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Formation and mobility of oxygen vacancies in $RuSr_2GdCu_2O_8$

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Oxygen vacancies are introduced in the RuO_2 and possibly CuO_2 planes of $RuSr_2GdCu_2O_8$ by annealing in vacuum above 600 K. The diffusive jumps of the O vacancies are accompanied by a reorientation of the local distortion, and are probed by measuring the elastic energy loss and modulus versus temperature at 1–10 kHz. An intense acoustic absorption peak develops near 670 K at 1 kHz and finally stabilizes after heating up to 920 K in vacuum. The analysis of the peak shows a barrier for the O diffusion of $\simeq 1.4$ eV, and a slowing down of Curie-Weiss type, with $T_C = 400-470$ K, due to the interaction among the O vacancies. A secondary peak is attributed to O vacancies trapped at defects in the RuO_2 planes, or to vacancies in the CuO_2 planes. No sign of structural phase transformation is found up to 920 K.

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I. INTRODUCTION

The ruthenocuprates are a relatively new class of high-T_C superconductors,[1] which is attracting much interest for the apparent coexistence of ferromagnetism and superconductivity.[2] In spite of a considerable experimental activity on these compounds, and notably on $RuSr_2GdCu_2O_8$ (Ru-1212), there are still several obscure points regarding their preparation and characterization, and it turns out that nominally identical samples may or may not be superconducting, depending on subtle details of the preparation process.[3] The O stoichiometry is considered as a possible source of nonuniform properties from sample to sample, but there is a great variety of results regarding the influence of the preparation on the O stoichiometry. Some studies find that the annealing at high temperature in vacuum or inert atmosphere causes considerable O deficiency,[1,4] while others find no influence at all[5,6] even up to 800 °C.[7] It has then proposed that the prolonged annealings affect the cation ordering,[8] the grain boundaries,[3] or the microstructure.[9] It seems that granularity has an important role,[6] since the near coincidence of the lattice parameters a, b, and $c/3$ results in the formation of small domains with c in any of the three almost equivalent directions. Therefore, some authors attribute the improvement in superconducting properties following long high-temperature anneals to increases in domain size, rather than change in cation composition or O content.[10] The possibility of a broad range of O stoichiometry would have implications regarding the amount of doping of the CuO_2 planes. In fact, from both bond valence sum calculations[10] and x-ray absorption spectroscopies[11] it is found that the Ru cations in Ru-1212 exhibit mixed valence Ru^{4+}/Ru^{5+}, with $[Ru^{4+}] = 0.4 - 0.5$. The fraction of Ru^{4+} is considered to be responsible for the doping of the CuO_2 planes, with $p = \frac{1}{2}[Ru^{4+}]$, due to the relative Cu/Ru stoichiometry. The value $p = 0.2 - 0.25$ deduced in this way, however, is much larger than that deduced from transport experiments, suggesting that most carriers are trapped by defects or by the ferromagnetic order.[10]

In the present work we address the issue whether O vacancies may be present in Ru-1212 by anelastic spectroscopy measurements. Such a technique is particularly suited, since, similarly to the well known case of $YBa_2Cu_3O_{6+x}$, an O vacancy in the RuO_2 or CuO_2 plane of Ru-1212 creates an anisotropic strain that reorients by 90° after a jump; therefore, the diffusive motion of the O vacancies gives rise to a well detectable anelastic relaxation effect.

II. EXPERIMENTAL

Polycrystalline samples of composition $RuSr_2GdCu_2O_8$ have been synthesized by solid state reaction of high purity stoichiometric powders of RuO_2, Gd_2O_3, CuO, and $SrCO_3$, following a well established procedure described in previous works.[12,13] The final step, aging at 1070 °C in flowing O_2 for one week followed cooling at 50 °C/h, resulted in the formation of a sintered ingot that was cut into bars. Some samples have been characterized structurally by x-ray powder diffraction and by magnetic susceptibility in a Quantum Design SQUID magnetometer. The superconducting transitions presented the two step behavior typical of granular high-T_c superconductors, with intragrain onset at $T = 45$ K and the intergrain one at $T = 19$ K. Figure 1 shows the field cooled and zero field cooled magnetization curves measured in a field of 0.55 mT, as described in Ref. 12. The anelastic measurements were made on a bar of $49.5 \times 4.8 \times 0.58$ mm^3.

