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Tuning the structure and magnetism of model systems under pressure

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Pressure provides a strong and clean means of tuning exchange interactions, J , in magnetic materials, yet it is not widely used and the relationship between J and interatomic separations, r , is poorly characterised and understood. The empirical relationship $J \propto r^{-n}$ - where n is typically in the range 9 - 12 - was proposed on the basis of studies on oxides and halides several decades ago, but has not been extended over many more classes of compound, and the theoretical basis of the expression has received scant attention. One reason for the paucity of experimental work is the fact that it is challenging to provide a reliable measure of J as a function of pressure, partly because cells for high-pressure magnetometry tend to obscure the signal from the sample unless the magnetisation is very high. We describe work that combines SQUID magnetometry under pressure using new, low-background cells with X-ray diffraction on the same samples held in a diamond anvil cell. Initial work has concentrated on materials in which the relation between the magnetic susceptibility and exchange interactions is relatively simple, and in which the magnetisation can be strong. To this end we selected cubic ferrimagnets in the form of Prussian Blue Analogues and found that they show a remarkable sensitivity of J towards r : $J \propto r^{-n}$ with n of the order of 30. These observations are in remarkable agreement with hybrid density functional theory calculations of the energy of different spin states in these materials as a function of cell parameter. These calculations also cast light on the origin of the particular sensitivity of J on r .

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High Pressure as a Tool to Study Structure and Function of Molecular Crystals

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The detailed structures of molecular crystals depend on the packing forces, and hence the distances between molecules. Similarly, dynamic processes including the rotation of moieties within molecular structures are dependent upon the strength of the interactions such as H-bonding between different components of the crystal structure. These forces can be directly modified by the reduction in inter-atomic distances through the application of pressure. Pressure is a cleaner and more effective probe than temperature of inter-atomic interactions in molecular crystals because it drives the volume directly through the PV energy term. In addition, the volume reduction easily induced experimentally by pressure is far greater than that obtained by cooling to 0K. The development of the diamond-anvil pressure cell along with the data reduction protocols for single-crystal diffraction, has made the determination of the structure of molecular crystals at pressures up to 10 GPa (100,000 atmospheres) routine [1]. Over this pressure range, unit-cell volumes of molecular crystals typically decrease by 30% and intermolecular distances by 15%. In $\text{Ru}_3(\text{CO})_{12}$, for example, this leads to the development of significant interactions between molecules without changes to the conformation of the carbonyl groups [2], thus disproving the previous idea that the choice of conformation was a result of packing forces. In organic-inorganic hybrid materials, the decrease in distances between the organic cations and the inorganic anionic frameworks leads to the formation of stronger H-bonding and the suppression of dynamic disorder of the cations that can clearly be determined from the displacement parameters obtained from refinement to high-pressure data. Further, in $[(\text{CH}_3)_2\text{NH}(\text{CH}_2)_2\text{NH}_3][\text{SbCl}_5]$, structure refinements show that pressure also induces a change in the electronic structure of the Sb atoms within the framework [3].

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