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Anelastic characterization and superconducting properties of $RuSr_2GdCu_2O_{8+\delta}$

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Since the discovery of the high Tc superconductors, many researches have been carried out on the different properties of these materials, especially on the transition temperature into the superconducting state. The rutheno-cuprates belong to a new class of composites, which were synthesized for the first time by Bauernfeind in 1995. Bernhard and collaborators discovered, in 1999, the coexistence of the ferromagnetism and the superconductivity in this phase, which is known as antagonistic phenomenon in the electromagnetism due to spin-charge interactions established in these states. However, the physical nature of the superconducting and magnetic states is still very obscure. The non-stoichiometric (interstitial) oxygen is considered as a possible cause for the non-uniformity of the sample properties. In this paper, results of mechanical spectroscopy in Ru-1212 samples are presented showing complex anelastic spectra, which were attributed to the mobility of the interstitial oxygen atoms in the Ru-1212 lattice.

Keywords: Mechanical Spectroscopy, Ru-1212, Oxygen Mobility

Caracterizacion anelastica y propiedades superconductoras de $RuSr_2GdCu_2O_{8+\delta}$

Desde el descubrimiento de los superconductores de alta Tc, muchas investigaciones han sido realizadas sobre las diferentes propiedades de estos materiales, especialmente sobre la temperatura de transición dentro del estado superconductor. Los cupratos de rutenio pertenecen a una nueva clase de compositos, los cuales fueron sintetizados por primera vez por Bauernfeind en 1995. Bernhard y colaboradores descubrieron, en 1999, la coexistencia del ferromagnetismo y la superconductividad en esta fase, lo cual es conocido como un fenómeno antagonistico en el electromagnetismo debido a las interacciones spin-carga establecidas en estos estados. Sin embargo, la naturaleza física de los estados superconductores y magnéticos aun no son muy claros. El oxigeno no-estequiométrico (intersticial) es considerado como una causa de la no-uniformidad de las propiedades de la muestra. En este articulo, los resultados de espectroscopia mecánica en muestras de Ru-1212 son presentados, mostrando un espectro anelástico complejo, el cual fue atribuido a la movilidad de los átomos de oxigeno intersticial en la red de Ru-1212.

Palabras clave: Espectroscopia mecánica, Ru-1212, Movilidad del Oxígeno

1. INTRODUCTION

The rutheno-cuprate $RuSr_2GdCu_2O_{8+\delta}$ (Ru-1212) belongs to a class of compounds that were synthesized for the first time in 1995 (1). This material is characterized by a triple perovskite cell similar to $YBa_2Cu_3O_{7-x}$ (YBCO), in which Y and Ba are substituted for Gd and Sr, respectively, and the CuO_2 planes are separated from one another not by means of Cu chains, but by RuO_6 octahedra (2). Magnetism and superconductivity can coexist because they are supposed to act in different layers, the first one in the layer containing Ru, and the second in the Cu layer.

The Ru-1212 presents a remarkable development in the study of competition between magnetism and superconductivity (3), this one varying between 0-40 K coexisting with spatially uniform ferromagnetism at 132 K. However this material still presents diverse obscure points about its preparation and characterization, making the sample superconducting or not depending on some "details" during the preparation process (4). This is a critical point. The need to avoid the formation of impurities, such as the ferromagnetic $SrRuO_3$ and to obtain phase as ordered as possible, led to the optimization of the synthesis process, which includes a first calcination, a heat treatment in N_2 atmosphere (5,6) and several annealings in flowing O_2 (6,7).

The oxygen stoichiometry has been considered as a possible cause for the non-uniformity in the superconducting properties of the samples. Thus, there is a great variety of studies that takes into account the influence of preparation conditions in the oxygen stoichiometry. In the Ru-1212, oxygen vacancies are possibly introduced in the RuO_2 planes through vacuum annealing above 600 K (8). The diffusive jumps of the oxygen vacancies are accompanied by changes in the local distortion due to this defect and it can be investigated by mechanical spectroscopy (internal friction) measurements, which are sensitive tools for the study of defects in solids and allow detailed investigations of the structural and kinetic processes in atomic scale (9).

