Short Communications

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Acta Cryst. (1977). A**33**, 678

Structural phase transition in the spinel $MgAl_2O_4$.

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(*Received* 29 *November* 1976; *accepted* 3 *February* 1977)

A new crystallographic phase transformation in $MgAl_2O_4$ is reported in which the low-temperature low-symmetry space group of $MgAl_2O_4$ transforms to the 'spinel' space group $Fd3m$ at ~450°C. The *in situ* electron diffraction experiments suggest that this is a second-order phase transformation.

Grimes's (1972, 1973) suggestion that the space group of the spinel structure may not be $Fd3m$ but $F\bar{4}3m$ has been supported by recent electron and X-ray diffraction evidence, in which the presence of $hk0$ reflections with $h+k=4n+2$ in $MgAl_2O_4$ (Hwang, Heuer & Mitchell, 1973) and some thiospinels, (Higgins, Speer & Craig, 1975) has been found at room temperature. However, in other compounds with the spinel structure, such as $LiFe_5O_8$, the room-temperature electron-diffraction patterns of the ⟨100⟩ reciprocal-lattice sections (Fig. 1) do not exibit these forbidden reflections, suggesting that the structure has the originally proposed space group $Fd3m$ (Bragg, 1915). Neutron diffraction experiments on magnetite by Samuelson (1974) and X-ray diffraction on $CuCo_2S_4$ by Williamson & Grimes (1974), also support the result that the space group of Fe_3O_4 or $CuCo_2S_4$ is $Fd3m$ at room temperature. The purpose of this communication is to report the observation of a structural phase transition in $MgAl_2O_4$ that transforms its space group to $Fd3m$ at high temperature.

Fig. 1(*a*) and (*b*) shows the symmetric ⟨100⟩ selected-area electron-diffraction pattern from a stoichiometric $MgAl_2O_4$ spinel single crystal grown by the Czochralski method. The electron-transparent specimen was prepared from the bulk crystal by ion thinning and examined in the Philips EM301 transmission electron microscope operating at 100 kV. Fig. 1(*a*) shows the presence of $hk0$ spots with $h+k=4n+2$ (*i.e.* 200, 420, *etc.*). The integrated intensity of the 200 spots as measured from microdensitometer traces is less than 1/1000 of that of the 400 spots. This is consistent with the estimation by Heuer & Mitchell (1975). On heating the specimen in the hot stage of the electron microscope to a temperature close to 450°C, the 'forbidden' spots disappear, as is evident in Fig. 1(*b*) taken from the same area of the foil (~2 μm in diameter). In order to prove that the extra reflections are representative of structural changes and not double diffraction or other effects, Fig. 2(*a*)–(*d*) shows selected-area diffraction patterns taken from the foil near the ⟨100⟩ orientation, tilted so as to excite the ⟨400⟩ reflection after the temperature changes as shown. The heating sequence, Fig. 2(*a*)–(*c*), shows the disappearance of the 200 reflection near 450°C, and the reflection subsequently reappears upon cooling, as in Fig. 2(*d*). Close examination of the corresponding images both in bright field and dark field with the 200 and 400 reflections does not show any changes in microstructure or morphological features. This strongly suggests that the observed symmetry is not accompanied by a solid-state phase transition involving nucleation and growth, by which two phases can coexist.

Assuming that the space group $MgAl_2O_4$ at room temperature is $F\bar{4}3m$ as suggested by Grimes (1972, 1973), this experimental result suggests that the nonequivalent octahedral sites of the room temperature $F\bar{4}3m$ phase become statistically equivalent at higher temperature because of thermal vibration. The transformation can be accomplished without any long-range diffusion. Application of Landau's theory of a second-order phase transition shows that it is possible for the transition $F\bar{4}3m \rightleftarrows Fd3m$ to occur by either a first or a second-order transformation (Haas, 1965). However, the experimental evidence that no microstructural changes are resolved within the limits of this experimental technique, suggests that the transformation is actually one of second order. It is possible that the other spinel structure compounds that do not give rise to $hk0$ reflections with $h+k=4n+2$ at room temperature may also transform and show reflections at lower temperatures. Hence it may be that this transformation could be a general one for oxide spinels and thiospinels.

This research was supported by the Energy Research and Development Administration through the Materials and Molecular Research Division of the Lawrence Berkeley Laboratory.

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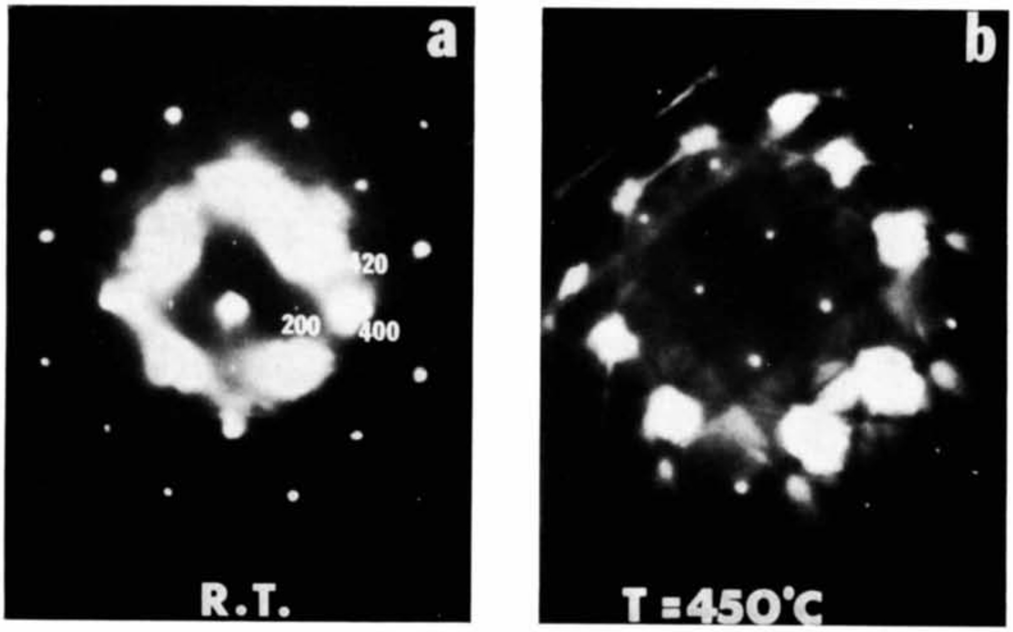

