LA-UR-13-22555
Approved for public release; distribution is unlimited.

Title: Emergent Properties of the Bose-Einstein-Hubbard Condensate in UO2(+x)

Author(s): Conradson, Steven D.
Durakiewicz, Tomasz

Intended for: Proposal

Issued: 2013-04-10

Research Goals

Condensates, systems composed of bosons that "crystallize" on the basis of the weak interactions between the wave functions of their constituent, ground state particles, are fundamental to the modern physics of emergent phenomena. Their superlative properties are evident in the names, *super*conductivity and *super*fluidity, in which, respectively, electrons and atoms or quasiparticles move without friction or dissipation. We have recently performed an extensive set of experiments on the strongly correlated Mott insulator $UO_{2(+x)}$ (Fig. 1) whose bizarre results are either best or only explained by emergent Bose-Einstein condensate-like behavior. However, instead of being composed of Cooper pairs in a lattice or several thousand highly separated ultracold atoms or quasiparticles of light and electrons in a resonant cavity, the condensates in $UO_{2(+x)}$ involve both electrons and ions undergoing complete, dynamical changes in their bonding, and although beginning at tens of K they also appear to extend to and through ambient temperature. **Clearly this is a most remarkable and totally unexpected behavior never before seen in a Mott insulator nor at high temperatures and that, because of the coupling to charge and spin, will result in unique correlated and emergent properties.** The goal of the proposed work is to explore this phenomenon to both more fully elucidate its origin and characteristics and to evaluate its technological potential that could be revolutionary.

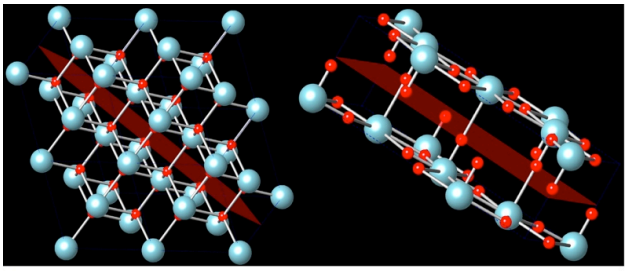


Figure 1. (Left) UO_2, showing (111) plane. (Right), α UO_3, showing (001) plane derived from UO_2 (111) plane after oxidation.

Background & Significance

In fermionic matter the Pauli exclusion principle compels each atom or particle to occupy a different state so that they are all unique. Since bosons are not subject to this requirement a set of them can all be in their ground state and their identical wave functions interact, albeit weakly, to form a correspondingly sparse and totally coherent lattice.[1] Because of the ground state requirement, BECs of atoms[2] require milli or μK temperatures, superfluidity in ^{4}He begins at 2.17 K, and recently almost massless polaritons[3] condense in special cavities at room temperature.[4, 5] A better known example is the condensation of Cooper pair quasiparticles resulting in superconductivity. There is, however, another possible mechanism for enhancing the attractive interactions. The unusual isotope effects[6, 7] in cuprates demonstrate that, whether their superconductivity is a homogeneous property of the spins or a local property of the charge inhomogeneities (most likely a combination of the two), the anharmonicity in the mixed valence material caused by these inhomogeneities and the on site Coulomb repulsion that make cuprates a poor and exotic metal have a crucial role. Can these have the same effect on a BEC? We have found that, in UO_2, the answer is most likely "yes." Neutron and x-ray scattering (Fig. 2) and x-ray absorption measurements on the three fluorite line compounds, UO_2, U_4O_9, and U_3O_7, showed identical results for UO_2 but a 1.7 Å U(VI)-oxo moiety in UO_{2+x} with both x-ray probes but only ≥2.15 Å U(V)-O bonds and narrower peaks with neutrons.[8] A difference between neutron and x-ray structures in cuprates[9-11] and manganites,[12, 13] was attributed to dynamical O polaron tunneling around a Cu[14, 15] that was activated by x-rays to give the dynamic/instantaneous structure factors $S(Q, \omega/t=0)$ that showed the two-site distribution of the polaron with ΔR=0.12 Å. [16-19] This mecha-

nism, however, is impossible in UO_{2+x} where ΔR=0.65 Å, many more atoms over a larger volume are involved, and the electronic structure is completely rearranged between the two states.

