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Charge Order at the Frontier between the Molecular and Solid States in Ba$_3$NaRu$_2$O$_9$

Simon A. J. Kimber,1,2,* Mark S. Senn,3 Simone Fratini,4 Hua Wu,5 Adrian H. Hill,1 Pascal Manuel,6 J. Paul Attfield,3 Dmitri N. Argyriou,2,7 and Paul F. Henry2,7

1European Synchrotron Radiation Facility (ESRF), 6 rue Jules Horowitz, BP 220, 38043 Grenoble Cedex 9, France
2Helmholtz-Zentrum Berlin für Materialien und Energie (HZB), Hahn-Meitner Platz 1, 14109, Berlin, Germany
3School of Chemistry, Joseph Black Building, King’s Buildings, West Mains Road, Edinburgh, EH9 3JH
4Institut Néel-CNRS and Université Joseph Fourier, Boîte Postale 166, F-38042 Grenoble Cedex 9, France
5Laboratory for Computational Physical Sciences, Surface Physics Laboratory and Department of Physics, Fudan University, Shanghai 200433, China
6ISIS Science and Technology Facilities Council, Rutherford Appleton Laboratory, Harwell Science and Innovations Campus, Didcot, OX11 0QX, United Kingdom
7European Spallation Source ESS AB, Box 176, 22100, Lund, Sweden

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We show that the valence electrons of Ba$_3$NaRu$_2$O$_9$, which has a quasimolecular structure, completely crystallize below 210 K. Using an extended Hubbard model, we show that the charge ordering instability results from long-range Coulomb interactions. However, orbital ordering, metal-metal bonding, and formation of a partial spin gap enforce the magnitude of the charge separation. The striped charge order and frustrated hcp lattice of Ru$_2$O$_9$ dimers lead to competition with a quasidegenerate charge-melted phase under photoexcitation at low temperature. Our results establish a broad class of simple metal oxides as models for emergent phenomena at the border between the molecular and solid states.

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Strong many body correlations between electrons in solids result in extremely diverse properties including insulating antiferromagnetism, charge order, and superconductivity. This is especially true in organic based materials like fullerides or the $\kappa$-(BEDT-TTF)$_2$X or (Pd[dmitt]$_2$)$_2$ salts, due to the narrow electronic bandwidth resulting from the overlap of molecular orbitals [1–3]. However, the contacts between molecules are weak, and organic bonding allows low-energy rotational and conformational degrees of freedom. Poorly crystalline or complex low symmetry structures [4–6] are thus common. This problem can be compounded by extreme air sensitivity, the inaccessibility of hydrogen to x-ray diffraction, and the incoherent background which it generates in neutron scattering experiments. Consequently, nearly all theoretical models of these materials rely on approximations that treat each molecular unit as effective sites on high symmetry lattices [3,7]. These models predict that Coulomb interactions drive electron localization, and that geometrical frustration is responsible for the observed competition between ground states [8]. However, the material-specific interplay between electronic correlations, local-degrees of freedom, and the lattice remains a significant challenge [9]. In this Letter, we show that simple metal oxides can provide new insight into the electronic properties which emerge between the molecular and solid states. Our model compound is Ba$_3$NaRu$_2$O$_9$, which has the 6$H$ hexagonal perovskite structure [Figs. 1(a) and 1(b)] containing isolated Ru$_2^{5+}$O$_9$ dimers of face-sharing octahedra which form triangular layers [10]. Previous reports have indicated poorly-metallic conduction around room temperature and a metal-insulator transition [11] associated with a structural distortion below 210 K. We synthesized single-crystal and powder samples of Ba$_3$NaRu$_2$O$_9$ which were characterized by magnetization and high resolution x-ray synchrotron measurements, performed using ID31 at the ESRF, detected a previously unreported monoclinic distortion [Fig. 2(a)] and further weak reflections that showed that the true space group is P2$_1$/c. The structural model was refined using x-ray data from a twinned single-crystal, and full details are given in the Supplemental Material [12]. The key feature of our low temperature P2$_1$/c structure is a splitting of the Ru$_2^{5+}$O$_9$ dimers into two symmetry inequivalent units, which suggests charge ordering (CO) [Fig. 1(b)]. Motivated by experiments on true molecular materials, we investigated the driving force for this transition using the following extended Hubbard model, with the dimers as effective sites.

$$\hat{H} = -t \sum_{\langle ij \rangle} (\hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + \text{H.c.}) + U_{\text{eff}} \sum_i n_{i\uparrow} n_{i\downarrow} + \sum_{\langle ij \rangle} V_{ij} n_i n_j$$

