

Superconductivity and Magnetism in the Ruthenocuprates

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Abstract - The ruthenocuprates are high temperature superconductors, which have raised a substantial interest due to the simultaneous presence of the transition metal magnetism and superconductivity. The compounds represent a complex and experimentally challenging research arena, with interesting recent experimental developments. Without striving for completeness, the author reviews some key properties of $\text{RuSr}_2\text{RECu}_2\text{O}_8$, $\text{RuSr}_2\text{RE}_{2-x}\text{Ce}_x\text{Cu}_2\text{O}_{10-y}$, and of few derivative compounds of the ruthenocuprate family.

Manuscript received September 20, 2007; accepted October 24, 2007. Reference No. CR3, Category 1.

I. INTRODUCTION

Physical properties of ruthenocuprates, which belong to the family of high-temperature superconductors (HTS), have raised substantial interest due to the presence of the Ru ion magnetic ordering reported to coexist with superconductivity. This is the only class in HTS where the transition metal magnetism is present and sets in at temperature T_m well above the superconducting T_c (e.g. for $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ $T_m \approx 132$ K and $T_c^{\text{on}} \approx 45$ K [1, 2, 3]). Since the mechanism of and prerequisites for the superconducting state in different parts of the HTSC phase diagram are still in debate, the ruthenocuprates seem to offer a unique research platform not only to explain the apparent coexistence of their superconductivity with magnetism, but also to possibly conclude on more universal features of superconductivity in cuprates.

The investigations of single crystals of intermetallics revealed that also for singlet state of pairing the superconductivity can coexist with ferromagnetism, not necessarily suppressed by the orbital pair breaking effect. This usually occurs in a narrow range of temperature and through the spatial modification of the order parameters. Sinusoidally modulated spiral magnetic structure ($T_c = 0.7$ K) was identified for reentrant superconductor HoMo_6S_8 ($T_{c1} = 1.8$ K, $T_{c2} = 0.6$ K) [4]. Spiral, spatially modulated magnetism coexisting with inhomogeneous nano-domain superconductivity was found in vicinity of $T_{c2} = 0.9$ K for ErRh_4B_4 ($T_{c1} = 8.8$ K) [5]. In Y_9Co_7 weak itinerant ferromagnetism ($T_c = 4.5$ K) was found to coexist with conventional superconductivity below $T_c \approx 2$ K [6].

Several years of intensive research generated a lot of experimental data and conclusions on the properties of ruthenocuprates, however, important questions remain open concerning the nature of the observed complex properties of these materials. This is so for both the intrinsic physical properties, and the nano-scale structural features which seem to play an important role in the determination of the properties.

The first simultaneous observation of superconductivity and the Ru ion magnetic order in a ruthenocuprate was published in 1997 for $\text{RuSr}_2\text{RE}_{1.4}\text{Ce}_{0.6}\text{Cu}_2\text{O}_{10-y}$ (RE is the rare earth ion Eu or Gd) [7]. This is the, so called, Ru1222-type phase (numbers reflect the number of metal atoms present in their distinct crystallographic positions per formula). Soon after, the muon spin rotation spectroscopy (μSR) experiments performed on $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ (the Ru1212-type phase) have confirmed the presence of bulk magnetic order below $T_m=133$ K in a sample, which was superconducting below 16 K [8,9]. The ferromagnetic-like and superconducting properties have been also reported for $\text{RuSr}_2\text{EuCu}_2\text{O}_8$ ($T_m = 132$ K, $T_c \leq 25$ K) [10,11,12], $\text{RuSr}_2\text{YCu}_2\text{O}_8$ ($T_m = 149$ K, $T_c \leq 39$ K) [13], and $\text{RuSr}_2\text{RECu}_2\text{O}_8$ for RE = Dy, Ho, Er [14,15].