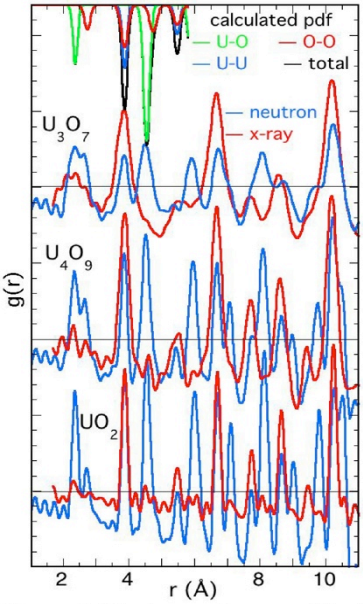


Figure 2. Neutron and x-ray pdfs of UO_2 (bottom), U_4O_9 (center), U_3O_7 (top), and a portion of the calculated neutron pdf of UO_2 (inverted across upper margin). The data are scaled arbitrarily to maximize their amplitudes within this figure.

In addition, the XAFS results of UO_2 at 35, 100, and 200K were identical while those in UO_{2+x} showed changes in the U-O near neighbor contribution despite the absence of any phase transitions or other phenomena that would alter their structures.[8] Finally, spectral features in the O K NEXAFS (Fig. 3) that reflect primarily the U states are wider than those for any other U-O compounds and do not display the standard separation between the U 5*f* and 6*d* states, indicative of broadening of the DOS.[20] Mixing of electronic states and their dressing with the excitation causing the tunneling were also predicted for dynamical polarons.[18]

The issue of the properties of mobile charges has been addressed by optical pump-probe experiments, exciting into the upper Hubbard band and probing inside the gap where the excited states would have relaxed to polaronic or excitonic quasiparticles.[21, 22] These also give unique results (Fig. 4). 3.14 eV excitation to the 5*f* states and lower fluence 4.71 eV to the 6*d* give peaks in the lifetimes at, respectively, 20 and 25 K, with the lifetime from 4.71 eV ten times larger. This peak may be associated with the only known transition below >200°C, to the AFM state at 30.1 K. The 3.14 eV excitation, however, shows a plateau rising to a cusp at 50–60 K in both the fast electronic and slow lattice relaxation. This pattern is indicative of a gap-opening transition, either superconducting or charge density wave, at the gap.[23] Its appearance with one of the excitation energies, highly unusual and demonstrating non-thermal behavior, proves that these features originate in the photoinduced quasiparticles and not within the lattice. The phonon spectra obtained by Fourier transformation of the psec-resolved real time data show, in addition to the 35 GHz collective mode induced by the pump,[24] another phonon at a very low 12–15 GHz hardening and splitting into multiple peaks with increasing temperature. This also indicates that the quasiparticles aggregate and condense into their own coherent phase.[25]

Every experiment we have performed on $UO_{2(+x)}$ has given results that cannot be explained with known physics. They are, however, easily explained if, invoking the known chemistry of U-oxides, the charge inhomogeneities that are polaronic quasiparticles are forming a BEC, or, in this Mott insulator, a Bose-Einstein/Hubbard Condensate where the quasiparticles repel each other when occupying the same site.[26-28] The oxidation of UO_2 to layered U_3O_8 and UO_3 occurs via a rearrangement of the O ions around the UO_2 (111) planes[29, 30] (Fig. 1) whose separation controls the stability of bridging and terminal U-oxo moieties along the [111] vectors through U sites. This same effect can occur dynamically and collectively. An acoustic phonon propagating in the UO_2 [111] direction will cause a coherent conversion of the U(V) to U(VI)-oxo sites within the extent of the displacement. The state will persist as long as the distance between the planes is within the range that stabilizes it, concomitantly reverting to the former when the collective motion re-crosses the boundary of this range. This excitation is facilitated by the uniquely flat U-O potential that causes U(VI) to exist continuously in all of the geometries from highly oblate trans-dioxo to fully octahedral,[31-34] but will also be stabilized by the energetics of BE/HCs that favor holon-doublon states over fermionic ones. [35] The energy of the oblate U(VI)

states that are highly mismatched with the cubic sites of fluorite is also reduced by the clustering of O and perhaps charge inhomogeneities in UO_{2+x}. The flatness of the U-O potential over the entire bond range may also cause the U(IV) ground and U(VI) excited state to intersect in a conical section, which is also known have highly unusual dynamical effects on the structure[36] and may be characteristic of the BE/HC. The observed tunneling over 0.65 Å is too large to occur at a single site, but it is orders of magnitude smaller than found for BECs where much larger gaps have been used to create Josephson junctions.[37-39] In addition, multiple phase transitions as observed in the optical experiment were predicted for BE/HCs even before the first one was created, with a stable Mott insulator below the superfluid state resulting from the opening of a gap and, even a third Bose glass phase in the presence of disorder.[26]

