X-Ray–Scattering Evidence for Sublattice Phase Transition in Stoichiometric Silver β-Alumina

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X-ray–scattering investigation of stoichiometric silver β-alumina reveals a clear phase transition between the high-temperature conducting-ions quasiliquid sublattice, and a low-temperature crystalline state. Preliminary, structural analysis of the low-temperature crystalline order confirms the type of organization previously deduced for the low-temperature short-range order of nonstoichiometric silver β-alumina.

Among the real superionic conductors, β-alumina which usually corresponds to the formula $11(Al_2O_3)1.3B_2O$ (with B=Na, Ag, K, Tl, etc.) has the particular feature that both the electrical[1] and structural properties of the conducting ions[2] display a continuous variation as a function of temperature, in contrast with other ionic conductor such as AgI[3] or $RbAg_4I_5$[4] in which a clear phase transition is observed between a high-temperature conducting sublattice liquid and a low-temperature nonconducting crystalline state.

The absence of phase transition in β-alumina crystals can be thought to be a direct consequence of the nonstoichiometry. Indeed it was already observed that crystals of slightly different compositions show appreciable differences for the extent of the local order between the conducting ions at a given temperature,[5] but this could also be attributed to variations of crystalline perfection or of compensating defects for the nonstoichiometry mechanism in cases where the samples are obtained by very different growing techniques. Since it has now been achieved to obtain nearly stoichiometric β-alumina crystals[6,7] with a formula $11Al_2O_3$-xB_2O ($x \simeq 1$), the question is raised whether this new compound behaves as the more usual ionic conductors with an order-disorder transition.

The purpose of the present paper is to report structural evidence of such a phase transition taking place at about room temperature in stoichiometric silver β-alumina. In a preliminary characterization, the long-range low-temperature order of the conducting-ion sublattice is found to be an extension of the type of short-range superstructure earlier deduced from the low-temperature diffuse scattering in nonstoichiometric silver β-alumina.[8]

As described in more detail in Refs. 6 and 9, stoichiometric silver β-alumina single crystals were obtained by thermal decomposition of nonstoichiometric ammonium β-alumina crystals at 500°C, followed by molten salt exchange in a bath of silver nitrate. No protonic species (such as H_2O) were detected by ir study and a nearly stoichiometric composition is given by the x-ray structure determination with the main-lattice reflections. Evidence of the existence of a phase transition was obtained by photographic x-ray scattering as previously used for a similar compounds,[2] intensity measurements of the low-temperature superlattice reflections were performed on a $P2_1$ Syntex four-circles diffractometer.

Evidence for the existence of a high-temperature conducting sublattice liquid state in stoichiometric β-alumina is given in the pattern of Fig. 1(a) taken at 700 K; besides sharp Bragg reflections from the main average lattice, several successive orders of a diffuse halo, characteristic

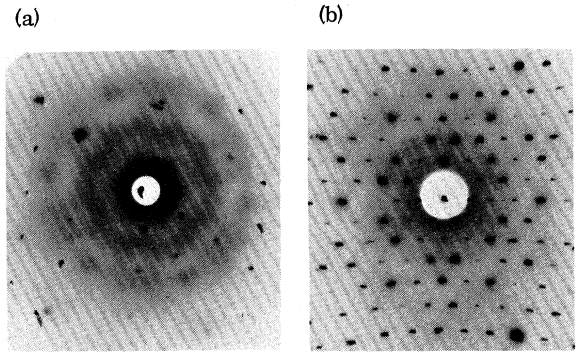

FIG. 1. X-ray scattering from stoichiometric Ag β-alumina with c axis parallel to incident beam (Mo $K\alpha$ radiation). (a) T = 295 K, exposure with oscillating crystal (±1°). (b) T = 700 K, exposure with fixed crystal.

of quasiamorphous or quasiliquid state are clearly visible. This diffuse halo recalls the earlier observations made at the same temperature on nonstoichiometric silver β-alumina[2] with, however, slight differences.