Fig. 1. Selected-area electron-diffraction patterns from $MgAl_2O_4$ in $\langle 100 \rangle$ orientation; (*a*) taken at room temperature showing 200, 420-type spots, (*b*) taken at ~450°C from the same area where these reflections have disappeared. The slight shift in the Kikuchi pattern is due to a slight buckling of the foil upon heating.

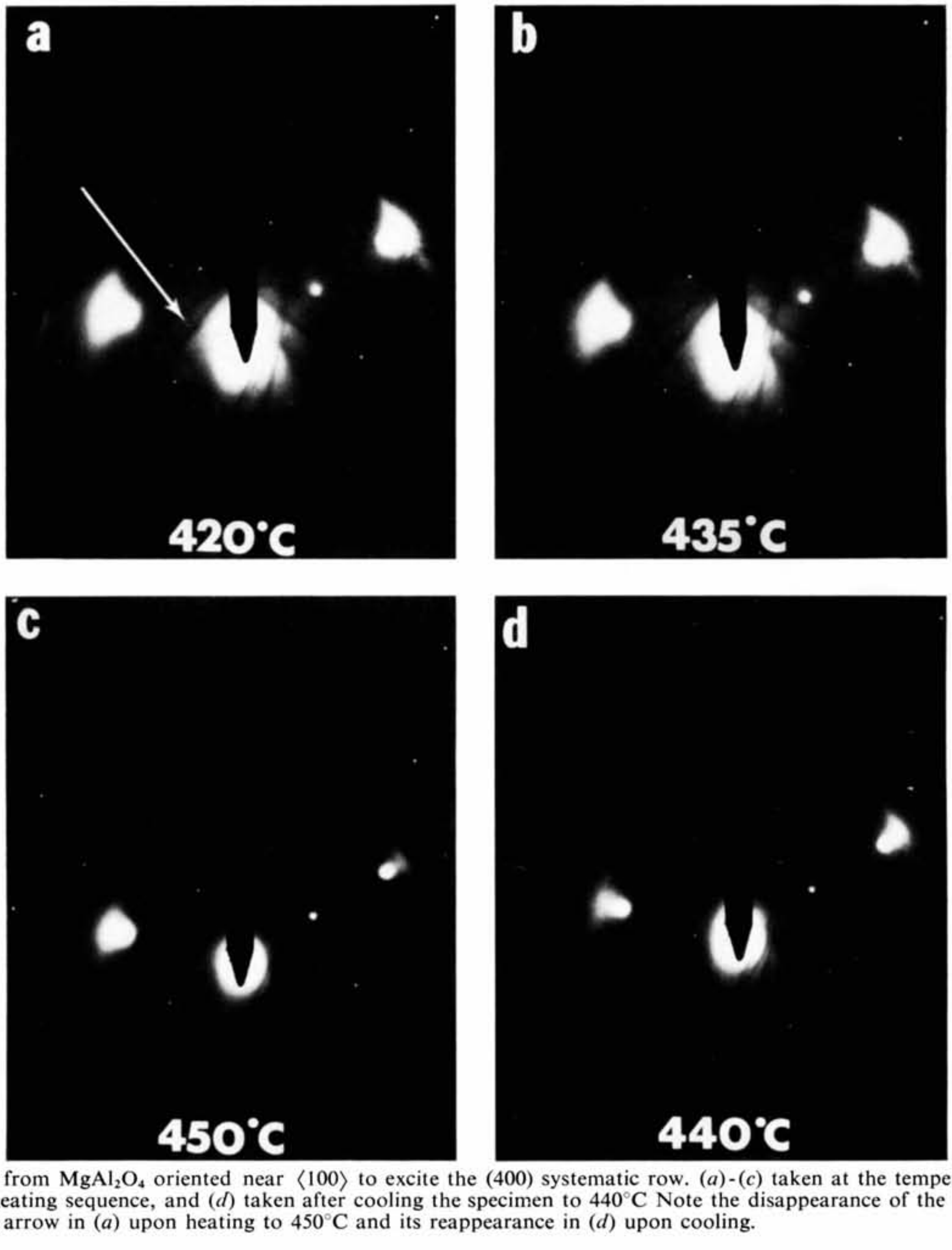

Fig. 2. SAD from $MgAl_2O_4$ oriented near ⟨100⟩ to excite the (400) systematic row. (*a*)-(*c*) taken at the temperatures shown during a heating sequence, and (*d*) taken after cooling the specimen to 440°C Note the disappearance of the 200 spot marked by an arrow in (*a*) upon heating to 450°C and its reappearance in (*d*) upon cooling.