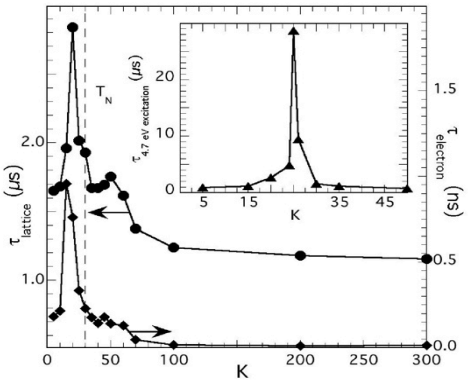
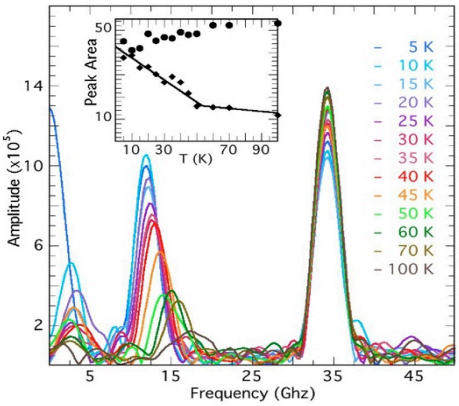


Figure 4. Ultrafast pump-probe results. (Upper) Electronic (lower - right scale) and lattice (upper, left scale) lifetimes with temperature, obtained with 1.6 eV probe. Main panel is with 3.1 eV pump into the U 5*f* states of the upper Hubbard band, the inset is with 4.6 eV pump into the U 6*d* states. (Lower) Phonon spectra from same experiments. The inset plots the areas of the 35 GHz collective mode and (with the line) and the 12–15 GHz peak that originates in a condensate of the photoinduced quasiparticles.



Given the consistency of this model with BE/HC physics and the lack of alternative mechanisms, we believe that our proposed condensate is stabilized by the anharmonicity following from dynamical charge transfer so that it occurs through ambient temperature. Its study will give new insights into quantum phenomena by enabling examination of condensates formed of atoms at ambient temperature as well as from this novel mechanism. In addition, BECs have possible applications in motion sensing and quantum computing. Furthermore, $UO_{2(+x)}$ has unique attributes that make it even more compelling. Its condensate is directly coupled to charge and occurs concomitant with magnetic ordering. In contrast to normal BECs, in $UO_{2(+x)}$ the coherence and subsequent condensation result from a collective electronic excitation coupled to a phonon that involves charge transfer. This indicates a much greater capability for modifying and controlling the BE/HC by alterations to the structure, exemplified by its effects on the electronic structure.[20] The superfluidity involves charge transport, so that up to whatever temperature it can be rendered continuous through the material – and based on the tunneling at least droplets appear to exist through 300 K – UO_2 with mobile charges could be a superconductor. Even if it is not, however, there are many other properties and applications that follow from a charge-based condensate coupled to magnetism. The significance apart from the relevance to BE/HCs and the coupling to emergent properties follows from the question about the emergent phenomena that will originate in coherent charge and spin degrees of freedom.

R&D Approach

The objective of this proposal is to confirm and further elucidate the BE/HC-like properties of $UO_{2(+x)}$ with charge inhomogeneities and to develop additional materials that exhibit it, including ones without defects that sustain and promote transport. Since this BE/HC-like behavior in

$UO_{2(+x)}$ is a totally novel and unanticipated finding and the only pertinent results are ours, our *preliminary studies* were already presented in the previous section.