Evidence for the existence of a lower-temperature crystalline 3D (three-dimensional) long-range order of the conducting-ions sublattice is shown in the pattern of Fig. 1(b) taken at 295 K. Besides the stronger reflections from the main lattice, weaker but sharp reflections corresponding to a hexagonal superlattice with $C=c$ and $A=a\sqrt{3}=9.68$ Å and oriented at 30° from the main lattice ($a=5.59$ Å) are observable. This 3D superstructure contrasts with the 2D short-range superstructure earlier observed at low temperature in nonstoichiometric silver β-alumina; in the conducting planes, however, the local order is the same.

Above 300 K, the superlattice reflections broaden and become undetectable around 500 K. In the c^* direction this broadening is more rapid than in a^* direction giving rise from about 315 K and upwards to streak characteristic of a short-range 2D order in the conducting planes. Microdensitometer readings along the a^* direction from patterns taken at intermediate temperatures between the two extreme cases of Fig. 1 show the evolution and the decrease of the coherence length in the silver layers as illustrated in Fig. 2.

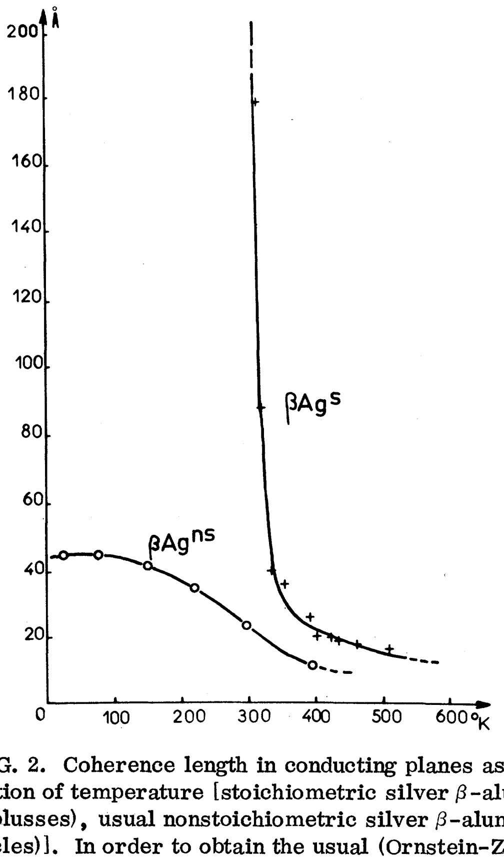

FIG. 2. Coherence length in conducting planes as a function of temperature [stoichiometric silver β-alumina (plusses), usual nonstoichiometric silver β-alumina (circles)]. In order to obtain the usual (Ornstein-Zernike) correlation length, the above coherence length must be divided by ($\pi\times 0.888$).

The relations between intensities ($I_{hkl}=I_{hkl}$) and the existence of reflections $h\,0\,\overline{2h}\,l$ with $l=2n+1$ for the superlattice reflections yield the hexagonal space group $P6_3/m$, with a 50% twinning and a translation of $z=\frac{1}{2}$ between the two types of domains. A preliminary analysis of the intensity of 340 superlattice reflections recorded on a four-circle diffractometer between two $\theta=0$ and two $\theta=50°$, using standard structure determination procedures for the silver and oxygen ions of the conducting planes, gives an agreement factor $R=9\%$ ($R=\sum|F_{\rm obs}-F_{\rm calc}|/\sum|F_{\rm obs}|$) with the superstructure schematically shown in Fig. 3. This corresponds to one silver ion per layer and per main β-alumina unit cell in agreement with the chemical formula of stoichiometric silver β-alumina. The superstructure only arises because of the off-centering from the theoretical Beevers-Ross[7] positions of the silver ions by 0.8 Å, and a corresponding off-centering of the oxygen ions by 0.3 Å, which accounts for the weaker intensity of the superlattice reflections compared to the Bragg peaks from the main lattice. The ratio of the intensity of the superlattice reflections relative to

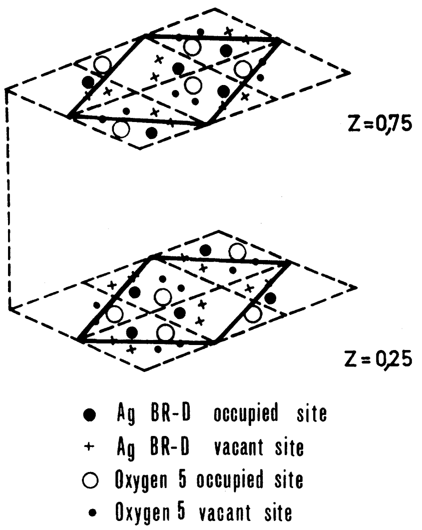

FIG. 3. Distribution of silver and oxygen ions in the layers of stoichiometric silver β-alumina.

