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Raman and weak ferromagnetism in Eu_2CuO_4

A.D. Alvarenga[a], D. Rao[a], J.A. Sanjurjo[a], E. Granado[a], I. Torriani[a], C. Rettori[a,*], S. Oseroff[b], J. Sarrao[c], Z. Fisk[c]

[a] *Instituto de Física "Gleb Wataghin", Universidade Estadual de Campinas, 13083-970 Campinas, São Paulo, Brazil*
[b] *San Diego State University, San Diego, CA 92182, USA*
[c] *Los Alamos National Laboratory, Los Alamos, NM 87545, USA and National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL 32306, USA*

Abstract

We show that there is a subtle instability of the T′ structure for the R_2CuO_4 (R = rare earth) compounds at the center of the R series with the boundary at R = Eu. Crystals grown in Pt crucibles and PbO flux show weak ferromagnetism (WF) and two temperature-dependent forbidden Raman peaks. Crystals grown in alumina crucibles and CuO flux do not show WF and the forbidden Raman peaks are much weaker. The WF and forbidden Raman peaks in Eu_2CuO_4 suggests that the instability of the T′ structure is associated with O(1) displacement in the CuO_2 planes.

1. Introduction

The $R_{2-x}M_xCuO_4$ compounds of T′-type structure (R = rate-earths and M = Ce, Th) have been intensively studied since their discovery. For R = Pr, Nd, Sm, Eu and $x \cong 0.15$, n-type superconductivity is achieved after appropriate thermal treatments in reducing atmospheres [1], but compounds with R = Gd to Tm are not superconductors for any doping concentration [2]. In R_2CuO_4, the Cu moments order antiferromagnetically (AF) below $T_N \cong 240$–280 K [3]. For heavier R these compounds show weak ferromagnetism (WF), with a boundary at R = Eu[4]. For R = Tb, Dy, Ho, Er, Tm and Y the T′ structure can be synthesized only under high pressure, with again a boundary for structural stability at the center of the R series [5]. The WF is due to a canting in the ***ab***-plane of the Cu moments away from perfect AF alignment. Although WF is forbidden in the T′ (14/mmm) structure, lattice distortions in the CuO_2 planes may allow WF. Lattice distortions in Gd_2CuO_4 and Tm_2CuO_4 were invoked to explain X-ray and Mössbauer data [6]. It was argued that a lateral displacement of the oxygen ions O(1) away from their symmetric positions in the CuO_2 planes gives rise to an antisymmetric Dzyaloshinsky–Moriya exchange interaction between the Cu moments [7, 8]. This distortion may also be responsible for the extra Raman lines seen in $Nd_{2-x}Gd_xCuO_4$ [9] and Gd_2CuO_4 [10, 11].

Here we give results of Raman and magnetization measurements in single crystals of Eu_2CuO_4, grown in Pt crucibles from PbO flux (hereafter, Pt/PbO) and in alumina crucibles from CuO flux (hereafter, Al_2O_3/CuO).

2. Experimental details

The crystals were of plate-like shape, with the ***c***-axis perpendicular to the large face. They were grown from stoichiometric mixtures of the oxides, using PbO and CuO fluxes in Pt and alumina crucibles, respectively. The Pb content was less than 1% of the Cu content [12]. In Raman experiments, we used the cold finger of a closed-cycle Displex He refrigerator, the 514.5 nm line of an

* Corresponding author.

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argon laser, and a Jobin Yvon T6400 triple spectrometer with a CCD camera. A backscattering geometry was used throughout. Magnetic measurements were made with a Quantum Design DC SQUID magnetometer.

3. Results and analysis

A group-theoretical analysis predicts four Raman active modes in the tetragonal T′ structure: $A_{1g} + B_{1g} + 2E_g$. Denoting by z the direction parallel to the crystal c-axis, the modes appear at the configurations: Y(ZZ)Y (A_{1g}), Y(ZX)Y (E_g) and Z(XX)Z (B_{1g}). In the Raman spectrum of the Pt/PbO sample, we identified Raman active modes at 229 cm^{-1} (A_{1g}), 499 cm^{-1} (E_g) and 324 cm^{-1} (B_{1g}) (Fig. 1). As in Nd_2CuO_4 [13] and Pr_2CuO_4 [14], the low-frequency E_g mode was not seen.

