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Authors' reply to Dr Sickafus's "Comment on 'Order–disorder phase transition induced by swift heavy ions in $MgAl_2O_4$ and $ZnAl_2O_4$ spinels'"

Dr Sickafus defends his analysis, presented in many of his articles (refer 2–6 of his comment or in [1]). His analysis is based solely on transmission electron microscopy (TEM) diffraction patterns. We explained in detail [2] why this method, using the Mott Bethe approximation for atomic form factors associated to electrons, as well as X-ray diffraction (XRD), can lead to an erroneous conclusion, as mentioned earlier [3], for the structure of $MgAl_2O_4$ spinel: Mg and Al atoms possess similar atomic form factors which leads to accidental extinctions of diffraction patterns and to *an apparent reduction* by two of the unit cell parameter as well as to *an apparent change* of the space group of $MgAl_2O_4$ for important values of the inversion parameter during irradiation.

To avoid such a problem, we also studied [2] in the same conditions an other spinel, $ZnAl_2O_4$. In this material, cations possess quite different atomic form factors and then TEM and XRD become efficient tools to describe the evolution of $ZnAl_2O_4$ under irradiation. We clearly showed that irradiation leads only to an order-disorder transition without any change of the space group ($Fd\bar{3}m$) in this spinel ($ZnAl_2O_4$). We maintain that it would be quite surprising to find that $MgAl_2O_4$, belonging to the same family, would exhibit a different behaviour under irradiation.

To confirm this point, XRD was complemented by other analysis techniques. Raman spectroscopy, insensitive to atomic form factors, was used to define the space group of irradiated $MgAl_2O_4$ samples [2]. The results show that the space group of different irradiated $MgAl_2O_4$ samples is $Fd\bar{3}m$, in concordance with previous works [3]. Moreover, two different local probes, nuclear magnetic resonance (NMR) and X-ray absorption near edge structure spectroscopy (XANES) were further employed [4]. NMR unambiguously shows the inversion of Mg/Al cations in irradiated $MgAl_2O_4$ spinels in agreement with an order disorder transition induced by irradiation as expected [2] whereas XANES on irradiated $MgAl_2O_4$ was unable to demonstrate the splitting expected in the case of the change of the space group during irradiation and clearly showed that Al tetrahedra exist in irradiated $MgAl_2O_4$ confirming our analysis [2].

Thus, to conclude, using different techniques, we confirm that an order disorder transition occurs in the irradiated $MgAl_2O_4$ spinel without any change of its space group ($Fd\bar{3}m$). We are undertaking investigations to understand the mechanism responsible for the order disorder transition enhanced by irradiation in these spinels.

References

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