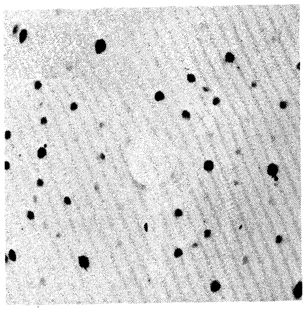

FIG. 4. X-ray scattering from stoichiometric Na β-alumina 100 K; c axis parallel to incident beam (Mo $K\alpha$).

the reflections from the main lattice is further of the expected order of magnitude with the assumption that the superlattice peaks are only due to the off centering of the ions from the theoretical positions within the conducting planes.

The occurrence for stoichiometric silver β-alumina of an order-disorder transition as in other silver superionic conductors clearly confirms that the nonstoichiometry of usual β-alumina is at the origin of the continuous behavior as a function of temperature of both the electrical and structural properties. If stoichiometry is achieved, β-alumina shows the expected conducting-ions sublattice melting at given transition temperature.

The preliminary analysis of the superlattice reflections of the low-temperature ordered phase, further confirms the type of ordering deduced from the limited diffuse scattering data obtained at low temperature with nonstoichiometric silver β-alumina.[2] In fact, in the conducting layers the long-range-ordered superstructure of the conducting ions in stoichiometric β-alumina can be considered as an extension of the partial order found in the earlier work: empty anti Beevers-Ross sites, and full occupation of strongly off-centered Beevers-Ross sites.

A more detailed structure determination of stoichiometric β-alumina, including the main-lattice reflections and the superlattice peaks only considered here, is presently under progress in the case of both silver β-alumina and sodium β-alumina which also reveals a low-temperature ordered sodium sublattice, as can be seen in the pattern shown in Fig. 4 and taken at 100 K.

Further experimental work on stoichiometric β-alumina single crystals used in the present study is clearly needed, including in particular detailed measurements as a function of temperature of the ionic conductivity. Very partial results available to date from measurements performed at only two temperatures reveal that the ionic conductivity of stoichiometric silver β-alumina in the high-temperature quasiliquid state (700°K) is three orders of magnitude higher than in the ordered room-temperature state (300 K). This difference is by about two orders of magnitude more important than for nonstoichiometric silver β-alumina, and is indeed consistent with the existence of a sharp phase transition.

We are grateful to G. Lucazeau, who studied stoichiometric β-alumina by Raman-scattering techniques,[7] for communicating his results prior to publication.

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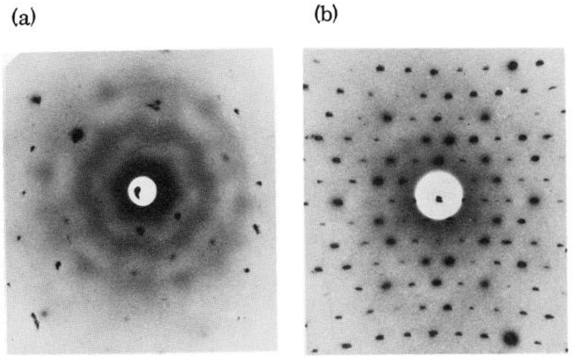

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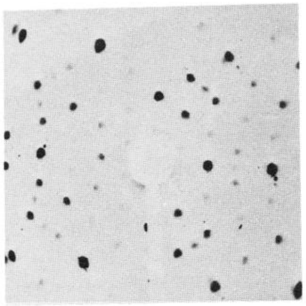

FIG. 4. X-ray scattering from stoichiometric Na β-alumina 100 K; c axis parallel to incident beam (Mo $K\alpha$).