The complex Young's modulus $E(\omega) = E' + iE''$, was measured as a function of temperature by suspending the bar on thin thermocouple wires and electrostatically exciting its flexural modes. The frequencies $\omega_i/2\pi$ of the first three odd flexural modes are in the ratios 1:5.4:13.3 with $\omega_1/2\pi \sim 0.8$ kHz, and are related to the real part of the Young's modulus through $\omega_i = \alpha_i \sqrt{E'/\rho}$, where α_i is a geometrical factor and ρ the mass density. The elastic energy loss coefficient, or the reciprocal of the mechanical quality factor,[14] is $Q^{-1}(\omega,T) = E''/E' = S''/S'$, where $S = S' + iS'' = E^{-1}$ is the elastic compliance; the Q^{-1} was measured from the decay of the free oscillations or from the width of the resonance peak.

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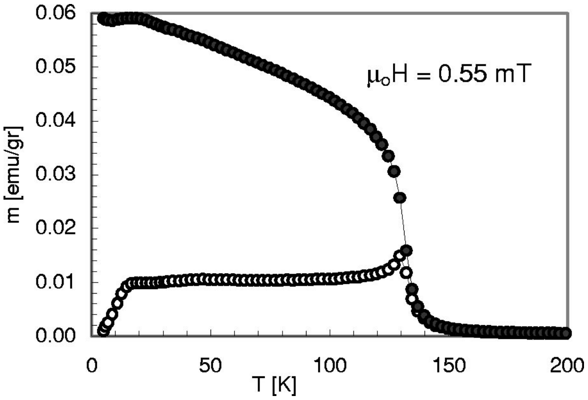

FIG. 1. Field cooled (closed circles) and zero field cooled (open circles) magnetization of an as-prepared sample at an external field of 0.55 mT.

An elementary relaxation process, such as the hopping of an O atom or vacancy with rate τ^{-1}, contributes to the imaginary part of the compliance with[14]

$$\delta S''(\omega,T)=\frac{cv_0(\lambda^{(2)}-\lambda^{(1)})^2}{2k_BT}\frac{\omega\tau}{1+(\omega\tau)^2}, \tag{1}$$

where $\lambda^{(i)}$ is the elastic dipole of the defect in configuration i: $c\lambda^{(i)}$ is the anelastic strain due to a homogeneous distribution of defects with molar concentration c, all in the ith configuration. Considering the relaxation from O atoms or vacancies in the RuO_2 or CuO_2 planes, and at first neglecting the small rotation of the RuO_6 octahedra about their c axis,[6,10] there are only two orientations $i=1,2$ of the elastic dipole, depending whether the O atom or vacancy (V_O) has the nearest neighboring Ru/Cu atoms along the y or x direction [corresponding to the O(1) and O(5) sites in YBCO (Ref. 15)]. The upper part of Fig. 2 shows a projection of the unrotated O octahedra on the ab plane with the two possible types of V_O; a and b are chosen following Ref. 6, while the x and y directions are at 45°, parallel to the Ru-O bonds. Strain is a centrosymmetric second rank tensor,[16] and can therefore be represented as an ellipsoid with the principal axes representing the deviations of the lengths with respect to the reference unstrained sphere (dotted circles).[17] The ellipsoids in Fig. 2 represent contractions around the V_O, more pronounced along the directions of the nearest neighbor Ru atoms. The lower part of the figure includes the (slightly exaggerated) rotations of the octahedra; the symmetry of the elastic dipoles, however, remains unaltered, as can be seen from the mirror planes passing through the V_O, which are still perpendicular to the x or y directions. Analogously to the case of YBCO,[18] if we call $\lambda_1=\lambda_{xx}^{(1)}$ and $\lambda_2=\lambda_{yy}^{(1)}$, then it is $\lambda_{xx}^{(2)}=\lambda_2$ and $\lambda_{yy}^{(2)}=\lambda_1$, while $\lambda_{zz}^{(1)}=\lambda_{zz}^{(2)}$ and $\lambda_{\mu\nu}^{(i)}=0$ for $\mu\neq\nu$. The anelastic strain associated with an O jump is therefore $\varepsilon_1-\varepsilon_2$, and causes relaxation of the $\delta(S_{11}-S_{12})$ compliance, with $\lambda_1-\lambda_2$ entering into Eq. (1); the factor 1/2 in that expression is appropriate for the case of a $\langle 100\rangle$ orthorhombic elastic dipole in a tetragonal crystal.[14] The above expression is peaked at $\omega\tau=1$, and since the measurements are made at the resonance frequencies ω_i as a function of temperature, one finds peaks at the temperatures T_i such that $\omega_i\tau(T_i)=1$. Therefore, measurements at different frequencies provide the temperature dependence of the rate $\tau^{-1}(T)$, which generally follows the Arrhenius law

