Heavy Atom Ferromagnets under Pressure: Structural Changes and the Magnetic Response

Masaki Mito,† Yuki Komorida,† Hideki Tsuruda,† John S. Tse,‡ Serge Desgreniers,# Yauso Ohishi,† Alicea A. Leitch,§ Kristina Cvrkalić,§ Craig M. Robertson,# and Richard T. Oakley†§

Faculty of Engineering, Kyushu Institute of Technology, Kitakyushu 804-8550 Japan, Department of Physics and Engineering Physics, University of Saskatchewan, Saskatoon, Saskatchewan S7N 5E2, Canada, Department of Physics, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada, Materials Science Division, Japan Synchrotron Radiation Research Institute (JASRI), Spring-8, Sayo, Hyogo 679-5198, Japan, and Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

Received September 28, 2009; E-mail: oakley@uwaterloo.ca

For decades the idea that molecular radicals might serve as building blocks for organic ferromagnets has fueled research into the structures and properties of light heteroatom radicals such as nitroxyls, verdazyls, and thiazyls. This work yielded a number of systems that order ferromagnetically, but the Curie temperatures of these materials are under 2 K, and their coercive fields are only a few Oersted. More recently, we reported a family of thia/selenazyl radicals that order ferromagnetically, but the Curie temperatures of these materials are under 2 K, and their coercive fields are only a few Oersted.

Moreover, their coercive fields (at 2 K) of 250 Oe for thia/selenazyl radicals are only a few Oersted. More recently, we reported a family of thia/selenazyl radicals that order ferromagnetically, but the Curie temperatures of these materials are under 2 K, and their coercive fields are only a few Oersted.

To explore the effect of structural modifications on the magnetic response of these heavy heteroatom ferromagnets, we prepared several isostuctural derivatives of 2a and found that minor changes in the degree of slippage of the radicals along the stacking direction led to major changes in magnetic behavior. Thus, while two of the modified radicals 2 (R1 = Et; R2 = Me, Br) ordered as ferromagnets, with similar Tc and Hc values to those of 2a, the other two variants 2 (R1 = CH2CF3, Pr; R2 = Cl) showed no indication of ordering above 2 K. This study illustrated the use of chemical pressure, that is, the introduction of a small perturbation by synthetic means to a known system, so as to modify structure and hence property. An alternative approach involves the application of physical pressure.

To probe the effects of physical pressure on these heavy heteroatom ferromagnets we have examined the crystal structure and magnetic properties of 4a over the pressure range 0–4 GPa. High pressure diffraction experiments were performed at BLX10U, Spring-8, using synchrotron radiation (λ = 0.51446 Å) and He as the pressure transmitting medium. Data were collected at room temperature on a powdered sample of 4a using a diamond anvil cell (DAC), and the structures were solved by simulated annealing methods starting from a molecular model of 4a taken from single crystal data (collected at 100 K). During the solution and Rietveld refinement, a rigid-body constraint was maintained for the molecule. As illustrated in Figure 1, all the lattice constants for 4a, which crystallizes in the tetragonal space group P4212m, contract smoothly with increasing pressure, indicating that there is no structural phase transition. The contraction is not, however, isotropic; compression along c, the stacking direction, is significantly greater than that along the a, b axes.

Figure 1. Unit cell of 4a (left) and percent contraction in unit cell dimensions relative to the ambient pressure structure (right).

While compression of the unit cell does not alter the packing of the radical π-stacks about the 4 points along the c-direction, it does alter the slippage of radicals (dy) along the π-stacks, as well as the interplanar separation (δ) between adjacent radicals. As may be seen in Figure 2, both δ and, to a greater extent, dy decrease with increasing pressure; in essence the radical π-stacks become more nearly superimposed under pressure.

Figure 2. Slippage (dy) and interplanar separation (δ) of adjacent radicals along the π-stacks of 4a as a function of pressure.
AC magnetic susceptibility measurements on samples of 4a were performed over the pressure range 0–1.6 GPa under hydrostatic conditions using a piston cylinder cell (PCC) in a SQUID magnetometer. In the sample chamber, crystals mixed with a pressure transmitting medium, Apiezon J oil, were held with a piece of lead as the manometer. Figure 3 (left) shows representative plots of the in-phase component of the susceptibility $\chi'$ (at 1 Hz) versus temperature $T$. The results indicate an initial increase in the ferromagnetic ordering temperature $T_C$, which reaches a maximum value of 21 K near 0.9 GPa. Beyond this pressure $T_C$ starts to retreat, so that by 1.6 GPa its value is near 18 K. Similar results were obtained from samples subjected to uniaxial compression (along $z$) and to quasi-hydrostatic compression in a DAC. The latter technique also allowed access to pressures above 1.6 GPa and revealed a continued decrease in $T_C$ to 16 K at 2 GPa, with little change thereafter to the limit of the experiment (4 GPa). The magnetic response, however, weakened significantly at higher pressures, suggesting partial collapse of the ferromagnetic network. Figure 4 (left) provides a composite of all the $T_C$ versus $P$ measurements.

Figure 3. Plots of the in-phase AC susceptibility $\chi'$ of 4a versus $T$ (left), and magnetization $M$ versus $H$ at 2 K (right), at different pressures.

Pressure dependent magnetization ($M$) measurements as a function of field ($H$) were also performed on 4a, under hydrostatic conditions, in a PCC. The coercive field $H_C$ (1250 Oe) obtained from the $M$ versus $H$ hysteresis loop at 0 GPa and $T = 2$ K (Figure 3, right) undergoes little or no change up to 0.55 GPa. With further compression to 1.6 GPa, the saturation moment at 50 kOe remains essentially constant, but the hysteresis loop contracts and $H_C$ drops to 880 Oe, suggesting that long-range ferromagnetic exchange pathways are compromised by pressure.10

![Diagram](image)

Figure 4. A composite plot of the $T_C$ values obtained for 4a from five samples examined under hydrostatic (PCC), uniaxial, and DAC conditions (left). DFT calculated $J_\pi$ values for 4a as a function of crystal structure geometry at different pressures are shown on the right.

To correlate the magnetic and structural data we have performed a series of DFT broken symmetry calculations at the UB3LYP/6-31G(d,p) level to estimate variations in the magnetic exchange interaction $J_\pi$ between neighboring radicals along the $\pi$-stacks of 4a as a function of pressure, using experimentally obtained coordinates. The results, shown in Figure 4 (right), indicate an initial increase in $J_\pi$ with pressure, that is, a stronger ferromagnetic interaction. This change, which can be related to a loss of overlap between adjacent singly occupied molecular orbitals occasioned by slippage of the $\pi$-stacks (a decrease in the value of $d_{\pi}$),6,11 is consistent with the observed increase in $T_C$ with pressure (Figure 4, left). However, with continued compression, the slippage of the $\pi$-stacks moves past the position of minimum (orthogonal) overlap, and $J_\pi$ begins to decrease, as does $T_C$. While the maxima in the $J_\pi$ and $T_C$ plots as a function of pressure do not coincide, the qualitative correspondence between the two profiles is appealing and suggests that physical pressure, like chemical pressure, can be used to alter the degree of $\pi$-stack slippage in radicals of this type. As a result, their magnetic (and perhaps conductive) properties can be fine-tuned.

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Supporting Information Available: Diffraction plots, table of crystal data and crystallographic (CIF) files for 4a; summary of magnetic measurements and DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

References


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