Tuning the Verwey transition as an orbital ordering

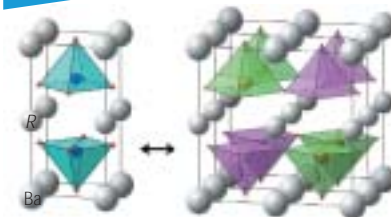P. Karen (University of Oslo)

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Figure 1: Valence mixing and charge ordering in $RBaFe_2O_5$. Divalent iron in green, trivalent in violet.

Accurate neutron powder diffraction results combining high resolution (D2B) and high-flux (D20) data unravel the mystery behind the Verwey transition. By varying the rare-earth element R in $RBaFe_2O_5$, it was possible to decouple the Verwey transition from the effect of the cooperative magnetic interactions in this perovskite-type structure. Given that the (thermally induced) valence-mixed $Fe^{2.5+}$ state, the obtained structural results suggest ordering of the doubly occupied Fe^{2+} dxz orbitals as the sole driving force for charge localization at the Verwey transition.

Magnetite, Fe_3O_4, has been utilized by various organisms for some 2×10^9 years [1], and it continues to attract attention to date. Ferromagnetic, stable and compositionally simple, it exhibits a sharp drop in electrical conductivity when cooled below the Verwey transition [2] temperature T_V. Although interpreted already by Verwey as ordering of di- and trivalent iron in the octahedral sublattice of the spinel-type structure of magnetite, structural details of this change have remained elusive for more than 50 years [3]. Electronic, magnetic and structural phase transitions in similar oxides have long been a source of extreme interest to chemists and physicists alike, in particular when competing ground states can be accessed through choices of chemical substitution as well as changes in temperature and/or pressure. Such tunable compounds provide a direct experimental window on the interrelationships between crystal structure, bonding, electronic band structure and magnetism. Recently a series of $RBaFe_2O_5$ double-cell perovskites (R = rare-earth element) has been synthe-

sized [4,5,6,7,8] in which the structural order of the large divalent Ba and small trivalent R creates one oxygen vacancy in the R layer, while the imbalance of these two ionic charges bestows iron with the semi-integer (mixed) valence of +2.5 valence units; the same as that in the octahedral sublattice of magnetite. Consequently, classical symptoms of the Verwey transition are detected upon cooling: an electrical conductivity drop, a latent-heat effect and a volume increase.

At high temperature, $RBaFe_2O_5$ is a Day–Robin class-III mixed-valence [9] paramagnetic conductor with a simple tetragonal structure. Below the Néel temperature of 430 K, an increasing orthorhombic distortion is associated with alignment of opposing magnetic moments in the direction of the shorter parameter b of the

orthorhombic lattice. Upon further cooling, some 30 degrees above the classical Verwey transition, a small caloric effect is observed where Mössbauer spectroscopy reveals a partial disproportionation into two states $Fe^{2.5-\epsilon}$ and $Fe^{2.5+\epsilon}$, corresponding to the Day–Robin class-II mixed valence. Upon further cooling, a full separation into integer Fe^{2+} and Fe^{3+} charges of the class-I mixed valence occurs at the Verwey transition proper (figure 1). The transition is not unlike water freezing into ice, only in this case an ice of localized ionic charges.

Recent advances in neutron powder thermodiffractometry's instrumentation enabled the collection of high quality data on time scales varying from a few minutes to microseconds - a temperature grid comparable to thermal-
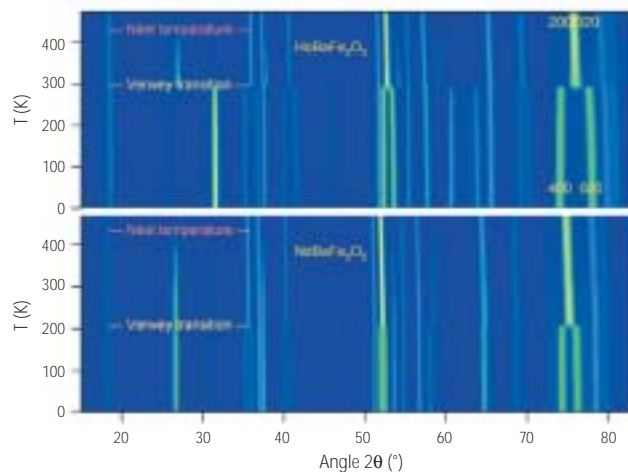

