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Phase Separations in Highly Correlated Materials

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The X-ray absorption near edge structure spectroscopy is a unique powerful local and fast experimental method to study complex systems since it probes the nanoscale structure around selected atoms giving evidence for different local and instantaneous phases present in multiscale highly correlated granular systems. Transition metals and rare earth oxides like manganites, cuprates or pnictides superconductors show a rich variety of different competing structural, electronic and magnetic phases, which spatially coexist forming complex lattice textures. Many recent experimental data have pointed out the presence of arrested phase separation and the interplay of different phases occurring from nano- to micrometer-scale. This scenario opens the possibility to manipulate the mesoscopic phases to get new material functionalities. Therefore there is increasing need to develop methods to probe morphology and phase distribution at multiple length scales. Actually, combining X-ray imaging at high spatial resolution with μ-XANES spectroscopy both mesoscale, nanoscale and atomic structural changes can be identified. The μ-XANES spectroscopy technique is rapidly growing to investigate adaptive matter, high temperature superconductors, complex materials showing arrested phase separation at the mesoscale.

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1. Introduction

It is well known that phase separation occurs where two or more phases with comparable free energies coexist giving two or more macroscopic phases each one with a large coherence length, however there is growing scientific interest for the case of arrested phase separations in transition metal oxides where two or more phases form complex textures extending in the mesoscale between the atomic scale and the macroscopic world, made of small domains with a size ranging from nanoscale to micron-scale. The mesoscale phase separation leads to strong anomalies or dramatic changes of system properties and material functionality. Clear anomalies are observed in the behaviour of different observable quantities such as the resistivity and the optical transmission [1, 2]. The origin of the mesoscale phase separation phenomenon responsible for a variety of unusual phenomena is due to the appearance of voxels of competing thermodynamic phases inside a host phase [3–6]. Transition metals and rare earth oxides, as for example high temperature superconductors, as cuprates or pnictides present multiple electronic states with different orbital symmetries at the Fermi energy and competing anisotropic Coulomb, magnetic and electron–lattice short range interactions together with long range Coulomb and elastic interaction, giving complex lattice architectures and a rich variety of different coexisting electronic and magnetic phases. Their interplay plays a key role in colossal magnetoresistance materials [7, 8], ferroelectrics [9, 10] and in high temperature superconductors (HTS) showing arrested phase separation at mesoscopic or nanoscopic length scales [11–15].

Many experimental data support the scenario that the competition and interplay among different phases at nano-, meso-, and micrometer scale are at the origin of the macroscopic behaviours observed in these systems. As a consequence, techniques suitable to probe morphology and phase distribution at multiple length scales are required to characterize these complex materials. Moreover, to study the multiscale phase separation from the nano- to the micronscale we need bulk experimental methods not averaged in time and in space, complementary to other techniques sensitive only to highly ordered/crystalline phases such as X-ray diffraction with micron size spots (μXRD).

Actually, macroprobe techniques, e.g., XRD, angle-resolved photoelectron spectroscopy, inelastic neutron scattering, etc. are excellent methods for characterizing materials but are not able to spatially separate the contributions of different coexisting phases in the nano- and microscale domain. Therefore, to image micrometer-scale lattice fluctuations of ordering of oxygen interstitials (O_i) in single crystals, we need microprobe based techniques such as μ X-ray absorption spectroscopy (μ-XAS) and μ-XRD, which take advantage of the highest spatial resolution made possible by synchrotron radiation sources.

Being a fast and local probe of a selected atom, the X-ray absorption near edge structure (XANES) spectroscopic technique represents a unique method suitable to investigate the distribution of a polymorph and of multiscale correlated systems at the nanoscale being a measure of multiple scattering resonances of the excited photoelectron in a nanocluster [16–18] and it has been used to probe the coexistence of different perovskite local structures [18, 19].

Highly correlated electron systems can be described as complex systems having a multiscale structure and a dynamics, unavoidably entangled well beyond the definition of a poorly-ordered or a disordered system. Combining

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X-ray imaging at high spatial resolution with μ-XANES spectroscopy both small structural distortions occurring at the atomic scale and weak chemical changes can be identified and correlated with 2D and 3D morphologies of complex systems. The technique has been already successfully applied to several systems such as high temperature superconductors, correlated materials where different "phases" coexist at the mesoscale.