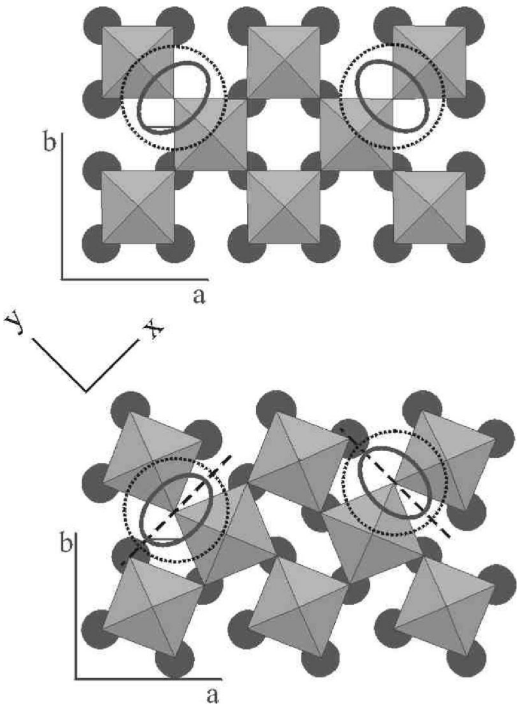

FIG. 2. Upper part: view of the RuO_2 plane with the RuO_6 octahedra put in evidence (the apical O atoms are not shown). The ellipsoids represent the elastic dipoles associated with the O vacancies. Lower part: the same view with the octahedra rotated about their c axes.

$$\tau^{-1}(T)=\tau_0^{-1}\exp(-W/k_BT), \tag{2}$$

where W is the energy barrier for the O jump. Assuming that E' and S' are almost constant over the temperature range in which the peak is observed, Eq. (1) describes also the peaks in $E''(\omega,T)$ and $Q^{-1}(\omega,T)$:

$$Q^{-1}\simeq\Delta\frac{\omega\tau}{1+(\omega\tau)^2}, \tag{3}$$

where the relaxation strength

$$\Delta(T)=\frac{\delta S''(0,T)}{S''}=\frac{cv_0(\lambda^{(2)}-\lambda^{(1)})^2}{S'k_BT} \tag{4}$$

corresponds to the static elastic susceptibility. A process characterized by a spectrum of relaxation times may be described by the Fuoss-Kirkwood distribution of relaxation rates,[14] yielding for the frequency dispersion factor $[1+(i\omega\tau)^{\alpha}]^{-1}$ instead of $[1+i\omega\tau]^{-1}$; the imaginary part of the dispersion to be inserted into Eqs. (1) and (3) therefore becomes

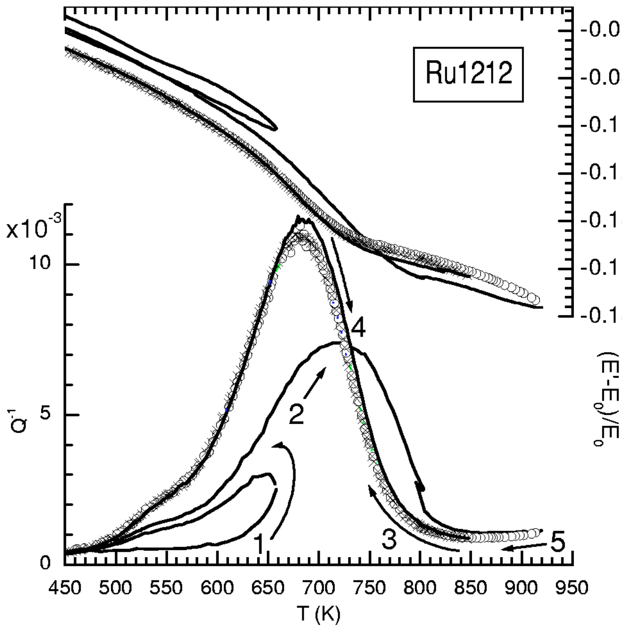

FIG. 3. Anelastic spectrum of Ru-1212 measured at 0.8 kHz during three heating and cooling cycles, in the sequence indicated by the numbers. Lower panel: elastic energy loss coefficient; upper panel: relative variation of the Young's modulus.