II. CRYSTAL STRUCTURE

The crystal structure of $\text{RuSr}_2\text{RECu}_2\text{O}_8$ is similar to that of the $\text{YBa}_2\text{Cu}_3\text{O}_7$ superconductor where Cu-O chains are replaced with RuO_2 layers leading to the octahedral coordination of Ru with oxygen ions. The structure has tetragonal symmetry. In analogy to $\text{YBa}_2\text{Cu}_3\text{O}_7$, the RuO_2 layers can be regarded as a charge reservoir for the CuO_2 planes, whose electrons form electronic bands responsible for the superconducting condensate. Synchrotron X-ray diffraction studies of $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ have shown that the RuO_6 octahedra are rotated around the c axis (of the elementary cell) and slightly tilted off this axis forming structural domains with characteristic sizes between 5 and 20 nm [16]. So far the only report on Ru1212-type monocrystals (with maximum $T_c^{\text{on}} = 54$ K) points to an anisotropic layered structure with Josephson junctions formed in stacks along the crystallographic c axis [17, 18]. Figure 1 shows a schematic representation of crystal structures of the two main phases discussed in this review: $\text{RuSr}_2\text{RECu}_2\text{O}_8$ (Ru1212) and $\text{RuSr}_2\text{RE}_{2-x}\text{Ce}_x\text{Cu}_2\text{O}_{10}$ (Ru1222).

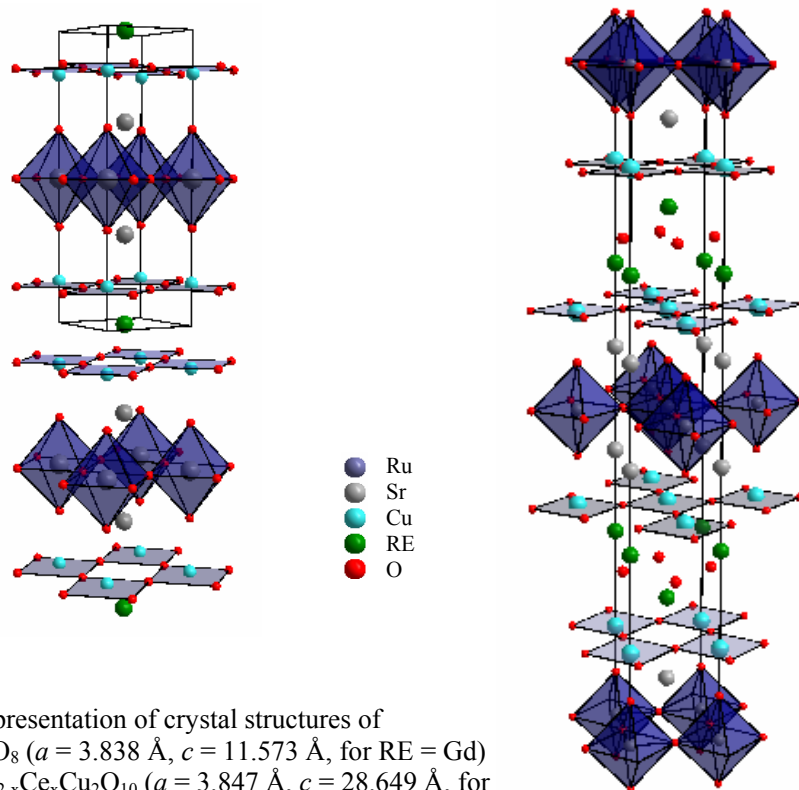


Fig.1. Schematic representation of crystal structures of $\text{RuSr}_2\text{RECu}_2\text{O}_8$ ($a = 3.838$ Å, $c = 11.573$ Å, for RE = Gd) and $\text{RuSr}_2\text{RE}_{2-x}\text{Ce}_x\text{Cu}_2\text{O}_{10}$ ($a = 3.847$ Å, $c = 28.649$ Å, for RE = Gd) compounds.

III. MAGNETIC ORDER AND PROPERTIES OF Ru1212 PHASE

The μSR spectroscopy experiments performed on polycrystalline samples show that the magnetic order remains homogeneous at microscopic scale and that it is not detectably altered at the temperature of superconducting transition [9]. However, the type and detail of this ordering remains a subject of discussion. Results of the detailed investigations by neutron