It is important to underline here that high-resolution experimental probes such as electron microscopy or the atomic force microscope, provide information only on surface atoms and from a limited numbers of layers below the surface. Both are not able to probe the presence of different nanoscale phases below the surface. Other experimental probes looking at the k-space such as XRD, neutron diffraction, and angular resolved photoemission, may provide only non-local and space averaged information.

Local structural probes with micrometer size spots such as the pair distribution function (PDF) or micro-XANES (μ-XANES) may investigate also nanoscale structures [19, 20] and nanoparticles [21, 22]. However, being an extremely fast probe ($\approx$ fs resolution) only XAS spectroscopy may provide information on local electronic and lattice fluctuations, in a complementary way to other techniques such as scanning μXRD [23, 24].

It will be shown in the next section how μ-XANES data of La_2CuO_{4+y}, the simplest cuprate superconductor with mobile oxygen interstitials whose μ-X-ray diffraction data clearly show the presence of a bulk multiscale structural phase separation. This result is extremely important because in this sample we may observe the coexistence of two competing macroscopic phases associated to two c-axis lattice constants [24].

The presence in the La_2CuO_{4+y} of two coexisting networks of ordered defects point out that for superconductors with higher T_c and, in general, for more complex materials the number of networks can be higher. Moreover, both the network number and the distribution of phases inside a phase-separated system are related to the superconductivity or to other peculiar properties of the material.

2. μ-XANES spectroscopy and heterogeneous materials

Figure 1 shows a simplified scenario describing cuprate heterostructures, in particular the distribution of different puddles, which can be formed in the CuO_2 plane and their different active atomic layers. Indeed, the phase separation occurring in cuprates may form different networks with different types of voxels. In this figure we simplified the description of the La_2CuO_{4+y}, i.e., the simplest cuprate, where two different types of puddles can be considered. Blue regions are magnetic puddles of ordered Cu spins, in Cu $3d$ orbital, while red are puddles of charge ordered holes in oxygen $2p$ orbital. These puddles can be associated to spin density wave (blue regions) and charge density wave (red regions) where superconductivity takes place in the interstitial space [23–26].

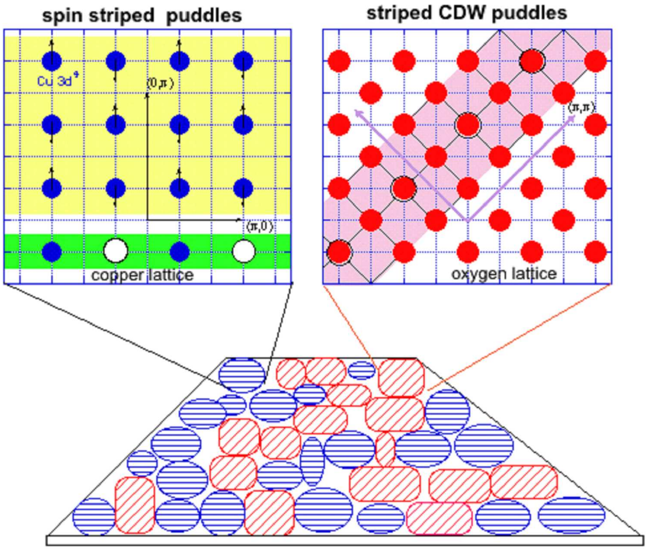

Fig. 1. A simplified description of a mesosystem like the CuO_2 showing active atomic layers in cuprate heterostructures. A complex phase separation forms networks of two different types of domains: magnetic puddles (blue) and superconducting puddles (red). Top left: Magnetic puddles comprise horizontal (or vertical) spin stripes in the Cu sublattice (blue dots), with spin indicated by black arrows. Top right: CDW puddles are made of diagonal stripes.

