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The Ordered Twin to Disordered Phase Transition in Modulated $[Ag(bipy)NO_3]_\infty$

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Objective

Characterize the phases associated with the order-disorder transition in polymeric $Ag(bipy)NO_3$

Method

Collect single crystal x-ray data sets as a function of temperature and refine structures above and below the phase transition temperature.

Results and Conclusion

$Ag(bipy)NO_3$, bipy = 4,4'-bipyridine = $C_{10}H_8N_2$, has two known crystal forms at room temperature [1,2,3]. The *Fddd* form contains a disordered nitrate ion and shows previously unreported planes of diffuse scattering indexable as $3k \pm l = 4n$ for the RT cell *a* 12.952(2), *b* 9.912(1), *c* 34.428(4) Å. Automated data collection used a Nonius KappaCCD diffractometer equipped with an Oxford Cyrostream 600. Synthetic precession photographs showed the symmetry was *Fddd* at 160 K and above but a loss of systematic absences indicated *F12/d1* (*i.e. C2/c*) at 150 K and below.

The 100 K structure, *C2/c*, *a* 12.751(1), *b* 9.860(1), *c* 18.379(2) Å, β 109.98(1) ° had twin components related by a rotation around **c***. The cell for *F12/d1* has $a' = a$, $b' = b$, *c'* 34.547(2) Å, β' 89.68(1) °. All intensities were obtained as the sum of two components. Refinement gave a 0.754(1):0.246 twin with no disorder and $R(F) = 0.021$ for 2293 (out of 2456) reflections with $I > 3\sigma(I)$. Along a chain, Ag atoms, $(3\mathbf{b} \pm \mathbf{c})/4$ apart, move 0.221(1) Å in opposite directions perpendicular to the chain. Chains are cross linked by Ag-Ag contacts of 2.958(1) Å and Ag-O contacts of 2.749(2) and 2.747 (2) Å. The chains zig-zag so that Ag atoms avoid closer contact with the nitrates.

The 200 K structure, *Fddd*, *a* 12.823(1), *b* 9.937(1), *c* 34.450(1) Å, was refined as a 1:1 disorder of all atoms initiated by disordering the 100 K structure. Constrained refinement gave $R(F) = 0.028$ for 1004 (out of 1270) reflections with $I > 3\sigma(I)$. The Ag displacement reduced to ±0.123(3) Å. The alternative orientation of the nitrate gave 3 Ag-O contact distances indicating an intermediate step for a change of local ordering. The 16.5° root mean square angular displacement of the nitrate (up from 10.1 °) showed that the nitrate ions readily rotate by 60 ° in their own plane to initiate the order-disorder phase change. The diffuse scattering indicates that mistakes in nitrate positions cause a localised straightening of the adjacent chains that moves substantial amounts of these chains along their lengths. In contrast, the actual position of a nitrate only affects the closest Ag atoms.

Keywords: disorder-order transition, diffuse scattering, twin structure, modulated structure

References

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