Methods and Proposed Experiments

Direct measurements of superfluidity and the excitation. The best confirmation of BEC-like properties would be a direct measurement. X-ray Photon Correlation Spectroscopy (XPCS) gives information on the rates and directions of atomic motions. Although it is not clear what its response would be to tunneling in a BEHC, the dynamics will nevertheless be expressed in the disorder of the sites that, on a time basis, are only fractionally filled. It should therefore be possible to extract the highly correlated component of these motions in the proposed condensate. XPCS requires a coherent source that must be the LCLS because of the small scattering factor of O relative to U. Another less definitive probe is ^{17}O NMR, expected to give an average signal for the different sites instead of resolving them. Inelastic neutron pair distribution function analysis could measure not only the atom positions in the excited state but also the energy required to create it. Finally, optical pump-x-ray probe diffraction of UO_2 would give direct structural information on the photoinduced quasiparticle condensate including its domain size.

Analysis of UO_2. One problem in this work is the absence of reliable data on the parent compound UO_2. The structure analysis that we are using to interpret our optical results was published in 1964–1966[40-42] and the 1972 description of α UO_3 was only derived from U_3O_8[32]. From modern experimental techniques we have found not only the anomalies resulting from the BE/HC but also the unique mechanism to which it is coupled. The origin of this behavior must reside in UO_2 itself, so we must repeat some of the original work. Synchrotron x-ray measurements of the structure from below the AFM transition through ambient temperature will probe additional transitions and instabilities. Elastic softening anomalies were reported,[43, 44] but more recent inelastic neutron scattering studies have focused on low energy magnetic excitations leaving gaps in the 50–150 meV energy range.[45, 46] From phonon dispersions at multiple temperatures we will identify soft modes associated with the U(IV) cubic- U(VI) layered excitation.

Creation of static, unpinned charges in UO_2. The most urgent question is whether UO_2 can be a superconductor and if so, does its T_c follow the BE/HC to and through room temperature. This probably cannot be answered with optical excitation because of the short lifetime and spatial extent of the quasiparticle phase and because of the difficulty of controlling the nonthermal relaxation. An alternative is ionic liquid gating, in which charge is injected into the surface of a material by direct application of a potential on the surface.[47] This technique may produce static charges whose density is partly controllable through the applied voltage. We will attempt to obtain the requisitely smooth (<5–10 Å) surface via oriented films grown by physical vapor deposition. The other problem, inducing redox chemistry with the applied potential, will be obviated if the voltage required for charge injection is comparable to the low excitation energy we have found for the system. Magnetic properties will be evaluated in addition to electrical ones.

Analysis of $UO_{2(+x)}$. An obvious yet crucial set of experiments is to watch the development of the pinned BE/HC as UO_2 is progressively oxidized. Isolated O atoms at concentrations below the clustering threshold should not trigger any of the BE/HC-like behaviors so that the dynamical signatures in, e.g., NMR should not be observed. It is also important to determine the BE/HC phase diagram even if at only a few values of x, which can be performed using NMR, XAFS, x-ray pdf, and possibly inelastic neutron diffraction or pdf measurements that show the dynamics. It is also possible that with relatively fine temperature intervals spectral/structural signatures can be found in these data that could be used to track additional condensate phases. From the other

direction, the signatures for the creation of the photoinduced quasiparticle condensate should vanish with increasing x because the polarons should be pinned by the adventitious O. Confirmation of this scenario can then be accomplished by performing the reflectivity experiments on UO_{2+x} samples. Single crystal samples can be prepared via the known oxidation of UO_2 crystals.

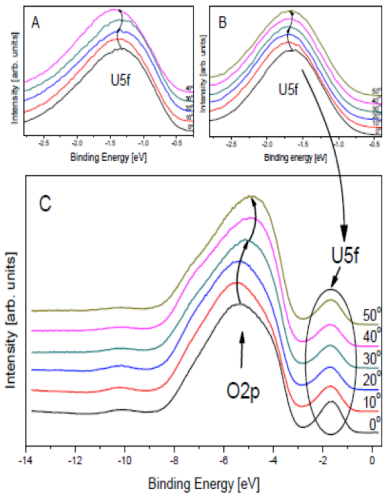


Figure. 5. Angle-resolved valence band photoemission obtained from a synchrotron light source (34 eV photons). a) the lattice-commensurate dispersion of the first characteristic 5f electron feature in the valence band, measured in the single crystal UO_2 cleaved in vacuum. A band dispersion on the order of 80 meV is indicated by arrows; b) the same feature as in (a), but measured in the epitaxial UO_2 film grown on an $LaAlO_3$ subtrate. The band dispersions and binding energies of the epitaxial UO_2 film are the same as those found in a single crystal case; and c) the full valence band spectra of epitaxial UO_2 film, including dispersive peaks within the O2p band located around binding energy of –5 eV. The angle of 0° stands for normal emission.

