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Prof. D. Keen,
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Submission for the PCG PANalytical Thesis Prize

Dear Prof. Keen,

Please find attached to this e-mail a copy of my thesis, entitled *Energetic Materials at Extreme Conditions*, for consideration for the PANalytical thesis prize for Physical Crystallography.

I am pleased to consider myself a physical crystallographer, since my research interests lie in understanding the effects of extreme conditions on the performance of energetic materials (explosives, pyrotechnics and propellants). This important class of materials can have applications ranging from fireworks to munitions and it is therefore critical that their performance is subject to stringent criteria regarding, for example: sensitivity to detonation; detonation velocity; and, chemical/thermal stability. Polymorphism and solid-state phase transitions may have significant implications and explosive performance may be highly dependent on the particular polymorph selected.

In order to model effectively the behaviour of energetic materials under operational conditions it is essential to obtain detailed structural information for these compounds. In many cases, the crystal structure obtained under ambient conditions is used as the basis for modelling properties under the elevated temperatures and pressures of detonation because structural information is simply not available at these extreme conditions. However, it is well documented that such extreme conditions can often lead to substantial changes in intermolecular interactions and molecular geometries, and can even induce phase transitions. My doctoral research therefore focussed on the identification and structural characterisation of polymorphs of energetic materials obtained at high pressures/ temperatures and the rigorous assessment of the effect of pressure and temperature on intermolecular interactions within these materials. Such experimental information is of great value to computational chemists and physicists who seek to improve the efficacy of their models of high-energy processes such as detonation and deflagration.

The structural complexity of these materials, as well as the difficulties of high-pressure studies, necessitated that I become skilled at a range of complementary techniques: X-ray diffraction (both single-crystal and powder), neutron powder diffraction and vibrational spectroscopy. Furthermore, throughout this work I have relied on experimental capabilities only available at central facilities, such as ISIS and Diamond.

I present structural data obtained during compression of the high explosives RDX and CL-20, as well as a series of inorganic azides, which allowed the determination of equations of state with greater precision than has previously been reported. The most exciting aspect of this work, however, was the recovery of a high-pressure/high-temperature form of RDX to ambient pressure by exploiting a variable-temperature insert for the Paris-Edinburgh cell. The unique capability to heat and cool rapidly *in situ* was developed in conjunction with this research programme – a prime example of the interplay between instrument advancement and scientific understanding.

The number of polymorphs identified in this work is a reflection, not only of the powerful effects that extreme conditions have in dramatically altering crystal packing, but also the technical advances that have facilitated the collection and refinement of complementary high-pressure structural data. Furthermore, this thesis demonstrates the unrivalled opportunity for obtaining novel materials that high-pressure studies provide and the exciting prospect of the recovery of high-pressure phases to ambient conditions, with dramatic implications for performance.

In addition to my thesis, I have included two academic referees (see below) who can attest to my experience and ability in physical crystallography.

Yours sincerely,

David Millar

References:

Dr Colin Groom (External Examiner)
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