$$\frac{\omega\tau}{1+(\omega\tau)^2}\rightarrow\frac{(\omega\tau)^{\alpha}\sin\left(\frac{\pi}{2}\alpha\right)}{1+(\omega\tau)^{2\alpha}+2(\omega\tau)^{\alpha}\cos\left(\frac{\pi}{2}\alpha\right)}. \quad (5)$$

III. RESULTS

Figure 3 presents three measurement runs in vacuum up to 660, 850, and 920 K; the lower panel contains the elastic energy loss coefficient, while the upper panel contains the relative change of the Young's modulus, where $E_0 = E'(T=0)$ refers to the as prepared state. During the first heating the dissipation is low, and starts increasing above 600 K (curve 1). This increase is due to the formation of O vacancies, as confirmed by heating the same sample in a UHV system equipped with a residual gas analyzer; the trace of the O_2 partial pressure started increasing at 600 K, indicating that this is the temperature of the onset of massive O loss. During the subsequent heating (curve 2 at $2-3$ K/min) a $Q^{-1}(T)$ peak develops and becomes stable after heating above ~ 850 K. In fact, the $Q^{-1}(T)$ curve measured on cooling (curve 3, open circles) is retraced during the subsequent runs: curve 4 on heating is slightly higher, but curve 5 on cooling (crosses) perfectly coincides with curve 3. This means that no further loss of O occurs, at least up to 920 K in vacuum. This fact again is confirmed by outgassing the same sample in the UHV system, and noting that the O outgassing rate at 900 K drops by two orders of magnitude within 10 min. The amount of O loss has been estimated from the mass variation after oxygenation and outgassing treatments, and ranges between 2.2 and 3 % per formula unit after outgassing at 900–1000 K for less than 1 h.

From the perfect coincidence of the $Q^{-1}(T)$ curves 3 and 5 measured on cooling, also very close to curve 4 on heating, we conclude that curves 3–5 represent a situation very close to equilibrium and their analysis is meaningful. The $E'(T)$ curves reflect the behavior of the acoustic losses, with a negative step in correspondence to the absorption peak.[14] A transformation to a more symmetric structure where the rotation angle of the RuO_6 octahedra about their *c* axes goes to zero may be expected at high temperature,[6] but there is no trace of it from room temperature to 930 K. Such a transformation should appear in the $E'(T)$ curves as a jump, dip or change of slope.

IV. DISCUSSION

The formation of O vacancies in the RuO_2 and possibly CuO_2 planes in Ru-1212 should have analogies with the partial filling of the CuO_x planes in $YBa_2Cu_3O_{6+x}$. From the structural point of view the CuO_2 planes of Ru-1212 correspond to the CuO_2 planes of YBCO, which remain stoichiometric, while the RuO_2 planes of Ru-1212 correspond to the CuO_x planes of YBCO.[6] Based on this structural analogy, we assume that the O vacancies form mainly in the RuO_2 planes. It is also plausible that such planes may accommodate V_O, in view of the mixed valence displayed by Ru both in Ru-1212 (Ref. 11) and Ru-1222;[19,20] in the latter compound, the O stoichiometry seems to affect the Ru valence,[20] again supporting the hypothesis of V_O in the Ru planes.