Photoemission and optical measurements. Probing the dynamics of the transient quasiparticle states in a Mott insulator can be achieved by using a combination of ultrafast reflectivity, angle-resolved photoemission (ARPES), time-resolved photoemission and time-resolved Terahertz spectroscopy. Our initial experimental results from ARPES implying ultra-weak f-electron hybridization with valence band electrons that is required for long range coherence and reflectivity measurements indicative of bipolaron pairing,[21] suggest the importance of polaron dynamics in optically pumped UO_2. Time-resolved photoemission and THz transmission spectroscopy were therefore focused on the polaronic and bi-polaronic response. The photoemission at ambient temperature found that the Mott structure persisted even at relatively high pump fluencies and a quadratic dependence on fluence of a fast response that indicates higher-order interactions and longer-range communication between the bipolaronic pairs in UO_2 (Fig. 5). Preliminary THz measurements at ambient temperature show a very long lived oscillatory response that is a predicted signature of a coherent bipolaronic condensate. Continuation of these experiments will map the coherent dynamical bipolaronic excitations in UO_2. The concentrated effort will provide information about the specific phonon modes associated with the generation of polarons and creation of conditions for the local condensation of pairs. This is the only way to directly link the low energy dynamics in UO_2 with high energy measurements on systems with different stoichiometry, which indicate instability towards increasing anisotropy. This anisotropy, present already in UO_2, together with very low carrier densities allows the low-scattering conditions necessary for local of bipolaronic pairs already at room temperature.

Extension to other elements. The possible BE/HC in UO_2 is understandable as a confluence of several factors, with the most important being the ease of the collective transformation from a cubic to a layered structure upon oxidation of the U. The neighboring light actinides, Np and Pu, exhibit this same property. We already have strong evidence that Pu does behave analogously in that PuO_{2+x} has been shown by XAFS to also possess Pu-oxo bonds[48, 49] despite Pu-oxides terminating at $PuO_{2.26}$ with no layered compounds. In addition, the Pu-oxo distances are 0.10–0.20 Å longer and in the reaction with H_2O oxidation competes with retention of H^+ as OH^- groups. These differences from U originate in the decrease in the energy of the 5*f* states that are 2.5 eV above the O 2*p* for U but overlap with them for Pu, with. Np between the two.[50] Np-oxides terminate at layered Np_2O_5. NpO_{2+x} has not been reported, but it will undoubtedly be found. These

compounds will be obtained via collaborators. For optical measurements it may be possible to borrow the PuO_2 crystal at the Radium Institute in St. Petersburg.

Synthesis of materials with unpinned BE/HCs. Best for characterization and required for many applications would be materials where, analogous to cuprates, iron pnictides, etc., presumably mobile charges are injected into stoichiometric UO_2 domains via the composition of the material. The problem is that, although the proposed mechanism involves layered U(VI)-oxo structures, cubic UO_2 that is a three-dimen-sional structure is also required and it is not amenable to forming layered compounds with separate functional domains. The alternative is to fabricate such materials by physical vapor deposition or molecular beam methods to form multilayers of UO_2 with another material. One candidate is $LaAlO_3$ that has already been used as a substrate for oriented UO_2 films. $La(Sr)AlO_3$ that would inject holes into UO_2 in a multilayer could conceivably be used when deposited under controlled O_2 pressure. Although this is the favored approach, ideas for stable layered compounds, perhaps by utilizing as a second material one with a strong two-dimensional component to its structure, will also be pursued. We note that the Cu-Cu distance in cuprates is almost identical to the U-U distance in UO_2, suggesting interesting possibilities.