Here $t$ is the interdimer hopping integral, $U_{\text{eff}}$ is the on-site (dimer) Coulomb repulsion, and $V$ is the interdimer...
Coulomb repulsion. In contrast to Mott insulating organic materials such as the \( /C20\text{-BEDT-TTF}\text{\textsuperscript{2}X}\) family, where \( V\) is commonly neglected \[9\], the experimentally determined stripe order could only be reproduced when \( V>U\text{\textsuperscript{eff}}\). This implies that the formation of molecular orbitals results in a reduced \( U\text{\textsuperscript{eff}}\) \[7\], and that the intersite electron-electron interactions play a fundamental role in the ordering mechanism. However, without breaking the threefold lattice symmetry, a striped ground state is still highly degenerate. We discovered that the full three-dimensional \( P\text{\textsubscript{2}}\text{\textsubscript{1}}\text{\textsuperscript{c}}\) structure could be rationalized by considering the tetrahedral linkages between the hcp network of dimers. Each tetrahedron of dimers contains two \( \text{Ru}^{5+}\text{O}_9\) and two \( \text{Ru}^{6+}\text{O}_9\) units (S1). Hence, so-called 'ice rules', which minimize the electrostatic energy of the molecular building blocks \[13,14\], act as directors for the fluctuating stripe order stabilized by the reduced \( U\text{\textsuperscript{eff}}\). On the macroscopic scale, the twinning in single-crystal samples has exactly the degeneracy predicted by this picture, as six orientational stripe domains of equal population are found. Our observations thus establish the \( \text{Ru}_2\text{O}_9\) dimers as the physically meaningful units in \( \text{Ba}_3\text{NaRu}_2\text{O}_9\). This analysis makes no prediction of the size of the charge separation between the sites. However, our precise refinement of \( P\text{\textsubscript{2}}\text{\textsubscript{1}}\text{\textsuperscript{c}}\) structure allowed us to examine structural parameters on the single-ion and molecular levels, and compare them to other members of the \( \text{Ba}_3\text{ARu}_2\text{O}_9\) family of known oxidation states. The valence of each individual Ru cation is reflected \[10\] by a linearly varying (Ru-O) distance [Fig. 2(b)], and the refined values for the \( P\text{\textsubscript{2}}\text{\textsubscript{1}}\text{\textsuperscript{c}}\) structure are in agreement with 'integer' separation into \( 5^+\) and \( 6^+\) oxidation states. Furthermore, detailed examination of the coordination environment [Fig. 2(d)] of the two sites provides evidence for ordering of orbital degrees of freedom. In order to separate out the effect of the intrinsic trigonal site distortion from electronic effects, we calculated the average length of perpendicular bond pairs. For the \( \text{Ru}^{5+}\) sites, which are orbitally nondegenerate with a \( t_2^3g\) configuration, these are extremely regular, and lie in the range 1.944(5)–1.9815 (8) Å. In contrast, the \( t_2^3g\) \( \text{Ru}^{6+}\) sites have four long bonds.
with average lengths in the range 1.943(5)–1.991(5) Å and two short bonds of average length 1.866(5) Å. An orbital ordering distortion therefore lifts the degeneracy of the doubly occupied $t_{2g}$ orbitals. In addition to these single-ion indicators of integer charge order, the interdimer Ru-Ru distances also vary linearly with the oxidation state [Fig. 2(c)]. This implies a well defined ‘bond order’ determined by the occupation of molecular orbital states and allows a precise estimate of the charge separation into 4.86(16)+ and 6.11(16)+ states. The Ru-Ru bond in the Ru$^{5+}$O$_9$ dimers is as short as that found in Ru metal (2.62 Å). Metallic bonding would make these sites non-magnetic, which is in accordance with the magnetic susceptibility below 210 K, which could be modeled assuming only $S = 1$ correlations from the Ru$^{5+}$O$_9$ dimers [Fig. 1(c)]. Finally, we used the precise P2/c coordinates to perform LDA + U calculations with $U = 3$ eV, which confirm that complete disproportionation into Ru$^{5+}$O$_9$ and Ru$^{6+}$O$_9$ pairs is found [Fig. 3(a)]. This is stabilized by the $S = 0$ dimer states, as antiferromagnetic coupling gives by far the lowest energy ground state. A small gap at the Fermi energy is found in accordance with Ref. [11]. These calculations confirm that the simplest molecular constraint, the desire to form closed shell configurations, stabilizes the complete charge segregation found below 210 K. We emphasize that our experimental and theoretical quantification of the degree of charge localization in Ba$_3$NaRu$_2$O$_9$ would have been effectively impossible for organic materials.