A. Oxygen hopping in YBCO

The case of YBCO is complicated, since only half filling of the available O sites can be achieved, with the formation of parallel Cu-O chains in the ortho-I phase. A complex *x-T* phase diagram results, which can be reproduced, for example, introducing three different short range O-O interaction energies (the so called ASYNNNI model).[15,21] The diffusive jumps of the O atoms in the CuO_x planes in the ortho-I phase have been studied by anelastic relaxation,[22–24,18] finding that hopping occurs over a barrier of ~ 1.1 eV; it has also been shown that there are actually two additional distinct hopping rates, with smaller activation energies, for O atoms belonging to chains in the ortho-II and tetragonal phases[25,26] and for isolated O atoms.[25,27] In spite of the numerous investigations, the anelastic spectrum due to O hopping in YBCO has not been quantitatively explained in terms of microscopic parameters such as the elastic dipole associated to an O atom and the short-range O-O interaction energies, e.g., of the ASYNNNI model. Still, it has been shown that the relaxation strength (the static elastic susceptibility) exhibits a Curie-Weiss enhancement and the relaxation rate a critical slowing near the orthorhombic/tetragonal phase transformation,[18] corresponding to the ordering of O in the O(1) sublattice. The anisotropy of the elastic dipole in YBCO is found to be $|\lambda_1 - \lambda_2| \simeq 0.02$ from the dependence of the cell parameters *a* and *b* on the O content both in the orthorhombic and tetragonal phases.[28] The same information can hardly be obtained from anelastic measurements on ceramic samples, due to the heavy corrections necessary for the angular averaging of the elastic constants and the porosity of the samples.[29]

B. O vacancies and related defects in Ru-1212

The case of Ru-1212 should be simpler, since the RuO_2 planes remain close to the full stoichiometry even after prolonged outgassing; this can be described in terms of a deficiency δ in $RuO_{2-\delta}$ with $\delta<0.03$, as deduced from the mass variation after oxygenation/outgassing treatments. This means that one can consider the dynamics of isolated or at most paired O vacancies with small concentration $c=\delta$, instead of more complex chain structures. One can therefore treat the O vacancy exactly as an O atom in a nearly empty CuO_x plane, and with an elastic dipole $\lambda^V=-\lambda^O$.

A complication arises from the fact that the main peak at $\sim$670 K (1 kHz) is accompanied by a shoulder at $\sim$530 K, indicating that there are actually two distinct relaxation processes associated with V_O in Ru-1212. There are various explanations for two distinct relaxation processes associated with V_O. One is that V_O may form stable pairs with a binding energy $-E_b$; in that case, the reorientation of the vacancy pair would require its temporary dissociation and the corresponding relaxation rate should have an activation energy increased by E_b over the barrier for hopping of a simple V_O. The corresponding anelastic relaxation peak would appear at higher temperature, analogously to the case of the diluted interstitial O atoms and O pairs in $La_2CuO_{4+\delta}$.[30] The problem with this interpretation is that the peak at lower temperature in Fig. 3, which should be due to isolated V_O, has definitely a smaller intensity than the peak at higher temperature. At these low concentrations, $\delta<0.03$, one would expect on the contrary that the isolated V_O predominate over the V_O pairs, rendering this explanation unlikely.

Another possibility is that the peak at lower temperature is associated with the complex of a V_O with a defect, for example, a Cu atom substituting a Ru atom (Cu_{Ru}). The fact that the temperature of the Cu_{Ru}-V_O relaxation is lower than that of V_O may be understood in terms of a Cu_{Ru} environment providing a lower barrier for O hopping, in accordance with the observation that the barrier for O hopping in the CuO_x planes of YBCO is 1.1 eV, lower than the barrier associated with the main peak in Ru-1212 (see later on). Support to the hypothesis of the existence of Cu_{Ru} defects comes from the fact that $Ru_{1-x}Cu_xSr_2GdCu_2O_8$ with mixed $Ru_{1-x}Cu_xO_2$ planes can actually be synthesized and is superconducting.[31] In addition, superlattice spots in electron diffraction patterns of Ru-1212 have been interpreted in terms of domains with intermixed and ordered Cu/Ru ions in the nominal RuO_2 planes[32] or, alternatively, with ordering of mixed valence Ru^{4+}/Ru^{5+} ions.[32] The presence of the minor peak in the anelastic spectra may be accounted for by Cu_{Ru} defects dispersed at a concentration much smaller than that of the V_O, i.e., $<1\%$, and acting as trapping centers for few V_O, but also by the minority regions of mixed Cu/Ru or also Ru^{4+}/Ru^{5+} devised in Ref. 32. Note that Cu_{Ru} defects in the RuO_2 planes require an equal amount Ru_{Cu} in the CuO_2 planes, or the presence of impurity phases rich in Ru.