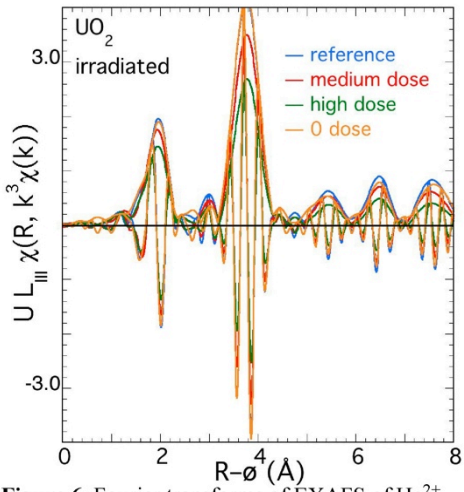


Figure 6. Fourier transforms of EXAFS of He^{2+} irradiated UO_2 samples. The reduction in amplitude with increasing dose without the the appearance of any new features indicate that the radiation causes non-specific disorder. The exception, the region around R=1.5 Å that increases, is shown by curve-fits to be an O with U-O around 1.7 Å, a U(VI)-oxo moiety. This result differs from oxidation in which the appearance of this O occurs with many new O shells above and below the original one.

Fabricating circuits and devices. Another remarkable result is our observation by XAFS of U(VI)-oxo moieties in UO_2 crystals that have been irradiated with H^+ and He^{2+} ions since modifications should be limited to the formation of interstitials. The structures determined by XAFS are much cleaner than those resulting from oxidation with O_2 or H_2O (Fig. 6), the only non-UO_2 O neighbor shell identified is the oxo one in contrast to the a plethora of U-O distances in UO_{2+x}. This demonstrates the propensity of UO_2 to form the U(VI)-oxo group coupled to and most likely stabilized by the BE/HC, even in situations where the average charge is only IV so that the creation of U(VI) ions must be balanced by U(III) sites elsewhere. More importantly, this result identifies a mechanism for patterning the BE/HC in UO_2. Devices based on the BE/HC can be fabricated by writing them into UO_2 with an ion beam.

Technical Challenges and Alternatives

Most of the proposed work is low risk. UO_2 is common, easily handled despite its mild radioactivity, and is already available as single crystals up to relatively large sizes as the result of a boule that was made at LANL 40 years ago. All of the experiments performed have either been reproduced, been verified by complementary methods, or been consistent in terms of opposite behavior for UO_2 and UO_{2+x} and similar behavior for U_4O_9 and U_3O_7. We also note that UO_{2+x} and PuO_{2+x} both display An-oxo bonds. The challenge is the interpretation and our ability to devise definitive experiments for both characterizing the phenomenon under study and its mechanism and in elucidating its properties, particularly ones that will have applications. Another challenge will be to develop materials and methods that maintain the BE/HC. This is, however, likely to become easier as more data are obtained and the condensate is better understood.

Expected Results

At the end of this project we expect to: 1) have a much deeper understanding of the behavior, mechanism, properties, and potential applications of the BE/HC-like behavior in $UO_{2(+x)}$ and possibly related materials; 2) have the capability to maintain the condensate either indefinitely or for sufficiently long periods of time for its direct characterization; and 3) have made complete or partial progress in developing stable or fabricated materials that exhibit the BE/HC as one of their properties. These results will provide a basis for additional studies and theory development and technologies based on this phenomenon.

1. F. Dalfovo, S. Giorgini, L. P. Pitaevskii and S. Stringari, Reviews of Modern Physics **71** (3), 463-512 (1999).

2. C. A. Regal, M. Greiner and D. S. Jin, Phys. Rev. Lett. **92** (4) (2004).

3. J. Kasprzak, M. Richard, S. Kundermann, A. Baas, P. Jeambrun, J. M. J. Keeling, F. M. Marchetti, M. H. Szymanska, R. Andre, J. L. Staehli, V. Savona, P. B. Littlewood, B. Deveaud and L. S. Dang, Nature **443** (7110), 409-414 (2006).

4. P. Littlewood, Science **316** (5827), 989-990 (2007).

5. R. Balili, V. Hartwell, D. Snoke, L. Pfeiffer and K. West, Science **316** (5827), 1007-1010 (2007).

6. H. Keller, A. Bussmann-Holder and K. A. Mueller, Materials Today **11** (9), 38-46 (2008).

7. A. R. Bishop, A. Bussmann-Holder, O. V. Dolgov, A. Furrer, H. Kamimura, H. Keller, R. Khasanov, R. K. Kremer, D. Manske, K. A. Mueller and A. Simon, Journal of Superconductivity and Novel Magnetism **20** (5), 393-396 (2007).