The integer charge separation motivates comparison with frustrated Ising spin models on the hcp lattice, which have the same ground state configuration [15]. Geometrical frustration of electronic degrees of freedom in molecular solids is additionally predicted to result in competition between charge-ordered and disordered states [14,16]. Although the P2/c phase of Ba$_3$NaRu$_2$O$_9$ has large (∼ 0.1 Å) atomic displacements, we discovered that the charge order is unusually sensitive to external perturbations. A comparison between the lattice parameters extracted from x-ray (ID31 at ESRF) and neutron (WISH at ISIS) diffraction experiments is shown in Fig. 3(b). Below ∼40 K these deviate strongly from each other. This was investigated by cooling a sample to 10 K before continuously measuring diffraction profiles with 31 keV x rays. We found that the P2/c charge-ordered structure transforms continuously to a higher symmetry C2/c structure in which only one Ru site is present. This phase was found to be stable for periods of several hours at 10 K, during and after irradiation, and was not observed by neutron powder diffraction down to 1.6 K, which also showed no evidence for long-range magnetic order. Band structure calculations predict metallic conduction in this phase.

The synchrotron x-ray data collected during the melting process show that local and lattice degrees of freedom are inextricably linked. As shown in Fig. 4(a), the average Ru$^{5+}$/Ru$^{6+}$ charge order, quantified by the difference between the Ru-Ru distances in the two dimers, decreases rapidly with an exponential time constant of 75(8) s. After 120–180 s, this charge order and the corresponding $(h+k) =$ odd superstructure reflections are completely suppressed showing that the average structure has transformed to C2/c symmetry. The very high resolution of the
synchrotron diffraction data makes a transition to an
intermediate charge glass of localized but spatially disordered
charges unlikely [17], as the microscopic lattice strain,
which measures local variations in lattice parameters, also
rapidly vanishes. The lattice distortion which breaks frus-
tration, parametrized by the $b/a$ ratio, is coupled to the
local order, and relaxes on a similar time scale (88(3) s).

A possible explanation for the CO melting is the dimen-
sional reduction into stripes [18] patterned by the ice-rule
constraints. X rays impinging on the sample generate a low
concentration of holes by the photoelectric effect. Based
on our minimal electrostatic model, these may freely de-
localize along the stripe direction, provided that $r \geq V - U_{eff}/4$, melting the charge order. That this charge-melted
phase exists in delicate balance with the charge order, is
shown by measurements on warming, as the $P2/c$ phase is
recovered on warming above 40 K with full recovery of the
lattice micro- and macrostrains. Future work will be
needed to determine the factors which set this temperature
scale. However, we note that $\chi(T)$ also reproducibly shows
a glassy transition [10] at similar temperatures [Fig. 1(c)],
which might indicate an intrinsic instability of the CO,
even in the absence of irradiation. Unlike other charge-
ordered metal oxides, Ba$_3$NaRu$_2$O$_9$ shows both fully
crystallized and liquidlike valence electron states at low
temperatures. However, the classic examples of oxide
close charge order are all found in structure types which have
infinite lattices of corner, edge or face-sharing coordination
polyhedra, like perovskites or spinels. The mechanism for
charge order is somewhat controversial in these materials,
as only fractional charge separation is found [19], with
strong evidence for Fermi surface nesting [20]. In contrast,
our results show that long-range electrostatic interactions
are responsible for charge ordering in Ba$_3$NaRu$_2$O$_9$.
Additionally, the comparatively simple crystal structures
highlight the role played by single-ion and molecular
degrees of freedom. Our results thus lend weight to a recent
theoretical investigation of $\kappa$-ET$_2$Cu$_2$(CN)$_3$, which
showed that intramolecular degrees of freedom must be
important in this related class of materials [21].

In summary, our results show that a combination of
single-ion and molecular degrees of freedom help to sta-
bilize charge order in Ba$_3$NaRu$_2$O$_9$. Our results are remi-
niscent of the true (organic) molecular solids and provide a
model system for studying frustrated strongly correlated
electrons. We note the presence of a vast library of unex-
explored related compounds [22], and predict the future
discovery of strongly fluctuating spin-liquid or supercon-
ducting ground states.

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*Corresponding author: kimber@esrf.fr