In this paper, it is reported mechanical spectroscopy study in Ru-1212 samples, in which complex anelastic spectra were found. This was attributed to the interstitial oxygen atoms mobility in the Ru-1212 lattice.

2. EXPERIMENTAL DETAILS

Polycrystalline samples of Ru-1212 were synthesized by the solid-state reactions method, using the mixture of high purity RuO_2 (99.99%), Gd_2O_3 (99.99%), $SrCO_3$ (99.99%) and CuO (99.99%) powders, supplied by Sigma-Aldrich (10). The synthesis process is illustrated in Fig. 1. The heating and cooling rate was 5 K/min.

The structure was determined by powder X-ray diffraction

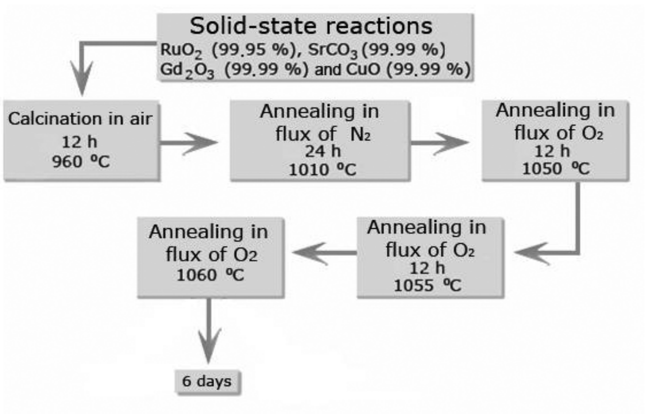

Fig. 1- Preparation details of $RuSr_2GdCu_2O_8$ samples.

in a Rigaku RINT2000 diffractometer, using CuK_α radiation. The magnetic susceptibility was measured using a quantum design SQUID magnetometer (10).

The mechanical spectroscopy measurements were performed in a torsion pendulum, operating with oscillation frequency around 40 Hz, temperature range between 100 and 400 K, heating rate of 1 K/min and vacuum lower than 10^{-5} Torr. This technique allows measuring the elasticity modulus (related to the oscillation frequency) and the elastic energy loss (the internal friction, Q^{-1}) as function of the temperature. In mechanical spectroscopy measurements, the samples are made vibrate in the fundamental mode (free vibrations), which gives rise to energy dissipation by heating due to internal friction. In the case of torsion pendulum, this energy loss per cycle is measured by the logarithmic decrement, which is proportional to the internal friction (9).

Aiming at removing the maximum amount of non-stoichiometric oxygen (δ), the Ru-1212 samples were annealed twice. The sample was heated up to 773 K at 10 K/min under vacuum lower than 10^{-9} Torr. The samples remained at these temperatures for 30 min and soon afterwards they were rapidly cooled by fast cooling of the furnace tube. The second annealing was performed under the same condition, but with temperature of 873 K.

The samples were annealed in oxygen atmosphere in order to recover oxygen content, δ. During the treatment, the samples were placed in equilibrium for 30 min at 973 K with 0.5 Torr of oxygen in a quartz tube connected to an ultra-high-vacuum (UHV) system. After reaching equilibrium, the tube was quenched in water.

3. RESULTS AND DISCUSSION

The X-ray diffraction pattern was analyzed by Rietveld method (10-13) and only the Ru-1212 single phase was showed. This analysis is shown in Fig. 2. The quality refinement indexes are R_{wp}= 6.85 %, R_F^2 = 4.06 %, R_F = 1.40 % and χ^2 = 1.40. Table I contains the unity cell parameters, density and weight percentage obtained for the Ru-1212 samples.