8. S. D. Conradson, D. A. Andersson, K. S. Boland, D. L. Clark, D. R. Conradson, A. L. Costello, F. J. Espinosa-Faller, N. J. Hess, G. H. Lander, J. S. Lezama-Pacheco, A. Llobet, J. Mustre de Leon, T. E. Proffen, D. E. Schwarz and S. A. Trugman, Phys. Rev. Lett. **submitted** (2013).

9. S. D. Conradson, I. D. Raistrick and A. R. Bishop, Science **248** (4961), 1394-1398 (1990).

10. T. Egami, B. H. Toby, S. J. L. Billinge, H. D. Rosenfeld, J. D. Jorgensen, D. G. Hinks, B. Dabrowski, M. A. Subramanian, M. K. Crawford, W. E. Farneth and E. M. McCarron, Physica C **185**, 867-868 (1991).

11. J. M. Deleon, S. D. Conradson, I. Batistic and A. R. Bishop, Phys. Rev. Lett. **65** (13), 1675-1678 (1990).

12. E. Dagotto, T. Hotta and A. Moreo, Physics Reports-Review Section of Physics Letters **344** (1-3), 1-153 (2001).

13. A. Moreo, S. Yunoki and E. Dagotto, Science **283** (5410), 2034-2040 (1999).

14. J. M. Deleon, S. D. Conradson, I. Batistic, A. R. Bishop, I. D. Raistrick, M. C. Aronson and F. H. Garzon, Phys. Rev. B **45** (5), 2447-2457 (1992).

15. J. M. Deleon, I. Batistic, A. R. Bishop, S. D. Conradson and S. A. Trugman, Phys. Rev. Lett. **68** (21), 3236-3239 (1992).

16. M. Arai, K. Yamada, S. Hosoya, A. C. Hannon, Y. Hidaka, A. D. Taylor and Y. Endoh, J. Supercon. **7** (2), 415-418 (1994).

17. J. M. DeLeon, S. D. Conradson, T. Tyson, A. R. Bishop, M. Salkola, F. J. Espinosa and J. L. Pena, in *Applications of Synchrotron Radiation Techniques to Materials Science III*,

edited by L. J. Terminello, S. M. Mini, H. Ade and D. L. Perry (1996), Vol. 437, pp. 189-199.

18. M. I. Salkola, A. R. Bishop, S. A. Trugman and J. M. Deleon, Phys. Rev. B **51** (14), 8878-8891 (1995).

19. M. I. Salkola, A. R. Bishop, J. M. Deleon and S. A. Trugman, Phys. Rev. B **49** (5), 3671-3674 (1994).

20. S. D. Conradson, D. A. Andersson, P. S. Bagus, E. R. Batista, K. S. Boland, J. A. Bradley, D. D. Byler, D. L. Clark, D. R. Conradson, N. J. Hess, M. B. Martucci, R. L. Martin, D. Nordlund, G. T. Seidler and X.-D. Wen, J. Am. Chem. Soc. **submitted** (2013).

21. Y. Q. An, A. J. Taylor, S. D. Conradson, S. A. Trugman, T. Durakiewicz and G. Rodriguez, Phys. Rev. Lett. **106** (20), 207402 (2011).

22. S. D. Conradson, Y. Q. An, G. Rodriguez, A. D. Taylor, T. Durakiewicz, A. R. Bishop and T. A. Tyson, Phys. Rev. Lett. **submitted** (2013).

23. V. V. Kabanov, J. Demsar and D. Mihailovic, Phys. Rev. B **61** (2), 1477-1482 (2000).

24. R. Yusupov, T. Mertelj, V. V. Kabanov, S. Brazovskii, P. Kusar, J. H. Chu, I. R. Fisher and D. Mihailovic, Nature Physics **6** (9), 681-684 (2010).

25. A. Bussmann-Holder, H. Keller, A. R. Bishop, A. Simon and K. A. Mueller, Journal of Superconductivity and Novel Magnetism **21** (6), 353-357 (2008).