powder diffraction (NPD) of both $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ and $\text{RuSr}_2\text{EuCu}_2\text{O}_8$ samples suggest the G-type antiferromagnetic (AFM) order with the magnetic moment per Ru ion in the c axis direction of approx. $1.2 \mu_B$ [13,19,20,21]. The analyses have been performed assuming single valence state, i.e. also the magnetic moment, for all Ru ions. The NPD data allowed only for small presence (up to $0.1 \mu_B$) of the ferromagnetic (FM) component [19]. To explain the observed macroscopic ferromagnetic characteristics, the canted alignment of the Ru spins has been proposed [20,21]. Magnetic field dependencies of the dc magnetisation in the ordered state show the FM-like hysteretic behavior with the magnetic remanence up to approx. 2% of the high field values and the coercive field up to 400 Oe. The Curie –Weiss dependence in the paramagnetic regime lead to positive values of the Curie temperature Θ indicating a ferromagnetic character of Ru spin interactions and $m_{\text{eff}}(\text{Ru}) \approx 3.2 \mu_B$ [12]. X-ray absorption near edge spectroscopy (XANES) experiments reveal presence of a comparable amount of Ru^{4+} and Ru^{5+} ions [22]. The mixed valence of Ru also has been seen in the nuclear magnetic resonance (NMR) experiments [23-27]. Interpretation of the NMR measured at different values of the external field led to the model of the AFM type-I structure with the Ru moments ferromagnetically aligned within RuO_2 planes and with substantial magnetic anisotropy between a - b and c crystallographic directions [27]. The analysis also suggests the reorientation type transition for values of the magnetic field much lower than the H_{c2} parameter. An interesting problem which appears unsolved is how to understand simultaneous presence of the itinerant-like Ru^{4+} and localized-like Ru^{5+} signals in the NMR spectrum. A discussion of the NMR and NPD experiments in context of ruthenocuprates for there considered phase separated structure consisting of FM and AFM domains has been presented in [28]. Recent measurements of the magnetization of $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ at high pulsed magnetic fields (up to 47 T) lead to estimation of the Ru moment at higher value of $1.8 \mu_B$ [29]. The ratio of Ru^{5+} : Ru^{4+} is there estimated at 87%:13%, which leads to an average Ru moment as expected for $p = 0.065/\text{Cu}$, where p is the effective charge doped per single Cu ion, which would depend on amount of charge transfer between Ru sublattice and CuO_2 planes. One should note, however, that earlier reports were providing quite different values of the p parameter: XANES data led to $p \approx 0.2/\text{Cu}$ [22], substantially larger than $p \approx 0.07/\text{Cu}$ also estimated from the transport measurements, and $p \approx 0.4/\text{Cu}$ was estimated based on measured Cu-O bond lengths in the crystal structure [16].

IV. SUPERCONDUCTING PROPERTIES OF Ru1212 PHASE

For many of the reported $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ samples, temperature onset of the superconducting transition, as well as the temperature at which material attains zero resistivity, remain quite dependent upon the conditions of the synthesis. There also have been reported non-superconducting samples of the $\text{RuSr}_2\text{GdCu}_2\text{O}_8$, synthesized at slightly different conditions [3,30,31]. It is worth to note that temperature of the magnetic transition of Ru sublattice in superconducting $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ is always slightly lower than for its non-superconducting counterpart. This feature has been discussed in [30], and recently further supported by results presented in [32]. Among several metal-substituted $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ phases, modest rise of T_c was reported for partial substitution of Sn^{4+} into the Ru position [33]. When compared with lowering of T_c by partial substitution of Nb^{5+} into the same crystallographic position (both substitutions diminish ordering temperature for Ru sublattice), maximum T_c to be achieved in the ruthenocuprate was estimated to be $65 \text{ K} \pm 10 \text{ K}$ [33].