The blue puddles (Fig. 1, upper left) form magnetic domains of the spin density wave order probed by magnetic nuclear and X-ray scattering. Spatially separated are the red puddles (Fig. 1, upper right) that contain the charge order probed by X-ray diffraction, extended X-ray absorption fine structure (EXAFS) and XANES, where within the oxygen sublattice we may found oxygen-poor and oxygen-rich stripes. Recently it has been shown that the distribution of the CDW domains shows a scale-free distribution, which determines a hyperbolic space for the superconducting phase [25] called superstripes phase [25, 26]. The difference observed among cuprate superconductors depends on the interplay and distribution of three different spatial domains, CDW, SDW, and the hole rich space in dopant rich domains. This last type of space is determined by self-organization of mobile dopants in the space layers [27, 28]. There are three fundamental parameters controlling the phase diagram of cuprates, namely temperature, doping and misfit strain [29, 30], they control the diversity of CDW scenario in different cuprates and the onset of SDW only beyond a critical value of the misfit strain.

The superconductivity is expected to take place at the interface and at the surface of CDW puddles giving a superstripes phase with spontaneous symmetry breaking of both gauge symmetries and lattice symmetries [25, 26]. The striped metallic phase induces a Fermi surface reconstruction that originated mini-bands and the opening of partial gaps in the density of states of ≈20–50 meV. This mechanism favours the occurrence of shape resonances in the striped puddles [31].

Actually, to fully understand the complex stripe-topology in layered systems or the presence of networks of voxels it is necessary to use techniques like micro/nano-XRD and micro/nano-XANES, the latter capable to probe the local lattice structure within a nanoscale cluster centered at the selected absorption site, being the only method suitable to support the reconstruction of the "network structure" at the atomic scale.

Previous neutron powder diffraction studies have shown the occurrence of a phase separation in La_2CuO_{4-y} for $y < 0.055$ [32] but only the average location of the oxygen interstitials (O_i) [33] was obtained.

The intrinsic self-organization of oxygen interstitials is better observed in layered crystals such as La_2CuO_{4-y} where due to the lattice misfit between the active and spacer layers, a large tensile strain occurs [29, 34, 35]. Moreover, oxygen interstitials shows a larger mobility in crystalline systems where an extra strain occurs due to the difference between the thermal expansion coefficients of the active and spacer layers.

The phase separation of oxygen-rich and oxygen-poor phase at higher concentration of O_i for $y > 0.055$ was not possible to be detected by neutron diffraction on single crystals but there were observed only superstructure satellites [36–38] with no information on the spatial location of multiple phases.

The spatial distribution of puddles in an optimally doped $La_2CuO_{4.1}$ ($T_c \approx 40$ K) [23] and in an underdoped $La_2CuO_{4.06}$ [24], was first obtained by scanning micro X-ray diffraction. It was pointed out that, at the optimum doping, O_i-rich puddles (ORP) form a scale-free network of superconducting puddles, which favours the high temperature superconductivity (HTS).

Using μ-XANES, we have collected space-resolved XANES spectra, probing the local structure around the La ion in the spacer layers [20]. Although, a XANES spectrum recorded over a μm size spot returns only the averaged ratio between ORP and O_i-poor puddles (OPP) in the same spot, XANES spectra collected in different points are different.

As a consequence, the underdoped sample ($y = 0.06$) shows a content of O_i intermediate between that of the La_2CuO_4 and of the optimally doped $La_2CuO_{4.125}$ sample. After establishing the relation between the variation of the main multiple scattering resonance (MSR) peak of the XANES spectra and the presence of O_i in the illuminated spots, it is possible to measure the variation of the intensity of the main MSR peak in the XANES spectra using X-ray spots of few μm. The distribution of ORP and OPP puddles is clearly shown by the maps of the space variation of the MSR in Fig. 2 [20].