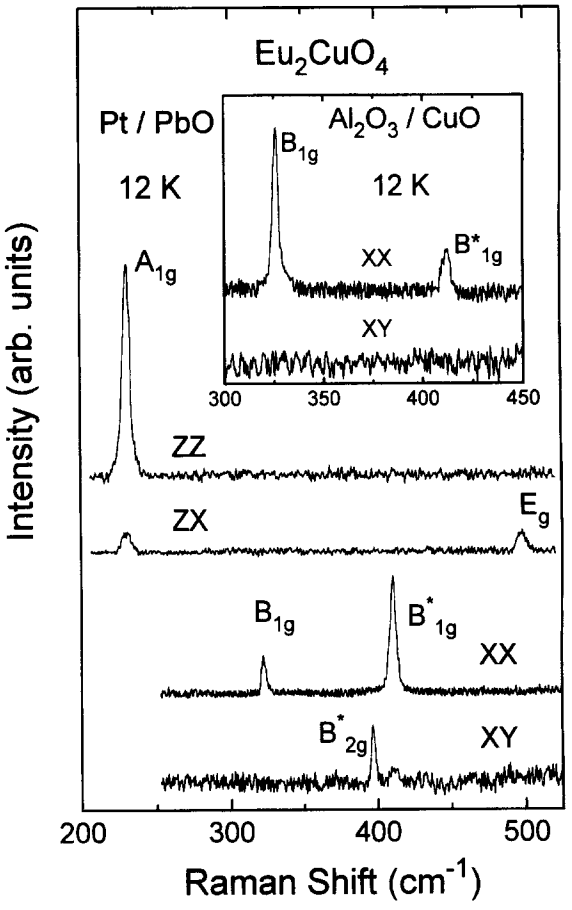

Fig. 1. Low-temperature Raman spectra of Eu_2CuO_4 grown in Pt/PbO and Al_2O_3/CuO for different polarizations. A_{1g}, B_{1g}, and E_g are the active Raman modes for the T′ structure. B^*_{1g} and B^*_{2g} are the anomalous Raman peaks (see text).

The peaks at 413 cm^{-1} for XX polarization and 398 cm^{-1} for XY polarization, which we label B^*_{1g} and B^*_{2g}, respectively [10, 11], do not correspond to any mode allowed in the T′ structure. We tentatively attribute them to local modes associated with oxygen displacements in the CuO_2 planes [7, 8]. The intensity of the B^*_{1g} peak, relative to the B_{1g} mode, is greater for samples grown in Pt/PbO than for those grown in Al_2O_3/CuO. The B^*_{2g} peak was not seen in Al_2O_3/CuO samples (inset of Fig. 1).

The most striking result is the temperature dependence of the intensity of the anomalous peaks (Fig. 2). The intensity of the B_{1g} mode was independent of temperature, so we used it to normalize the intensity of the B^*_{1g} peak. In another set of measurements we observed the B_{1g}, B^*_{1g}, and B^*_{2g} peaks simultaneously, by rotating the incoming polarization about 22° away from the X-axis without using analyzer. The intensities of the B^*_{2g} and B^*_{1g} had almost the same temperature dependence.

Magnetization in the ***ab***-plane was measured at 100 K, after field cooling (FC) and zero-field cooling (ZFC) (Fig. 3). The sample grown in Pt/PbO showed hysteresis

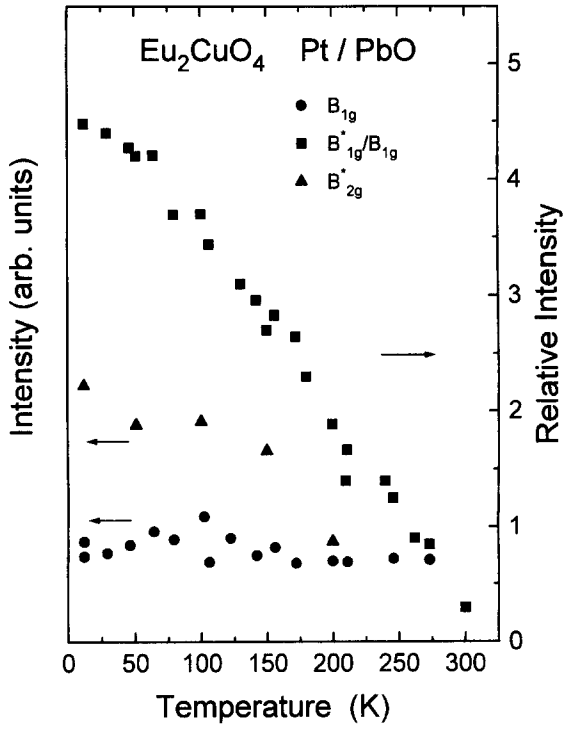

Fig. 2. Temperature dependence of the Raman intensity of the B_{1g} mode (full circles); the relative Raman intensity between the anomalous B^*_{1g} peak and the B_{1g} mode (full squares); and the Raman intensity of the anomalous B^*_{2g} peak and the B_{1g} mode (full squares); and the Raman intensity of the anomalous B^*_{2g} peak (full triangles).