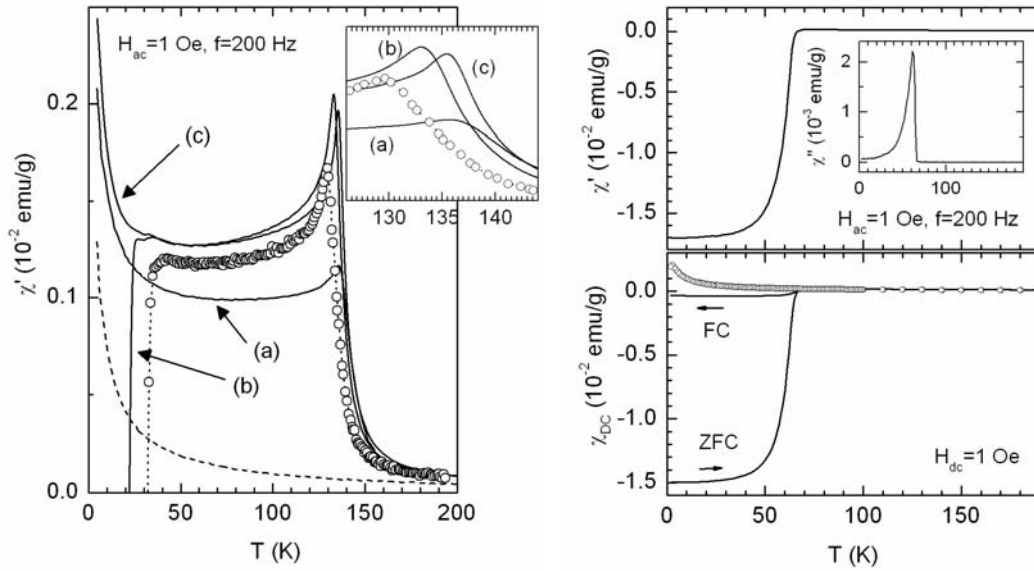


Fig.2. Magnetic and superconducting transitions for the Ru1212-type compounds. Left – real component of *ac* susceptibility (only positive part shown) of $\text{RuSr}_2\text{GdCu}_2\text{O}_8$: (a)→(b)→(c) represent the sequence of annealings which convert the same material from non-superconducting (*NSC*) to superconducting and then again to *NSC*; open circles: other sample after annealing in 600 bar of oxygen; dashed line: paramagnetism of $\text{GdBa}_2\text{Cu}_3\text{O}_{6.2}$. Right – *dc* magnetisation and *ac* susceptibility of $\text{Ru}_{0.5}\text{Sr}_2\text{GdCu}_{2.5}\text{O}_{8-y}$: lines represent sample synthesized in 600 bar of oxygen, open circles: same sample subsequently annealed in Ar flow at 650 °C. [30,35]. Symbols *FC* and *ZFC* refer to the *field cooled* and *zero field cooled* regimes of *dc* magnetisation, respectively. In the *FC* regime, magnetisation is measured on cooling in external magnetic field. In the *ZFC* regime the material is cooled down in absence of the external field, then the field is applied and magnetisation is measured on warming (upon application of the field at low temperature then induced superconducting currents can effectively screen whole volume of the sample, what precludes from concluding on a bulk Meissner state based on the *ZFC*-type of measurement).

Interestingly, there have been reported substituted compounds $\text{Ru}_{1-x}\text{Sr}_2\text{RECu}_{2+x}\text{O}_{8-y}$ ($\text{RE}=\text{Gd}, \text{Eu}, x < 0.7$), which were synthesized at high pressure of oxygen and for which the onset of the superconducting T_c reached as high as 72 K [34, 30]. Figure 2 presents relevant superconducting transitions for $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ [30] and $\text{Ru}_{0.5}\text{Sr}_2\text{GdCu}_{2.5}\text{O}_{8-y}$ [35], for which sequences of annealing were applied to change properties from the non-superconducting to superconducting, and again to non-superconducting [30]. Whereas no detectable difference in oxygen concentration was found between non-superconducting and superconducting samples of $\text{RuSr}_2\text{GdCu}_2\text{O}_8$, the case of $\text{Cu} \rightarrow \text{Ru}$ substituted phases seems to be different. The oxygen content was there reported to reversibly change during post synthesis annealing at ambient pressure, which causes simultaneous change of T_c [30]. It resembles the well known effect of the oxygen-concentration-driven modification of T_c in $\text{REBa}_2\text{Cu}_3\text{O}_{7-y}$ superconductor. The details of this effect for ruthenocuprates remain to be investigated. For the $\text{Cu} \rightarrow \text{Ru}$ substituted phases the muon spin rotation spectroscopy evidenced bulk magnetic order at low temperatures with the onset temperature increased for the non-superconducting sample of same cation composition. [30,35].