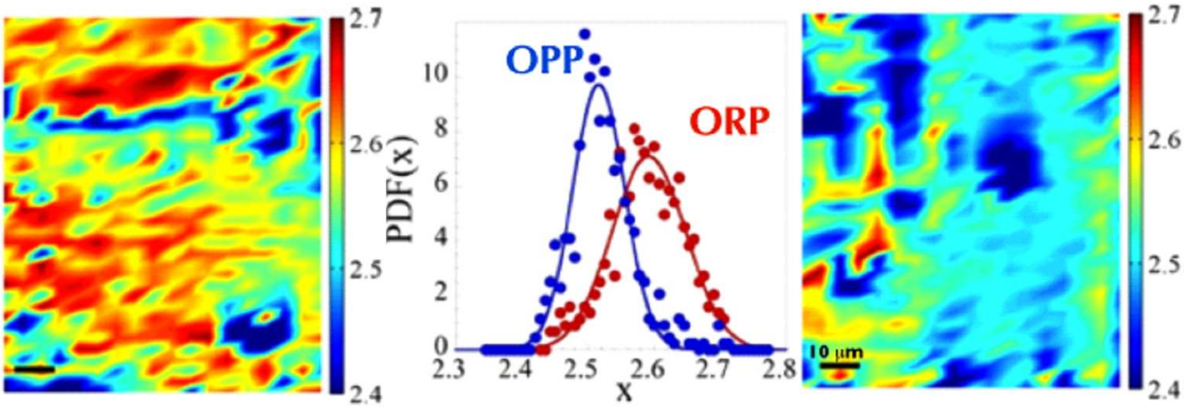

Fig. 2. Maps of the position dependent intensity of the MSR in the XANES spectra at the La L3-edge of a $La_2CuO_{4.06}$ crystal (intensity in the colour bars). The maps shown are ≈ 145 × 32 μm^2 (the bar is 10 μm) and has been collected at 10 s/step. In the central panel the probability density function PDF(x) of the multiple scattering resonance (MSR) for the two regions with different distributions of oxygen interstitials.

In this figure two regions of ≈ 145 × 32 μm (left and right panels) with different distributions of ORPs are compared. The patterns are obtained starting from the statistical analysis of the two regions shown in the central panel of Fig. 2. The x-axis of the central panel is the intensity of the XANES resonance (MSR) observed at the La L_3 edge, which ranges from ≈2.4 to 2.75 in units of the absorption jump. The Gaussian distribution corresponding to the left panel refers to an oxygen-rich region. It is peaked at ≈2.6 and its width ranges from 2.45 to 2.75 (red), while the distribution of the right panel corresponds to an oxygen-poor region. It is peaked at 2.5 and its width ranges from ≈2.4 to 2.65 (blue). Different distributions of ORP's and OPP's clearly occur in different locations of the investigated crystal.

μ-XANES mapping at the La L_3-edge provides also a strong experimental support to the percolative superconductivity scenario in high temperature cuprates superconductors [20]. Moreover, percolation of superconducting puddles has been recently observed also in iron selenide superconductors [15, 39–41].

3. Mesoscience and the phase separation scenario in correlated materials

Also transition metal oxides (TMO) offer a wide spectrum of properties, which provide the foundation for a broad range of potential applications. Many of these properties originate from interactions among spin, lattice, and charge degrees of freedom. Among TMO's, the vanadium dioxide (VO_2) is one of the most challenging and studied systems because it undergoes to a hysteretic metal–insulator transition (MIT) [42, 43] and a structural phase transition (SPT) from monoclinic to rutile phases [44], upon heating or cooling through a temperature range near room temperature ($\approx$340 K) with a change in conductivity by several orders of magnitude. This complex multiphase material is actively investigated because of its potential application as switching devices as well as for fundamental researches looking at the understanding of multiphase correlated electron systems.

Still now, the driving mechanism of the MIT transition is still matter of debate setting against the strong electron correlation present in many Mott–Hubbard systems with the electron–lattice coupling describing a Peierls transition [45–49].

Nanoscale phase separation and lattice complexity are key elements of all transition metal oxides including VO_2, which show a MIT [50, 51]. The vanadium K-edge XANES high-resolution spectroscopy has been shown to have the sensitivity to probe the local structure changes associated with the MIT transition [52]. Moreover, a local probe such as XANES may investigate simultaneously both the MIT and the SPT, monitoring the local behaviour of VO_2 films at the O K-edge [53].

The MIT transition in VO_2 films is strongly affected by doping and/or strain induced by the substrate, with large changes in the resistance of the material, shifts of the transition temperature and even the formation of new intermediate structural phases [54, 55]. Moreover, at the onset of the phase transition, nanoscale metallic domains emerge from the insulating host of VO_2.