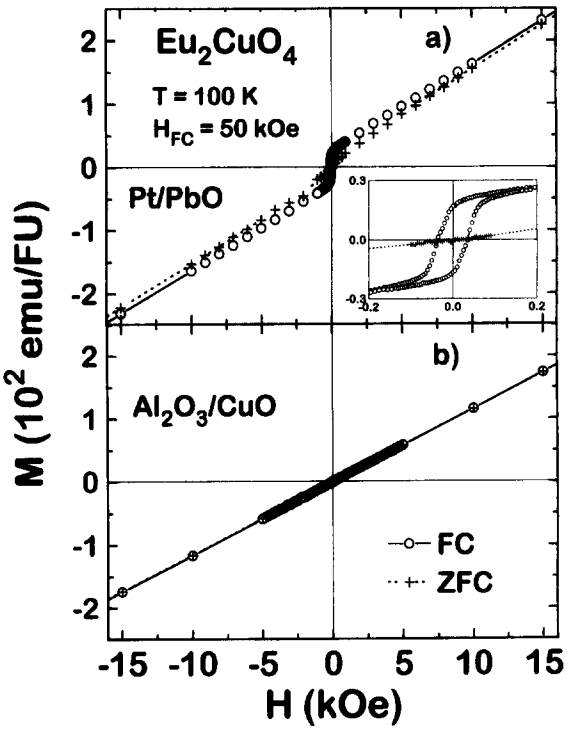

Fig. 3. Eu_2CuO_4 ***ab***-plane magnetization at $T = 100$ K for ZFC and ***ab***-plane FC for (a) crystals grown in Pt/PbO and (b) crystals grown in Al_2O_3/CuO. The inset shows the FC hysteresis with $M_r \simeq 18(3)$ emu/FU and $H_c \simeq 40$ Oe.

and WF after FC (Fig. 3(a)). The remnant magnetization M_r and the coercive field H_c depended on temperature and cooling field. We obtained the saturation values $M_r^s \cong 22(5)$ emu/FU and $H_c^s \cong 50$–70 Oe, at $T = 20$ K after FC in 50 kOe. However, ZFC magnetization was reversible and (at $T \simeq 100$ K) approached the FC magnetization above ≈ 10 kOe (Fig. 3(a)). For our applied fields, the anisotropy within the ***ab***-plane was negligible and no hysteresis or WF were detected perpendicular to the ***ab***-plane. We found no hysteresis or WF in samples grown in Al_2O_3/CuO (see Fig. 3(b)).

4. Discussion

We measured slightly larger lattice parameters for samples grown in Pt/PbO than for samples grown in Al_2O_3/CuO. The difference may be due to contamination by Pt from the crucible, by Pb from the flux, or both. Pt atoms replacing Cu atoms in the lattice may cause displacement of O(1) atoms, thus being responsible for the WF and stronger anomalous Raman peaks found in samples grown in Pt/PbO. Owing to their large ionic radius, Pb atoms would probably substitute Eu atoms, and hence not contribute directly to the O(1) displacements.

Our Raman and WF results, along with other work [15], show that a subtle instability in the T′ structure occurs at a value of about $a_0 \cong 3.905(5)$ Å for the ***ab***-plane lattice parameter. Compounds with $a < a_0$ show WF, whereas those with $a > a_0$ may become superconductors when properly doped with Ce [15].

Since the anomalous Raman B_{1g}^* peak (Fig. 2) is still seen above the Néel temperature ($T_N = 241$ K, determined by the appearance of WF), the distortions responsible for the B_{1g}^* and B_{2g}^* peaks may be associated with short-range magnetic ordering. Spin-dependent phonon Raman scattering [16] may be responsible for the greater intensity of the B_{1g}^* and B_{2g}^* peaks at lower temperatures. However, lattice contractions, resulting in a larger number of these distortions, also could increase the intensity of these Raman peaks at low temperatures.

5. Conclusions

Our results suggest that the anomalous Raman peaks in Eu_2CuO_4 are related to the WF. That the anomalous peaks appear at about the same energy for all the R_2CuO_4 compounds showing WF, regardless of crucible and flux used, supports the assumption that these peaks are associated with local vibrations due to O(1) displacement. However, lattice dynamics calculations are needed to see if the anomalous Raman peaks can actually be associated with O(1) displacement in the CuO_2 planes.

Acknowledgements

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