V. STRUCTURAL MODIFICATIONS AND PROPERTIES of the Ru1212 PHASE

In further discussion of the properties of parent $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ one should note important role of local scale modifications of the crystal structure. Such modifications seem to readily occur in this compound in form of vacancies or interstitial defects in transition metal sublattices. It was pointed out in [30,29] that detailed knowledge of the compositional and structural uniformity, as influenced by differing routes of material processing, may remain crucial to understand differences in superconducting and magnetic behavior. There also seems to exist a rationale for further investigation of the $\text{Cu} \rightarrow \text{Ru}$ substituted phases for them being candidates to include in models for nano-scale structural inhomogeneities discussed for parent compound [28,29]. Recently published detailed investigation of the sample of superconducting and ferromagnetic $\text{RuSr}_2\text{GdCu}_2\text{O}_8$, by means of high-resolution transmission electron microscopy (HRTEM) and high-resolution scanning transmission microscopy [36], analyzes local modifications present in the crystal structure. Authors conclude that the crystal structure is inhomogeneous and at nano-scale is built of two phases, which formulas are $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ and $\text{RuSr}_4\text{Gd}_2\text{Cu}_3\text{O}_{15-y}$, latter being described as periodic alteration of CuO_4 planes and RuO_6 octahedra along c axis, by $\text{Ru} \rightarrow \text{Cu}$ substitutions occurring in the host matrix. The 90° rotations and anti-phase boundaries were also mapped. An earlier investigation of the local crystal structure of $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ by selected area electron diffraction (SAED) shows presence of superstructure [16]. Results of electron diffraction and high resolution electron microscopy reported in [37] for $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ ($T_c \approx 20$ K) and $\text{RuSr}_2\text{Gd}_{1.5}\text{Ce}_{0.5}\text{Cu}_2\text{O}_{10-y}$ ($T_c \approx 43$ K) conclude for both samples the presence of nano-size domains along c axis, which are created by different ordering of rotated RuO_6 octahedra. HRTEM analysis for $\text{RuSr}_2\text{EuCu}_2\text{O}_8$, which we performed, confirms the presence of 90° domains (Fig.3, left side picture) and also reveals shear plane faults with displacement vector $1/6\langle 332 \rangle$, which should result in local Ru, Cu and O ion deficiencies and discontinuity of propagation of the Ru-O slabs in the structure (Fig.3, right side picture) [38].

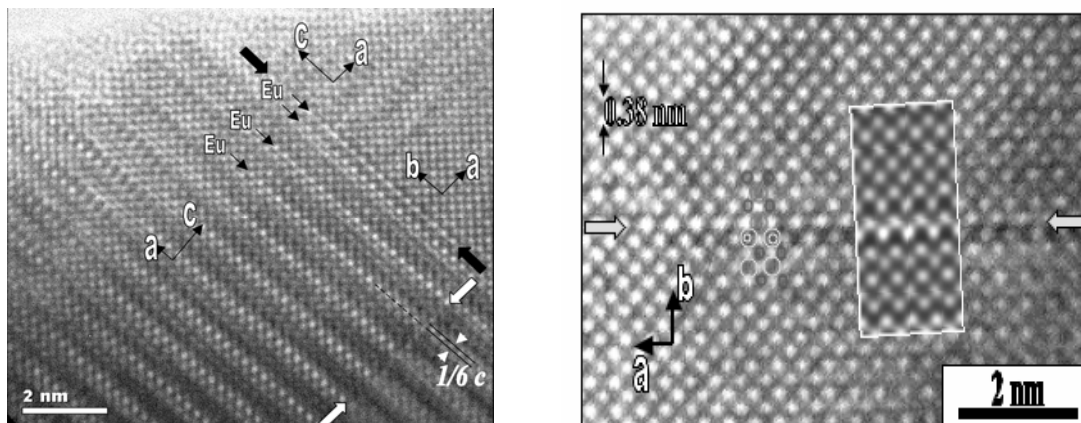


Fig.3. HRTEM images of $\text{RuSr}_2\text{EuCu}_2\text{O}_8$: left - 90° domain boundaries, right - crystallographic shear plane fault (central inset presents the result of simulation for the $1/6\langle 332 \rangle$ displacement vector, which is embedded in appropriate part of the image) [38].

