Pressure-induced Spin-pairing in Gillespite, $BaFe^{II}Si_4O_{10}$

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THE rapid increase in crystal-field splitting with decreasing metal–ligand distance[1] implies that high pressures will tend to cause spin-pairing in compounds of high-spin transition-metal ions, and Fyfe[2] has argued (from the decrease in ionic radius on spin-pairing) that polymorphic transitions of possible geophysical importance should occur in oxide and silicate minerals of iron(II) at pressures corresponding to depths within the Earth's mantle.

Most silicate and oxide minerals contain iron(II) in octahedral or tetrahedral co-ordination, with crystal-field splittings much less than those required to cause spin-pairing, but in gillespite,[3,4] high-spin Fe^{II} in square-planar co-ordination shows much larger splittings, resulting from the short ($4 \times 1{\cdot}97$ Å) metal–oxygen distances. Spin-pairing should thus occur in gillespite at relatively low pressures, leading either to an intermediate-spin state, which has a possible stability interval in square-planar systems,[5,6] or to a fully spin-paired state.

A clearly visible, instantaneous and reversible colour change (red to colourless) occurred when a (001) cleavage flake of gillespite was subjected to 26 kbar mean applied pressure in a Van Valkenberg diamond-anvil apparatus.[7] The absorption spectrum (3500—10,000 Å) of the low-pressure form shows a single absorption band ($\epsilon_{1\text{ atm.}} = 2{\cdot}3$), which broadens, intensifies, and shifts to the blue with increasing pressure, disappearing at the transition point to give the featureless spectrum of the high-pressure form. The gillespite was recovered unaltered after the run. Laue photographs taken under pressure (beam $\parallel c$: of poor quality) and examination between crossed polars (subject to interference from piezobirefringence of the diamond anvils) gave no indication of any departure from tetragonal symmetry during the transition. No further change occurred when the pressure was increased slowly to 80 kbar.

At low pressure, the order of increasing 3*d*-orbital energies[4] is $d_{z^2} < d_{xz,yz} < d_{xy} < d_{x^2-y^2}$, with separations $d_{z^2} - d_{xz,yz}$ (A) of $\sim$1000 cm.$^{-1}$, $d_{z^2} - d_{xy}$ (B) of 7500 cm.$^{-1}$, and $d_{z^2} - d_{x^2-y^2}$ (C) of 19000 cm.$^{-1}$. Assuming local D_{4h} symmetry,[4] and no change in the order of *d*-orbital energies with increasing pressure, three spin-states are possible: ${}^5A_{1g}$ (1 atm.), ${}^3E_g$ and ${}^1A_{1g}$. Adopting the simplest possible model[6] in which the exchange energy (K) is constant, and the number of parallel electron spins is 10, 7, and 6 for ${}^5A_{1g}$, ${}^3Eg$ and ${}^1A_{1g}$ configurations respectively, the stable spin-states are given by:

$$ {}^5A_{1g} \begin{array}{l} \nearrow {}^3E_g \text{ if } 3K > C - A + J/2 \text{ and } K > B - (A + J/2) \\ \searrow {}^1A_{1g} \text{ if } 4K > C + B - 2A \text{ and } K < B - (A + J/2) \end{array} $$

where J is the separation of the $d_{xz,yz}$ orbitals in the ^3E_g state. Provided the ratio $(C-A)/(B-A)$ remains approximately constant with increasing pressure, this calculation predicts at most a narrow stability interval for the ^3E_g state in gillespite if J is small and K is taken[8] as 8810 cm.$^{-1}$.

The rapidity and reversibility of the reaction, and its marked effect on the absorption spectrum indicate an electronic rather than a reconstructive or displacive mechanism for the transition, and the elimination of the $^5A_{1g}-5B_{1g}$ absorption at 5000 Å, the absence of observable peaks in the absorption spectrum of the high-pressure form, the failure to observe deviations from tetragonal symmetry, and the preceding calculation point to $^1A_{1g}$ rather than $^5A_{1g}$ or ^3E_g as the stable state at high pressures. All available data are thus compatible with spin-pairing $^5A_{1g} \rightarrow {}^1A_{1g}$ as the cause of the transition.

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