26. M. P. A. Fisher, P. B. Weichman, G. Grinstein and D. S. Fisher, Phys. Rev. B **40** (1), 546-570 (1989).

27. M. Greiner, O. Mandel, T. Esslinger, T. W. Hansch and I. Bloch, Nature **415** (6867), 39-44 (2002).

28. C. Kollath, A. M. Laeuchli and E. Altman, Phys. Rev. Lett. **98** (18) (2007).

29. L. Desgranges, G. Badinozzi, D. Simeone and H. E. Fischer, Inorg. Chem. **50** (13), 6146-6151 (2011).

30. L. Desgranges, G. Baldinozzi, G. Rousseau, J.-C. Niepce and G. Calvarin, Inorg. Chem. **48** (16), 7585-7592 (2009).

31. M. T. Weller, P. G. Dickens and D. J. Penny, Polyhedron **7** (3), 243-244 (1988).

32. C. Greaves and B. E. F. Fender, Acta Crystallogr, Sect. B: Struct. Sci. **28** (DEC15), 3609-3614 (1972).

33. P. C. Debets, Acta Crystallographica **21**, 589-& (1966).

34. R. Engmann and P. M. D. Wolff, Acta Crystallographica **16** (10), 993-& (1963).

35. K. A. Al-Hassanieh, F. A. Reboredo, A. E. Feiguin, I. Gonzalez and E. Dagotto, Phys. Rev. Lett. **100** (16) (2008).

36. I. B. Bersuker, *The Jahn-Teller Effect*. (Cambridge University Press, New York, 2006).

37. M. Albiez, R. Gati, J. Folling, S. Hunsmann, M. Cristiani and M. K. Oberthaler, Phys. Rev. Lett. **95** (1) (2005).

38. S. Levy, E. Lahoud, I. Shomroni and J. Steinhauer, Nature **449** (7162), 579-U578 (2007).

39. K. C. Wright, R. B. Blakestad, C. J. Lobb, W. D. Phillips and G. K. Campbell, Phys. Rev. Lett. **110** (2) (2013).

40. B. T. M. Willis, Solid State Comm. **2** (1), 23-23 (1964).

41. B. T. M. Willis and R. I. Taylor, Physics Letters **17** (3), 188-& (1965).

42. B. C. Frazer, G. Shirane, D. E. Cox and C. E. Olsen, Physical Review **140** (4A), 1448-& (1965).

43. G. Dolling, R. A. Cowley and A. D. B. Woods, Can. J. Phys. **43** (8), 1397-& (1965).

44. P. D. V. Duplessis, G. H. Lander, A. M. Strydom and B. Fak, Physica B **180**, 321-322 (1992).

45. R. Caciuffo, G. Amoretti, P. Santini, G. H. Lander, J. Kulda and P. D. Du Plessis, Phys. Rev. B **59** (21), 13892-13900 (1999).

46. R. Caciuffo, P. Santini, S. Carretta, G. Amoretti, A. Hiess, N. Magnani, L. P. Regnault and G. H. Lander, Phys. Rev. B **84** (10), 104409 (2011).

47. J. Jeong, N. Aetukuri, T. Graf, T. D. Schladt, M. G. Samant and S. S. P. Parkin, Science **339**, 1402-1404 (2013).

48. S. D. Conradson, B. D. Begg, D. L. Clark, C. den Auwer, M. Ding, P. K. Dorhout, F. J. Espinosa-Faller, P. L. Gordon, R. G. Haire, N. J. Hess, R. F. Hess, D. W. Keogh, L. A. Morales, M. P. Neu, P. Paviet-Hartmann, W. Runde, C. D. Tait, D. K. Veirs and P. M. Villella, J. Am. Chem. Soc. **126** (41), 13443-13458 (2004).

49. S. D. Conradson, B. D. Begg, D. L. Clark, C. den Auwer, M. Ding, P. K. Dorhout, F. J. Espinosa-Faller, P. L. Gordon, R. G. Haire, N. J. Hess, R. F. Hess, D. W. Keogh, G. H. Lander, D. Manara, L. A. Morales, M. P. Neu, P. Paviet-Hartmann, J. Rebizant, V. V. Rondinella, W. Runde, C. D. Tait, D. K. Veirs, P. M. Villella and F. Wastin, J. Solid State Chem. **178** (2), 521-535 (2005).

50. I. D. Prodan, G. E. Scuseria and R. L. Martin, Phys. Rev. B **76** (3) (2007).