Recent results using X-ray absorption spectromicroscopy [53] showed that it is possible to induce an electronic transition without inducing a structural transition in thin film of VO_2 during a heating–cooling cycle. This experiment is an additional demonstration of the relevance of used techniques with high spectral, time and spatial resolution, to accurately study inhomogeneous media such as phase separated materials and with complex multi-dimensional phase diagrams.

4. Conclusions

The mesoscale science represents an extraordinary opportunity for discovering and controlling new materials where atomic granularity, quantization of energy, and simplicity of structure and function mix together offering a new horizon to materials science. In the last half-century, and especially in the last decade, great advancements in the observations at small length and time scales allowed to reveal many atomic and molecular contributions that are responsible of many macroscopic behaviours. Moreover, many experiments pointed out the presence in many materials of a mesoscale architecture that promotes the emergence of new behaviours and new functionality to materials [56].

Being a fast and local probe a selected atomic element, XANES spectroscopy is a powerful fast and local spectroscopic method suited to investigate the distribution of phases of a sample in the mesoscale domain, down to the micrometer scale and below using small spots [16]. Actually, this technique is also unique when applied to investigate the nature of multiscale highly correlated systems such as transition metal and rare earth oxides or superconductors such as cuprates or pnictides [57]. All these systems offer a rich variety of nanoscale structural, electronic and magnetic phases sometimes coexisting among them, which are at the origin of their mesoscopic and macroscopic behaviours so that the capability to probe morphology and phase distribution at multiple length scales is mandatory.

μ-XANES spectroscopy allows probing the local lattice structure within a nanoscale cluster centered at the selected absorption site. Mapping the edge of a RE or of a TM provide the opportunity to describe and measure the distribution of two or more coexisting networks, e.g., of ordered defects, spin stripes and/or lattice stripes. The experiments performed on the La_2CuO_4 samples show that the arrangement of ORP's in the real space points out the presence of different percolation regimes. Moreover, the percolation phenomenon has a strong influence in the superconducting properties as shown in the case of La_2CuO_4.

Recently arrested mesoscale phase separation has been confirmed in uranium oxides [58–60] as recently shown in the UO_{2+x} system [60, 61], iron based superconductors [62], $BaPb_{1-x}Bi_xO_3$ systems [63] and it is expected in a new high temperature superconductor, pressurized sulphur hydride with T_c =203 K [64, 65]. A new quantum physics of complex system is growing where the Fano resonances (called also the Feshbach resonances or shape resonances in different fields) between localized and delocalized states or between the Bose–Einstein condensate (BEC) and Bardeen–Cooper–Schrieffer (BCS) condensates, contribute in the presence of anisotropic interactions, multiband Hubbard models, or near Lifshitz electronic transitions [66–69]. Finally, the interplay of nano- and micrometer-scale factors is typically at the origin of mesoscopic and macroscopic behaviours so that the capability to probe morphology and phase distribution in complex systems at multiple length scales is now mandatory.

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References

[1] M. Fäth, S. Freisem, A. Menovsky, Y. Tomioka, J. Aarts, J.A. Mydosh, *Science* **285**, 1540 (1999).

[2] J. Hollinger, A.A. Jahnke, N. Coombs, D.S. Seferos, *J. Am. Chem. Soc.* **132**, 8546 (2010).

[3] A. Bianconi, *Int. J. Mod. Phys. B* **14**, 3289 (2000).

[4] A. Bianconi, D. Di Castro, G. Bianconi, A. Pifferi, N.L. Saini, F.C. Chou, D.C. Johnston, M. Colapietro, *Physica C Supercond.* **341-348**, 1719 (2000).

[5] V.I. Yukalov, E.P. Yukalova, *Phys. Rev. B* **70**, 224516 (2004).

[6] V.I. Yukalov, *Phys. Rep.* **208**, 395 (1991).

[7] M.B. Salamon, M. Jaime, *Rev. Mod. Phys.* **73**, 583 (2001).

[8] E. Dagotto, T. Hotta, A. Moreo, *Phys. Rep.* **344**, 1 (2001).

[9] V.I. Yukalov, *Ferroelectrics* **82**, 11 (1988).