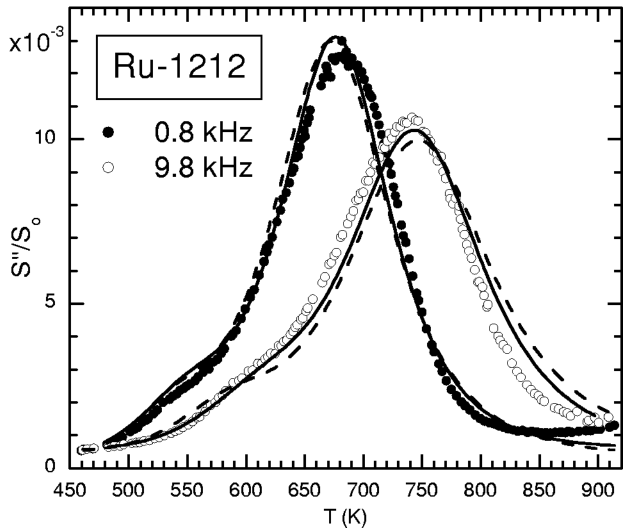

FIG. 4. Elastic energy loss of Ru-1212 measured during the last cooling cycle (curve 5 of Fig. 1), measured at two frequencies. The lines are fits as described in the text.

It is also possible to explain the minor peak in the anelastic spectra without invoking Cu/Ru intermixing, but supposing that V_O can form also in the CuO_2 planes of Ru-1212, at concentrations lower than in the RuO_2 planes. In this case the peak at lower temperature would be due to the minority of faster V_O in the CuO_2 planes. In what follows we will focus on the main peak.

C. Fit of the relaxation curves and Curie-Weiss response

Attempts to fit the main peak in terms of Eqs. (1)–(5) yield a mean relaxation rate with $\tau_0^{-1}\simeq 4\times10^{17}\ s^{-1}$ and $E=1.9$ eV, with a broadening parameter $\alpha=0.7$; such a value for τ_0^{-1} is too high for an O vacancy or any defect. In addition, it is impossible to reproduce the marked decrease of the peak intensity with increasing temperature (see the curve at higher frequency in Fig. 4). These features suggests a Curie-Weiss-like enhancement of the relaxation strength, as in YBCO,[18] due to the long range elastic interactions among the V_O. The effect of the long range elastic interaction among elastic dipoles has been treated in connection with the O atoms in YBCO (Ref. 18) and also the interstitial O atoms in bcc metals.[33,34] The interaction causes a tendency to cooperative alignment of the dipoles and results in a factor $(1-T_C/T)^{-1}$ that multiplies both the relaxation strength Δ and time τ, where $T_C\propto c(1-c)$ is the temperature below which the elastic dipoles at concentration c start aligning in a same direction. Note that the elastic dipoles can describe equivalently O atoms or vacancies, with opposite sign, and in the present situation it is natural to refer to vacancies. The relaxation process is then described by

$$dS''=S'\tilde{\Delta}\frac{\omega\tilde{\tau}}{1+(\omega\tilde{\tau})^2}, \qquad (6)$$

$$\tilde{\Delta}=\frac{cv_0(\lambda_1-\lambda_2)^2}{S'k_B(T-T_C)}, \qquad \tau'=\frac{\tau}{1-T_C/T}.$$

The divergence of the relaxation time on approaching T_C from above results in a $\tau^{-1}(T)$ that is steeper than Eq. (2), and therefore in a higher apparent energy barrier W and prefactor τ_0^{-1}, as presently observed. The divergence in the relaxation strength results in a peak intensity increasing more than as $1/T$ with decreasing T.

