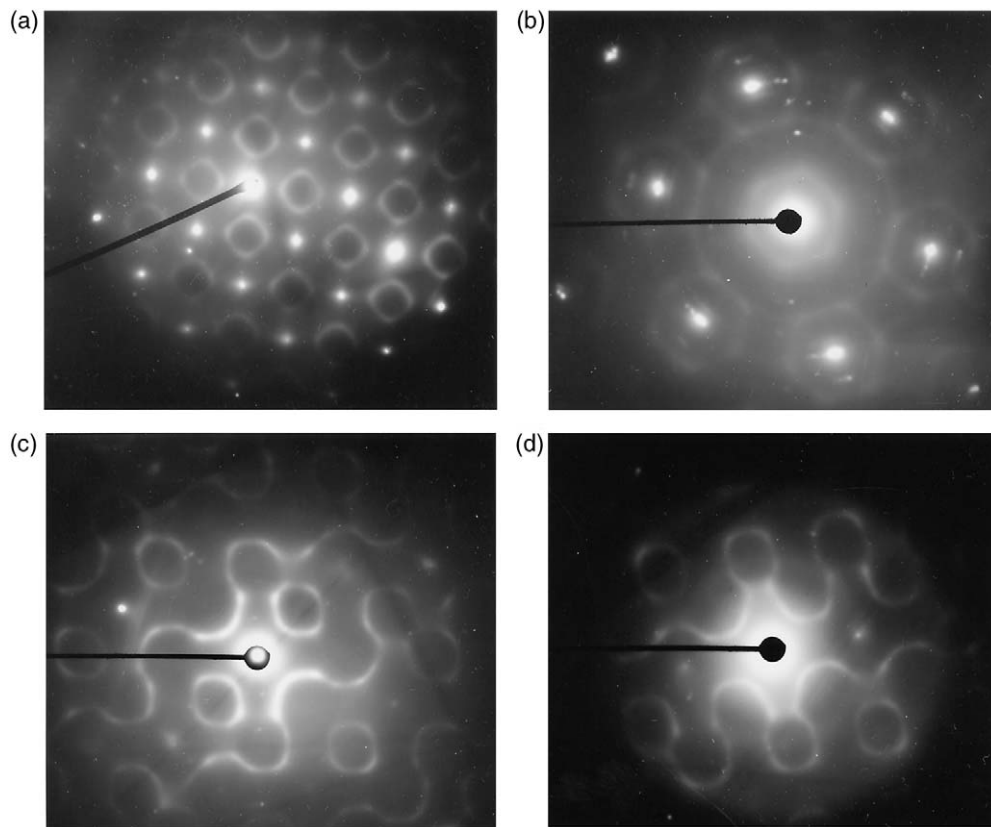Long exposure of the studied samples to electron

Fig. 5. Diffuse intensity loci from some of the studied $Li_{2(1-x)}Sn_{(1-x)}Co_xO_3$ compounds; (a) [001], and (b) [111] electron diffraction patterns for x = 0.1, (c) [114] for x = 0.125, and (d) [013] for x = 0.1375.

bombardment lead to diffraction patterns in which the diffuse intensity tends to disappear. Atomic re-ordering seems to be occurring under the influence of the electron beam. Finally, the diffuse intensity tends to become zero-dimensional, and it is located in superstructure spots. Evidently the electron beam supplies enough energy to gradually activate the transition of the small metastable regions from short-range states to the more stable long-range ones, making the diffuse scattering disappear.

4. Conclusions

In conclusion, complex oxides, like $Li_8CoSn_4O_{13}$, offer an example of the occurrence of diffuse electron scattering due to short-range order in the structure, which is rather scarce. What

we conclude is that the diffuse scattering from the new $Li_{2(1-x)}Sn_{(1-x)}Co_xO_3$ synthesised compounds can be explained by the formation of short-range order microdomains, as a transition state, induced by the introduction of cobalt atoms into the long-range-ordered Li_2SnO_3 structure.

Acknowledgements

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