[10] Y. Yamada, T. Iwase, K. Fujishiro, Y. Uesu, Y. Yamashita, I. Tomeno, S. Shimanuki, *Ferroelectrics* **240**, 1629 (2000).

[11] A. Bianconi, *Solid State Commun.* **91**, 1 (1994).

[12] A. Bianconi, M. Missori, *Solid State Commun.* **91**, 287 (1994).

[13] G. Campi, D. Innocenti, A. Bianconi, *J. Super. Novel Magn.* **28**, 1355 (2015).

[14] A. Ricci, N. Poccia, G. Campi, B. Joseph, G. Arrighetti, L. Barba, M. Reynolds, M. Burghammer, H. Takeya, Y. Mizuguchi, Y. Takano, M. Colapietro, N.L. Saini, A. Bianconi *Phys. Rev. B* **84**, 060511 (2011).

[15] A. Bianconi, N. Poccia, A.O. Sboychakov, A.L. Rakhmanov, K.I. Kugel, *Supercond. Sci. Tech.* **28**, 024005 (2015).

[16] J. Garcia, A. Bianconi, M. Benfatto, C.R. Natoli, *J. Phys. Coll.* **47**, C8-49 (1986).

[17] A. Bianconi, S. Della Longa, C. Li, M. Pompa, A. Congiu-Castellano, D. Udron, A. Flank, P. Lagarde, *Phys. Rev. B* **44**, 10126 (1991).

[18] A. Bianconi, M. Missori, H. Oyanagi, H. Yamaguchi, Y. Nishiara, S. Della Longa, *Europhys. Lett.* **31**, 411 (1995).

[19] D. Andrault, M. Muñoz, N. Bolfan-Casanova, N. Guignot, J.-P. Perrillat, G. Aquilanti, S. Pascarelli, *Earth Plan. Sci. Lett.* 293, 90 (2010).

[20] N. Poccia, M. Chorro, A. Ricci, Wei Xu, A. Marcelli, G. Campi, A. Bianconi, *Appl. Phys. Lett.* **104**, 221903 (2014).

[21] C. Balasubramanian, B. Joseph, P. Gupta, N.L. Saini, S. Mukherjee, D. Di Gioacchino, A. Marcelli, *J. Electron. Spectrosc. Relat. Phenom.* 196, 125 (2014).

[22] C. Balasubramanian, B. Joseph, P.B. Orpe, N.L. Saini, S. Mukherjee, K. Dziedzic-Kocurek, J. Stanek, D. Di Gioacchino, A. Marcelli, submitted to *Phys. Chem. Chem. Phys.*.

[23] M. Fratini, N. Poccia, A. Ricci, G. Campi, M. Burghammer, G. Aeppli, A. Bianconi, *Nature* 466, 841 (2010).

[24] N. Poccia, A. Ricci, G. Campi, M. Fratini, A. Puri, D. Di Gioacchino, A. Marcelli, M. Reynolds, M. Burghammer, N.L. Saini, G. Aeppli, A. Bianconi, *Proc. Natl. Acad. Sci.* 109, 15685 (2012).

[25] G. Campi, A. Bianconi, N. Poccia, G. Bianconi, L. Barba, G. Arrighetti, D. Innocenti, J. Karpinski, N.D. Zhigadlo, S.M. Kazakov, M. Burghammer, M. von Zimmermann, M. Sprung, A. Ricci, *Nature* **525**, 359 (2015).

[26] A. Bianconi, G. Bianconi, S. Caprara, D. Di Castro, H. Oyanagi, N.L. Saini, *J. Phys. Condens. Matter* **12**, 10655 (2000).

[27] A. Ricci, N. Poccia, B. Joseph, D. Innocenti, G. Campi, A. Zozulya, F. Westermeier, A. Schavkan, F. Coneri, A. Bianconi, H. Takeya, Y. Mizuguchi, Y. Takano, T. Mizokawa, M. Sprung, N.L. Saini, *Phys. Rev. B* **91**, 020503 (2015).

[28] N. Poccia, M. Fratini, A. Ricci, G. Campi, L. Barba, A. Vittorini-Orgeas, G. Bianconi, G. Aeppli, A. Bianconi, *Nature Mater.* **10**, 733 (2011).