In the current discussion of the properties of ruthenocuprates which tends to focus on compounds of highest available structural quality, reservations have been voiced with regard to the volume character of observed superconductivity. Detailed measurements of the dc magnetisation discussed in [39] are interpreted as confirming the presence of Meissner effect

and suggesting existence of a spontaneous vortex phase (SVP) in the temperature range immediately below the onset of superconducting transition. However, analysis of the temperature dependencies of field cooled (*FC*) *dc* magnetisation at low temperatures that was measured with use of the moving sample magnetometer, leads to conclusion that the observed diamagnetic-like signal is rather caused by presence of the magnetic field profile along path of the sample. Nevertheless, granular character of polycrystalline samples, which were investigated, precluded authors from concluding on lack of a Meissner state [40].

VI. THE STRUCTURE AND PROPERTIES OF THE Ru1222 PHASE

Second class in family of ruthenocuprates are the compounds described with formula $\text{RuSr}_2\text{RE}_{2-x}\text{Ce}_x\text{Cu}_2\text{O}_{10-y}$ (RE = Eu or Gd). Crystal structure of these compounds is similar to the structure of Ru1212-type. The difference is that instead of single RE layer embedded in between two Cu-O planes, there is a $(\text{RE}_{2-x}\text{Ce}_x)\text{O}_2$ fluorite-type layer and then part of the structure above it is shifted by vector $(\frac{1}{2}, \frac{1}{2}, 0)$ in respect to the part below (see Fig.1). The fluorite-type layer supports variable oxygen occupancy, which is denoted with parameter *y* in the formula. Disordered rotations and tilts of the RuO_6 octahedra were also mapped for $\text{Gd}_{2-x}\text{Ce}_x\text{RuSr}_2\text{Cu}_2\text{O}_{10}$, $x=0.5, 0.7$ samples, by synchrotron x-ray diffraction and neutron diffraction for $x=0.7$ [41]. Temperature dependencies of the *dc* magnetisation indicate that magnetic properties of these compounds are more complex than those of $\text{RuSr}_2\text{RECu}_2\text{O}_8$. There are two characteristic temperatures $T_m > T_{\text{irr}}$ (for solid solution $\text{Eu}_{2-x}\text{Ce}_x\text{RuSr}_2\text{Cu}_2\text{O}_{10-y}$ reported in the range $T_{\text{irr}} = 80 \text{ K} - 125 \text{ K}$ and $T_m = 160 \text{ K} - 215 \text{ K}$ [42,43]), which are introduced for description of magnetic ordered state. For temperatures below T_{irr} the *dc* magnetisation is strongly field hysteretic, which was interpreted as a weak ferromagnetic property of the compound. Below T_{irr} , there is substantial *FC-ZFC* (field-cooled vs. zero-field cooled) temperature irreversibility, especially observed at small value of the magnetic field. Beyond the ferromagnetic domain effect at low temperatures, the *dc* magnetisation reflects contribution from a diamagnetic response of the superconducting phase, which is induced in Ru1222-type at suitable Ce and oxygen concentration [42,41]. For $\text{RuSr}_2\text{Gd}_{1.5}\text{Ce}_{0.5}\text{Cu}_2\text{O}_{10}$ the maximum $T_c^{\text{on}} \approx 52 \text{ K}$ was reported in [44]. The coercive field decreases to zero at T_{irr} and reappears at temperatures between T_{irr} and T_m with significantly smaller value [43]. The upper characteristic temperature, T_m , which marks initial increase of magnetisation, is also dependent on both Ce and oxygen concentration. For $\text{Eu}_{2-x}\text{Ce}_x\text{RuSr}_2\text{Cu}_2\text{O}_{10-y}$, for x changing from 0.5 to 1.0, T_m was reported to increase from 125 K to 165 K, and for $x = 1$ sample was found to change from 165 K to 215 K after depleting oxygen from the structure [42]. The specific heat anomaly reported at T_c for superconducting $\text{Gd}_{1.4}\text{Ce}_{0.6}\text{RuSr}_2\text{Cu}_2\text{O}_{10-y}$ was interpreted as confirming volume character of superconducting phase [45]. It remains open, however, if it is a common feature for all of the Ru1222-type ruthenocuprates, for which superconducting phase was reported. XANES spectroscopy, unlike its results for $\text{RuSr}_2\text{GdCu}_2\text{O}_8$, reveals only single 5+ valence state of Ru [46,47]. It appears to limit possible ways for realization of charge doping. This is further discussed in [41] where synchrotron x-ray diffraction and magnetisation experiments for $\text{Gd}_{2-x}\text{Ce}_x\text{RuSr}_2\text{Cu}_2\text{O}_{10-y}$ led authors to conclude that charge doping in Ru1222-type structure is caused by varying oxygen content and Ce substitution, but not by the Cu/Ru bands overlap, as it has been suggested for $\text{RuSr}_2\text{GdCu}_2\text{O}_8$.

