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High pressure studies of the high temperature superconductors $RBa_2Cu_3O_{9-\delta}$ with R: Y, Eu and Ho up to 60 GPa

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The crystal structure of the superconducting compounds $RBa_2Cu_3O_{9-\delta}$ where R is one of the rare earth metals Ho, Eu or Y, has been studied at room-temperature at pressures up to 60 GPa by synchrotron X-ray powder diffraction in a diamond anvil cell using the energy dispersive method At increasing pressure the compounds show semilar behavior with a bulk modulus in the range 140–176 GPa and a phase transition from an orthorhombic to a tetragonal structure at around 20 GPa. The transition is without a volume change and shows no hysteresis.

Introduction

The crystal structure of $RBa_2Cu_3O_{9-\delta}$ (R = Y, Pr, Sm, Eu, Gd, Dy, Ho, Er, Tm) has been established [1]. There has been evidence of an effect of pressure on the resistance and the superconducting transition temperature of these materials [2] for pressures up to 1.8 GPa. A more detailed structural investigation of $YBa_2Cu_3O_{9-\delta}$ for pressures up to 12 GPa [3] did not give any evidence of a structural transition, but an orthorhombic to tetragonal phase transition has been observed for changes in temperature and in oxygen content [4]. We present in this paper X-ray diffraction measurement for pressures up to 60 GPA of the structures of $RBa_2Cu_3O_{9-\delta}$ (R = Y, Eu, Ho).

Material

The samples were all prepared from analytic grade materials. For the Y-containing compound, CuO, $BaCO_3$, and Y_2O_3, in the molar proportions of 6:4:1 were mixed, carefully ground and heated to 900 °C for 4 h. This material was then reground, compressed into tablets and heated in a flow of O_2 at 900 °C for 16 h followed by slow cooling (50 °C/h). For the Ho compound, BaO_2 was used instead of the carbonate, otherwise the procedure was the same. The resistivity of the samples was measured before the high pressure diffraction eperiments with the results for the superconducting transition temperature T_c and the 10%–90% resistivity transition region ΔT_c shown in Table 1. The high pressure diffraction experiments were performed with a diamond anvil cell of the Holzapfel-Syassen type. The sample was placed in a liquid medium consisting of a 4:1 mixture of methanol and ethanol. A piece of ruby was added for pressure determination. The total sample volume corresponds to a cylinder < 100 μm diameter × 60 μm thickness.

Method

X-ray diffraction spectra were measured using the energy dispersive technique with synchrotron-radiation at HASYLAB DESY-laboratory [5]. For each com-

Table 1. Transition temperature T_c and ΔT_c (10%–90%)

	$T_c(K)$	$\Delta T_c(K)$
$YBa_2Cu_3O_{9-\delta}$	91.5	2.0
$EuBa_2Cu_3O_{9-\delta}$	92.5	1.5
$HoBa_2Cu_3O_{9-\delta}$	91.5	2.0