[29] N. Poccia, A. Ricci, A. Bianconi, *Adv. Condens. Matter Phys.* **2010**, 261849 (2010).

[30] S. Agrestini, N.L. Saini, G. Bianconi, A. Bianconi, *J. Phys. A Math. Gen.* **36**, 9133 (2003).

[31] A. Perali, D. Innocenti, A. Valletta, A. Bianconi, *Supercond. Sci. Tech.* **25**, 124002 (2012).

[32] J. Jorgensen, B. Dabrowski, S. Pei, D. Richards, D. Hinks, *Phys. Rev. B* **40**, 2187 (1989).

[33] C. Chaillout, J. Chenavas, S.W. Cheong, Z. Fisk, M. Marezio, B. Morosin, J.E. Schirber, *Physica C Supercond.* **170**, 87 (1990).

[34] D. Di Castro, G. Bianconi, M. Colapietro, A. Pifferi, N.L. Saini, S. Agrestini, A. Bianconi, *Europ. Phys. J. B Condens. Matter Com. Sys.* 18, 617 (2000).

[35] N. Poccia, M. Fratini, *J. Supercond. Novel Magn.* **22**, 299 (2009).

[36] B.O. Wells, R.J. Birgeneau, F.C. Chou, Y. Endoh, D.C. Johnston, M.A. Kastner, Y.S. Lee, G. Shirane, J.M. Tranquada, K. Yamada, *Z. Phys. B* **100**, 535 (1996).

[37] B.O. Wells, Y.S. Lee, M.A. Kastner, R.J. Christianson, R.J. Birgeneau, K. Yamada, Y. Endoh, G. Shirane, *Science* **277**, 1067 (1997).

[38] P.G. Radaelli, J.D. Jorgensen, A.J. Schultz, B.A. Hunter, J.L. Wagner, F.C. Chou, D.C. Johnston, *Phys. Rev. B* **48**, 499 (1993).

[39] V. Ksenofontov, G. Wortmann, S.A. Medvedev, V. Tsurkan, J. Deisenhofer, A. Loidl, C. Felser, *Phys. Rev. B* **84**, 180508 (2011).

[40] Z. Shermadini, A. Krzton-Maziopa, M. Bendele, R. Khasanov, H. Luetkens, K. Conder, E. Pomjakushina, S. Weyeneth, V. Pomjakushin, O. Bossen, A. Amato, *Phys. Rev. Lett.* **106**, 117602 (2011).

[41] M. Eisterer, M. Zehetmayer, H.W. Weber, J. Jiang, J.D. Weiss, A. Yamamoto, E.E. Hellstrom, D.C. Larbalestier, N.D. Zhigadlo, J. Karpinski, *Supercond. Sci. Technol.* **23**, 054006 (2010).

[42] V. Eyert, *Ann. Phys.* 11, 650 (2002).

[43] C.N. Berglund, H.J. Guggenheim, *Phys. Rev.* **185**, 1022 (1969).

[44] M. Marezio, D.B. McWhan, J.P. Remeika, P.D. Dernier, *Phys. Rev. B* **5**, 2541 (1972).

[45] M. Nakano, K. Shibuya, D. Okuyama, T. Hatano, S. Ono, M. Kawasaki, Y. Iwasa, Y. Tokura, *Nature* **487**, 459 (2012).

[46] R.M. Wentzcovitch, W.W. Schulz, P.B. Allen, *Phys. Rev. Lett.* **72**, 3389 (1994).

[47] T.M. Rice, H. Launois, J.P. Pouget, *Phys. Rev. Lett.* **73**, 3042 (1994).

[48] M.M. Qazilbash, M. Brehm, B.-G. Chae, P.-C. Ho, G.O. Andreev, B.-J. Kim, S.J. Yun, A.V. Balatsky, M.B. Maple, F. Keilmann, H.-T. Kim, D.N. Basov, *Science* **318**, 1750 (2007).

[49] M.K. Liu, M. Wagner, E. Abreu, S. Kittiwatanakul, A. McLeod, Z. Fei, M. Goldflam, S. Dai, M.M. Fogler, J. Lu, S.A. Wolf, R.D. Averitt, D.N. Basov, *Phys. Rev. Lett.* **111**, 096602 (2013).