Fig. 3 shows a typical field cooled and zero-field cooled

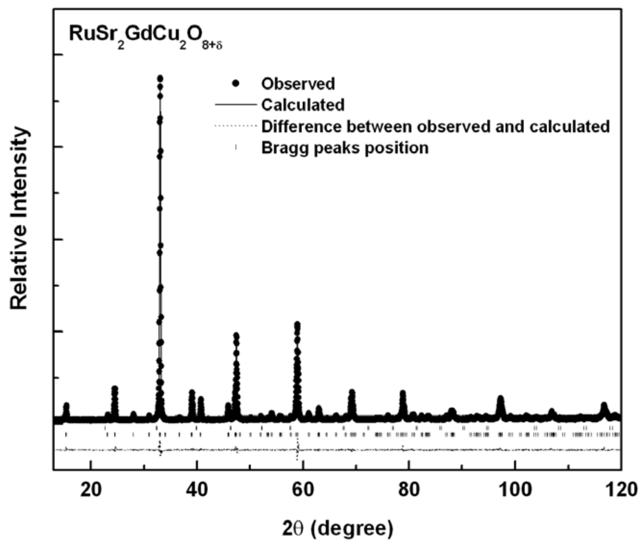

Fig. 2- Rietveld refinement profile for Ru-1212 sample.

TABLA I. WEIGHT PERCENT, UNIT CELL PARAMETERS AND DENSITY FOR RU-1212 SAMPLE

a (Å)	3.8384(4)
c (Å)	11.5711(2)
volume (Å³)	170.482(5)
density (g/cm³)	6.720
wt % (RCSG)	98.67(7)
wt % ($SrRuO_3$)	1.4(6)

curve for Ru-1212. The superconducting transitions presented the two-step behavior, which is typical of granular high-Tc superconductors (14), as presented in this case.

In Fig. 4 the mechanical spectroscopy curves are presented for the Ru-1212 samples, measured in the as-sintered (as-received) condition and after two heat treatments in UHV. Two relaxation peaks are observed at 210 K and 300 K in the curve for the as-receive sample, which shifts to higher temperature at higher frequencies (not shown here), denoting their thermally activated nature. These peaks disappear after the sample was submitted to heat treatments, showing that the annealing in UHV reduces the excess oxygen. The effect of reducing the amount of excess oxygen is to reduce the peaks, indicating that these peaks are due to excess oxygen.

In mechanical spectroscopy measurements, a relaxation process gives origin to a peak in the anelastic spectrum in

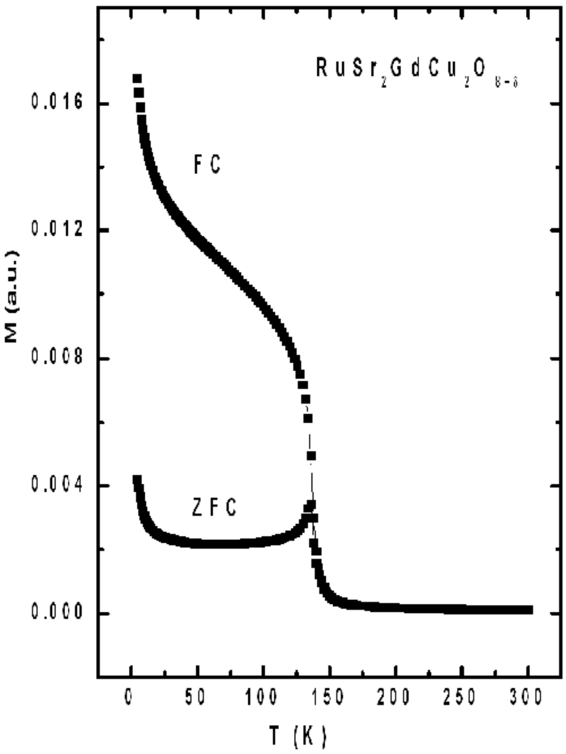

Fig. 3- The ZFC and FC dc magnetization for the Ru-1212 sample.