Figure 4 presents a fit with Eq. (6), without relying on the usual approximation that the elastic compliance S' or modulus E' and therefore also the resonance frequencies $\omega_i \propto \sqrt{E'}$ are constant. Therefore, instead of Q^{-1}, Fig. 4 reports $S''(\omega,T)/S_0 = Q^{-1}(\omega,T)S'(\omega,T)/S_0$ with $S_0 = S'(\omega,0)$ and $S'(\omega,T)/S_0 = [\omega_i(T)/\omega_i(0)]^{-1/2}$. This correction for the temperature dependence of the frequency and elastic compliance improves slightly the fit. The dashed curve is obtained with $W = 1.33$ eV, $\tau_0 = 1\times 10^{-14}$ s, $T_C = 460$ K for the main peak and $W = 1.4$ eV, $\tau_0 = 2\times 10^{-17}$ s, $\alpha = 0.63$ for the smaller peak. The fit is not perfect, but the main process can be described with very reasonable parameters; in addition, there is no need of introducing an additional broadening, since the theoretical curve has already the correct width. The introduction of broadening, e.g., through the Fuoss-Kirkwood distribution with Eq. (5), introduces the additional parameter α and allows slightly better fits to be obtained, such as the continuous curve with $W = 1.46$ eV, $\tau_0 = 1.1\times 10^{-15}$ s, $T_C = 470$ K, $\alpha = 0.82$ for the main peak and $W = 1.10$ eV, $\tau_0 = 2\times 10^{-14}$ s, $\alpha = 0.7$ for the smaller peak. A probable origin of the peak broadening is the high density of antiphase boundaries between domains with opposite senses of rotation of the octahedra.[10,6] It appears, however, that the introduction of a broadening is not the main ingredient for improving the accordance of the data with the Curie-Weiss expression (6); possibly the mean field treatment[33] of the interactions among the elastic dipoles is not adequate, or some changes of the electronic or structural properties of Ru-1212 make the barrier for O hopping temperature dependent, over a wide range of temperature (500–900 K) where the peak is observed. For example, the angle of rotation of the RuO_6 octahedra about their c axes has been found to decrease almost linearly when temperature increases from 0 to 300 K,[6] and it might well continue decreasing at higher temperatures. Still, from the fits shown in Fig. 4 and others not reported here, it appears that the main peak is due to hopping of the O vacancies with an activation energy of 1.3–1.4 eV; in addition, there is considerable critical slowing of the hopping dynamics and enhancement of the elastic susceptibility on approaching an ordering temperature $T_C = 400-470$ K. The ordering would consist in the preferential occupation of sites of one type, namely, with the nearest neighbor Ru atoms along either x or y (see Fig. 2), and would result in a slightly orthorhombic cell. It would be similar to the tetragonal-to-orthorhombic transformation in YBCO, where O occupies preferentially the O(1) instead of the O(5) sites, but not necessarily with the formation of chains of vacancies. The minor relaxation at lower temperature is almost completely masked by the main relaxation process, and the fit does not yield reliable values of the parameters.

D. Relaxation strength and comparison with YBCO

A reliable estimate of the shape factor $|\lambda_1 - \lambda_2|$ of the elastic dipole tensor associated with an O vacancy cannot be done at present. In fact, Eq. (1) refers to a single crystal excited on pure $\varepsilon_1 - \varepsilon_2$ mode, while a ceramic sample requires averaging of the elastic constants over the solid angle and corrections due to porosity.[29] The same is true for YBCO, were the shape factor can be estimated from the structural data at different O contents ($|\lambda_1 - \lambda_2| = 0.19$ in Ref. 28 or 0.25 from the data in Ref. 35). A comparison between Ru-1212 and YBCO in the ortho-I phase[18,22–25] shows that the peaks due to O hopping have comparable intensities in both materials. This may at first indicate that Ru-1212 has much larger $|\lambda_1 - \lambda_2|$ than YBCO, since in the present case the concentration of elastic dipoles is <0.03 (the concentration of vacancies), while in $YBa_2Cu_3O_{\sim 6.9}$ the molar concentration of mobile O atoms or vacancies is ~ 1. It should be considered, however, that in the case of orthorhombic YBCO, the O atoms jump between sites that are energetically inequivalent, and this reduces the relaxation strength by a factor[36] $4n_xn_y$, where n_x and n_y are the equilibrium fractions of occupied sites of type x or y; in the ortho-I phase it is $n_x \ll n_y$ and therefore $n_xn_y \ll 1$. The relatively small amplitude of the peak in the ortho-I phase of YBCO should therefore be attributed to this effect; indeed, the relaxation strength reaches values as high as 1 near the tetragonal-to-orthorhombic transition of YBCO,[18] where $n_x \simeq n_y \simeq 1/2$.