Figure 2: Bragg-peak altitude plot from neutron thermodiffractometry of $HoBaFe_2O_5$ and $NdBaFe_2O_5$.
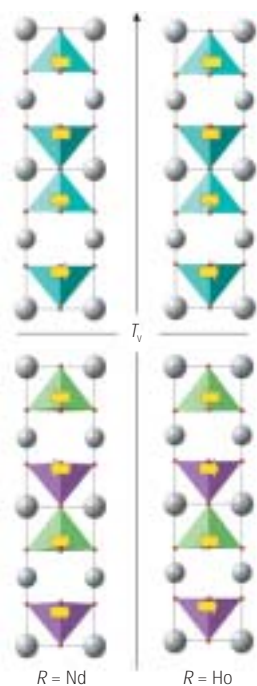
Figure 3: Magnetic coupling along c in $RBaFe_2O_5$ above and below the Verwey transition temperature T_v.

analysis. Such a dense cadence of structural snapshots is highly complementary to the structural still lifes obtained using high-resolution neutron diffraction.

In the thermodiffractometry experiment, we have observed a striking difference between the cooperative magnetic interactions in $HoBaFe_2O_5$ and $NdBaFe_2O_5$ (figure 2), despite isotypism at high temperature: In $HoBaFe_2O_5$ the Verwey transition is accompanied by reversal of the direct Fe–Fe magnetic coupling across the rare earth layer. In $NdBaFe_2O_5$, however, the larger Nd^{3+} ion increases the Fe–Fe distance, weakens the Fe–Fe magnetic interaction and decouples the magnetic ordering from the Verwey transition. The Fe–Fe interaction in $NdBaFe_2O_5$ remains the same (ferromagnetic) all the way to low temperatures. We see no discontinuity in Bragg reflections typical of the cooper-

ative magnetic order at T_v. Remarkably, the magnitudes of the ordered magnetic moments, determined from high-resolution diffraction data (D2B), do not change across the Verwey transition even when the type of order changes as in the case of the Ho variant. This suggests that the Verwey transition is not driven by the magnetic interactions. There are some subtler and equally important changes induced by varying the R^{3+} ionic size along the lanthanide series of elements. The Verwey transition temperature decreases when R grows larger, and, for R = Nd, the symmetry of the charge-ordered class-I MV phase is reduced from $Pmma$ to $P2_1ma$. With some additional data for other R variants we can draw the conclusion that the charge-ordered state is destabilized upon increasing the R size. This allows structural tuning of the Verwey transition via changing the R ion—an ion that may otherwise appear uninvolved in the ordering of the ionic charges of iron. Having decoupled the magnetic order from the Verwey transition, we could consider the electrostatic (Coulombic) order as the driving force for ordering of the two different, Fe^{2+} and Fe^{3+}, ionic charges. However, the structural ordering pattern (figure 1), we

Figure 4: Graphical representation of the typical shape of the d_{xz} orbital.

determined from the high-resolution diffraction data, violated the simple electrostatic condition [10] for point-charge approximation. Such condition calls for charges alternating in all three directions and we did not see this. In itself this suggests participation of orbital ordering, because it means that the stable (ground) state can only be understood when the spatial charge distribution of the iron ions is considered (as opposed to considering point-charges only). The last step was to correlate the observed orthorhombic distortion of the perovskite-type lattice with the typical shape of the d_{xz} Fe^{2+} orbital (figure 4).

Within such a distortion, this orbital is the one being ordered, energy minimized and doubly occupied in the Fe^{2+} ion that has 6 valence electrons. Given the easy deformability of Ba (manifested in its unsymmetrical structural environment) it is the "hard" R atom (with symmetrical structural environment) that controls the distortion hence the stability of the orbital ordering. This may be similar to the role that seemingly little involved inorganic anions play in molecular iron entities such as valence-mixed biferrocenium cations that also undergo charge localization and ordering at low temperatures [11]. Finally, to come back to the high interest in magnetite, it is worth pointing out that it is the nano-crystals of Fe3O4 that are in fact present in the ancient magnetosomes of the magnetotactic bacteria; as mentioned earlier.
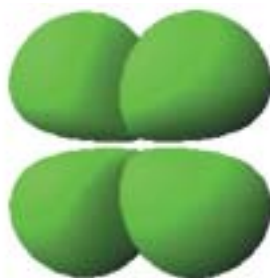
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