[50] A. Bianconi, N. Poccia, A.O. Sboychakov, A.L. Rakhmanov, K.I. Kugel, *Supercond. Sci. Technol.* **28**, 024005 (2015).

[51] A. Ricci, N. Poccia, G. Campi, F. Coneri, L. Barba, G. Arrighetti, M. Polentarutti, M. Burghammer, M. Sprung, M. von Zimmermann, A. Bianconi, *New J. Phys.* **16**, 053030 (2014).

[52] A. Bianconi, *Phys. Rev. B* **26**, 2741 (1982).

[53] S. Kumar, J.P. Strachan, M.D. Pickett, A. Bratkovsky, Y. Nishi, R.S. Williams, *Adv. Mater.* 26, 7505 (2014).

[54] J.P. Pouget, H. Launois, J.P. D'Haenens, P. Merenda, T.M. Rice, *Phys. Rev. Lett.* **35**, 873 (1975).

[55] T. Yao, X. Zhang, Z. Sun, S. Liu, Y. Huang, Y. Xie, Ch. Wu, X. Yuan, W. Zhang, Z. Wu, G. Pan, F. Hu, L. Wu, Q. Liu, S. Wei, *Phys. Rev. Lett.* 105, 226405 (2010).

[56] A. Ricci, G. Campi, N. Poccia, A. Bianconi, in: *Nanoscale excitations in emergent materials - NEEM 2015*, Eds.: A. Marcelli, C. Balasubramanian, Superstripes Press, Rome 2015, p. 96.

[57] A. Bianconi, in: *Nanoscale excitations in emergent materials - NEEM 2015*, Eds.: A. Marcelli, C. Balasubramanian, Superstripes Press, Rome 2015, p. 16.

[58] J. Petiau, G. Calais, D. Petitmaire, A. Bianconi, M. Benfatto, A. Marcelli, *J. Phys. Coll.* 47, C8-949 (1986).

[59] J. Petiau, G. Calais, D. Petitmaire, A. Bianconi, M. Benfatto, A. Marcelli, *Phys. Rev. B* **34**, 7350 (1986).

[60] S.D. Conradson, D. Manara, F. Wastin, D.L. Clark, G.H. Lander, L.A. Morales, J. Rebizant, V.V. Rondinella, S.D. Conradson, *Inorg. Chem.* **43**, 6922 (2004).

[61] S.D. Conradson, S.M. Gilbertson, S.L. Daifuku, J.A. Kehl, T. Durakiewicz, D.A. Andersson, A.R. Bishop, D.D. Byler, P. Maldonado, P.M. Oppeneer, J.A. Valdez, M.L. Neidig, G. Rodriguez, *Sci. Rep.* **5**, 15278 (2015).

[62] R. Caivano, M. Fratini, N. Poccia, A. Ricci, A. Puri, Z.-A. Ren, X.-L. Dong, J. Yang, W. Lu, Z.-X. Zhao, L. Barba, A. Bianconi, *Supercond. Sci. Technol.* **22**, 014004 (2009).

[63] P. Giraldo-Gallo, Y. Zhang, C. Parra, H.C. Manoharan, M.R. Beasley, T.H. Geballe, M.J. Kramer, I. R. Fisher, *Nature Commun.* **6**, 8231 (2015).

[64] A. Bianconi, T. Jarlborg, *Europhys. Lett.* **112**, 37001 (2015).

[65] A. Bianconi, T. Jarlborg, *Novel Supercond. Mater.* **1**, 37 (2015).

[66] A. Bianconi, A. Valletta, A. Perali, N.L. Saini, *Solid State Commun.* **102**, 369 (1997).

[67] A. Bianconi, *J. Supercond.* **18**, 625 (2005).

[68] K. Kugel, A.L. Rakhmanov, A.O. Sboychakov, N. Poccia, A. Bianconi, *Phys. Rev. B* **78**, 165124 (2008).

[69] F.V. Kusmartsev, M. Saarela, *Int. J. Mod. Phys. B* **29**, 1542002 (2015).