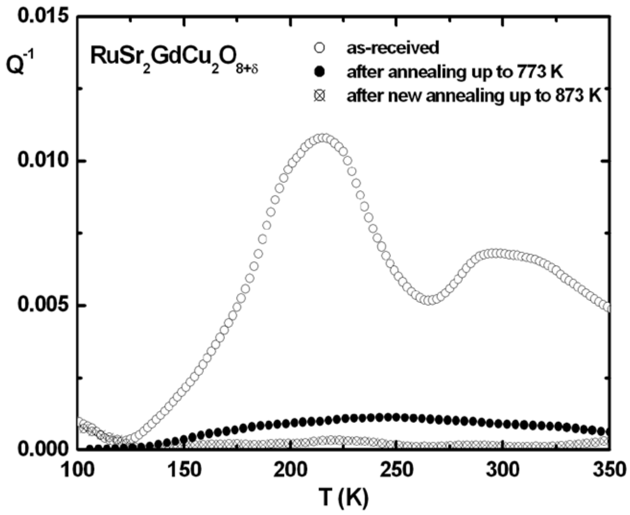

Fig. 4- Mechanical Spectroscopy for Ru-1212 sample after the sintering and after two heat treatments.

function of temperature. The intensity of the peak is related to the concentration of the relaxing entities and the position of the peak is determined by the mobility of these entities (9).

In order to confirm that the peaks are connected with the mobility of interstitial oxygen (excess oxygen atoms, δ), after the mechanical spectroscopy measurements, the sample was submitted to the annealing in oxygen atmosphere and was submitted to another round of mechanical spectroscopy measurements.

Fig. 5 shows the anelastic spectrum for the sample after oxygen charge. For a comparison, the curve obtained for the sample after the last annealing in UHV is demonstrated in Fig. 5, too. Fig. 5 shows that with the oxygen charge, the peaks reappear. Thus, these peaks are really strongly related to the presence of interstitial (excess) oxygen, because with the heat treatments in vacuum, such processes tend to decrease significantly, appearing again after the sample has been submitted to annealing in oxygen atmosphere.

On the contrary, with the YBCO only half filling of the available oxygen sites can be achieved, with the formation of parallel Cu-O chains in the ortho-I phase. 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 $RuO_{2-\delta}$, obtained by oxygenation/outgassing treatments (16)

These peaks are clearly related to the interstitial oxygen. The intensity of the peaks decreases/increases as the amount of the non-stoichiometric oxygen decreases/increases. Then, these observed two relaxation peaks, are associated with the additional oxygen atoms, attributed to the short-range diffusion of the additional oxygen atoms in RuO_2 planes. A more consistent analysis of these processes requires new measurements with higher amounts of interstitial oxygen, which are in course.

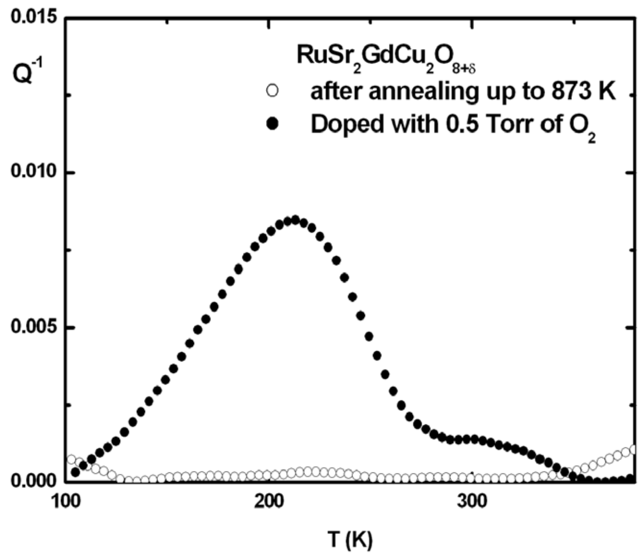

Fig. 5- Mechanical Spectroscopy for Ru-1212 sample after the annealing and after oxygen charge.

4. CONCLUSIONS

The Ru-1212 superconducting samples were analyzed by using mechanical spectroscopy in the Hz range (torsion pendulum). The obtained spectra present at least two relaxation peaks located at 210 and 300 K.

The observed peaks are clearly related to the additional oxygen atoms and can be explained by the short-range diffusion of interstitial oxygen in the RuO_2 planes.

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