An estimate of the order of magnitude of $|\lambda_1 - \lambda_2|$ in Ru-1212 can be made as follows: the polycrystalline average of the reciprocal Young's modulus E^{-1} assuming uniform stress from grain to grain of a tetragonal crystal (a different approximation would be that of uniform strain), is[14,16]

$$\langle E^{-1}\rangle = \frac{1}{5}(2S_{11}+S_{33}) + \frac{1}{9}(2S_{44}+S_{66}+4S_{13}+2S_{12}), \tag{7}$$

of which only $\delta(S_{11}-S_{12})$ relaxes according to Eq. (1); therefore[37] $\delta\langle E^{-1}\rangle = \frac{4}{45}\delta(S_{11}-S_{12})$ and, assuming that the porosity affects in the same way $\delta\langle E^{-1}\rangle$ and $\langle E^{-1}\rangle$, the relaxation strength becomes (including the Curie-Weiss correction)

$$\Delta = \frac{\delta E^{-1}}{E^{-1}} = \frac{2}{45E^{-1}}\,\frac{cv_0}{k_B(T-T_C)}(\lambda_1-\lambda_2)^2. \tag{8}$$

The effective Young's modulus of our sample was $E \sim 40$ GPa (the low value is due to a porosity of nearly 50%), $v_0 = 170$ Å^3 and assuming $c = 0.02$, and $\Delta = 0.022$ at 680 K from the fit of Fig. 4 with $T_C = 460$ K, we find $|\lambda_1 - \lambda_2| \simeq 0.10$. There are several sources of error in such an estimate, from the polycrystalline average to the V_O concentration, but 0.1 is a very reasonable value for the shape factor of the V_O; it is $4-5$ times larger than the value estimated for YBCO, but $5-10$ times smaller than the shape factor of interstitial O, N and C atoms in bcc metals.[14] It can be concluded that the high-temperature relaxation processes in Ru-1212 can consistently be interpreted in terms of hopping of V_O, with a shape factor somewhat larger than in YBCO.

E. Possible influence of the O vacancies in the transport properties of Ru-1212

The flat high-temperature anelastic spectrum of Ru-1212, after the initial oxygenation treatment, indicates absence of O vacancies or interstitial O atoms; it can be safely stated that the concentration of such O defects is at least 10 times smaller than after O outgassing, namely, of the order of 0.2% or less. This means that the level of the O vacancies may be kept as low as $\delta \leqslant 0.002$ also without treatments at high O_2 pressures, and should not exceed in any case $\delta = 0.02-0.03$. The latter values are estimated from the mass variation after oxygenation/outgassing treatments up to 1000 K, and correspond to a rather stable concentration of V_O, as deduced from the stability of the anelastic spectra during aging in vacuum at high temperature. Unless assuming that a V_O may neutralize or trap more than two holes, even a concentration $\delta \sim 0.03$ of V_O would not explain the discrepancy between the hole concentration deduced from the valence of Ru and that deduced from transport experiments.[10] The present study, therefore, even though demonstrates the existence of O vacancies in Ru-1212, supports the view that the origin for the poor superconducting properties often found in Ru-1212 is not in the O stoichiometry.

V. CONCLUSION

It has been shown that $RuSr_2GdCu_2O_{8-\delta}$ may be prepared with very low ($\delta < 0.2\%$) O deficiency, also without treatments in high O_2 pressure, and annealing in vacuum above 600 K introduces O vacancies in the RuO_2 and/or CuO_2 planes. The structural analogy with the cuprates of the YBCO family suggests that most of the vacancies are formed in the RuO_2 planes. The diffusive motion of these vacancies gives rise to an intense anelastic relaxation process, measured as a peak of the elastic energy loss coefficient around 670 K at 1 kHz. The concentration of the O vacancies reaches a plateau estimated as $\delta = 0.02-0.03$ from the mass variation after treatments up to 1000 K in vacuum or O_2 atmosphere. The analysis of the peak shows that the barrier for the O diffusion is of $\simeq 1.4$ eV, and the long range elastic interaction among the O vacancies causes an enhancement of the relaxation strength and time of Curie-Weiss type, with $T_C = 400-470$ K.

A minor peak at ~ 530 K might be due to O vacancies trapped at defects, such as Cu substituting Ru in the RuO_2 planes, or to vacancies in the CuO_2 planes. No sign of structural phase transformation appears in the elastic modulus and absorption curves versus temperature up to 930 K.

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