Complex macroscopic characteristics of magnetic and superconducting states of Ru1222-type phase called for investigation of spatial homogeneity of the materials and consideration of phase separation effects of either structural or electronic origin. Recent investigation of magnetic and superconducting $\text{RuEu}_{1.4}\text{Ce}_{0.6}\text{Sr}_2\text{Cu}_2\text{O}_{10}$ by means of muon spin

rotation spectroscopy (μ SR) provides analysis of volume character of there observed internal magnetic field in broad range of temperatures [48]. It was shown that in temperature range $T_{\text{irr}} < T < T_m$ the magnetic phase accounts only for approximately 15% of the sample volume. The result seems to confirm presence of magnetic clusters in single crystallites of the compound, because the estimation of maximum amount of impurity phases present in this sample led to a considerably smaller volume. Such scenario for phase separation was proposed in [49]. An alternative may be the presence of inclusions of other structurally related magnetic phase, which could be dispersed at nano-scale in a whole volume of the grain. A candidate phase is the Sr(Ru,Cu)O₃ perovskite, which was brought up in [43]. The μ SR data for this sample, for temperatures below 77.6 K which also marks sudden drop in *ZFC* magnetisation, reveals presence of magnetism in a whole volume. Since the sample is superconducting below approximately 40 K, below this temperature the μ SR data seems to indicate coexistence of superconductivity with magnetism. It should be noted, however, that properties of some of reported samples may differ and we should very cautiously build a universal picture. Recent detailed analysis of neutron powder diffraction and polarized neutron transmission data collected for superconducting ($T_c = 35$ K) RuSr₂Eu_{1.2}Ce_{0.8}Cu₂O₁₀ interprets there found magnetic signals as originating not in the main Ru1222-type phase, although complexity of the sample did not allow to relate the signal to particular minority phases. [50].

VII. CONCLUDING REMARKS

The research literature for Ru1212- and Ru1222-type ruthenocuprates is so extensive that only a part of published results could be mentioned in the review. Several important questions concerning the observed properties of these compounds remain open. The unusual superconducting characteristics leave us with interesting possibility of creation of a spontaneous vortex phase, which seems to await further experimental clarification. A rationale exists to investigate details of the magnetically ordered state. Recent results of investigation of nano-scale structural features refocus our attention on the role of anti-site doping and metal atom deficiencies resulting in nano-scale features, possibly spatially ordered, rather than on the uniformly defect structural matrix. Such features could selectively support superconducting condensate and alter the anisotropy of magnetic interactions. Proposed phase separation scenarios would need to be evaluated within this framework.

Our insight into properties of ruthenocuprates could be made far more complete via experiments on suitable single crystals, which, unfortunately, are not readily available. Selected parent and doped compounds, which were already investigated for modification of magnetic and superconducting states, seem to remain a quite unexplored area for research. Interesting possibility was recently presented by A. Mclaughlin *et al.* with the μ SR and neutron diffraction results [51]. They claimed to reveal the effect of Ru-induced magnetic order in the Cu ion subsystem for Ru1222-type compounds for hole doping in the range: $p = 0.02 - 0.059$, *i.e.* at a verge of the superconducting state. Low temperature magnetic order observed with the μ SR for selected compositions of Ru_{1-x}Sr₂RECu_{2+x}O_{8-y} phases also seem interesting for further research [30 and therein].

Acknowledgements

The author would like to acknowledge an opportunity to contribute in collaborative research in subject of the article with several research groups in Europe and in the US. Sincere thanks

are due to Prof. Jan Klamut for valuable discussions, and to Prof. Joe Budnick for his critical reading of the manuscript.

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