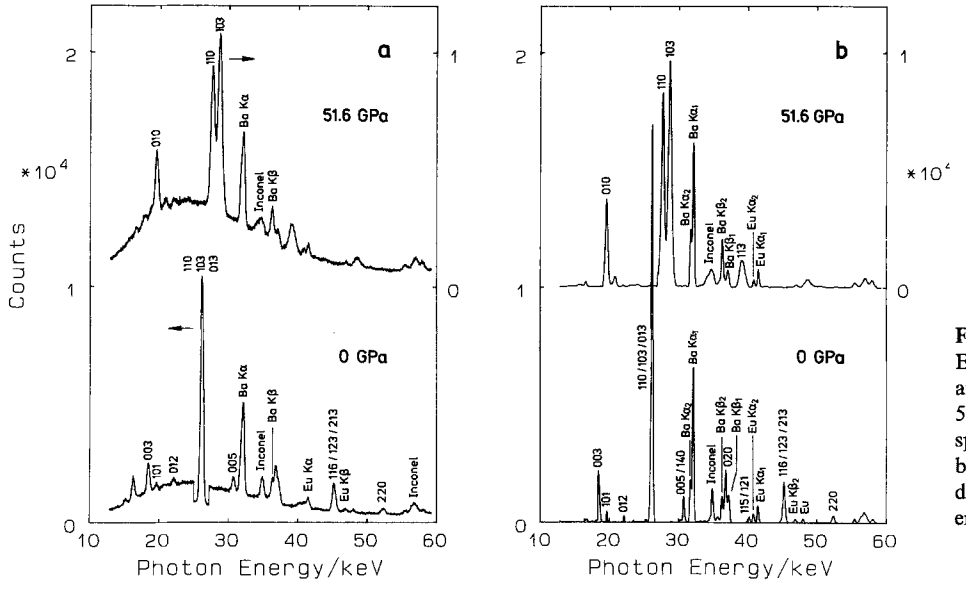

Fig. 1. a Spectra as measured for $EuBa_2Cu_3O_{9-\delta}$. Lower spectrum at ambient pressure; upper at 51.6 GPa. **b** The corresponding spectra after escape correction, background subtraction and deconvolution by the maximum entropy method

pound 10 to 20 spectra were recorded for pressures up to 60 GPa. An example is shown in Fig. 1a where spectra measured for $EuBa_2Cu_3O_{9-\delta}$ at ambient pressure and at 51.6 GPa are displayed. The rather large background and the resolution obtainable with the energy-dispersive method makes the identification of close lying peaks particularly difficult. As part of the broadening of the peaks due to the electronics is well-understood, the maximum entropy deconvolution procedure [6] may be used to yield an improved estimate of the "true" spectrum. In Fig. 1b the results of such deconvolution (after correction for escape [7] and background subtraction [8]) for the spectra in Fig. 1a are shown.

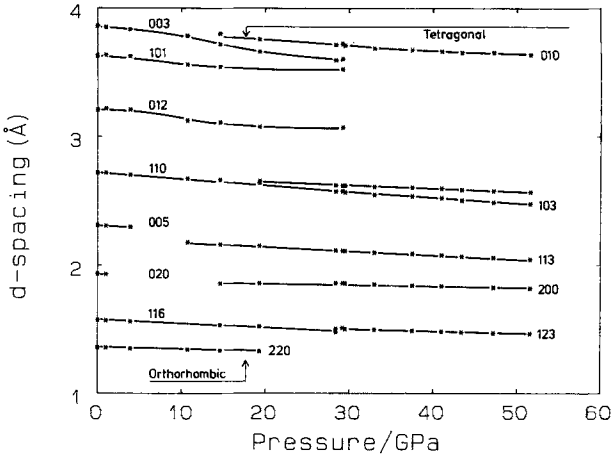

Fig. 2. Observed *d*-values as a function of pressure for $EuBa_2Cu_3O_{9-\delta}$. The lines are only meant to guide the eye

Results

The *d*-values corresponding to the observed peaks were obtained as a function of pressure, and an example for $EuBa_2Cu_3O_{9-\delta}$ is shown in Fig. 2. More detailed values for ambient pressure and for a pressure just above the transition point are given in Table 2, together with the measured intensities. The goodness of the fit as characterized by the reliability factor:

$$R = \Sigma |d_{obs} - d_{cal}| / \Sigma d_{obs} \quad \text{in percent}$$

is also shown in Table 2. Indexing at ambient pressure is consistent with the orthorhombic structure and the intensities were in rough agreement with those calculated according to the spacegroup *Pmmm* and the atomic positions as given in [1]. It is noted, that with the small amount of material and the parallel synchrotron beam, texture is to be expected and the mea-

Table 2. Measured *d*-spacings for $EuBa_2Cu_3O_{9-\delta}$ for different pressures

Assumed			*d*-spacing(Å)	Pressure		
h	*k*	*l*	0.0(GPa)	intensity	19.3(GPa)	intensity
0	1	0			3.759	s
0	0	3	3.861	s	3.663	w
1	0	1	3.625	w		
0	1	2	3.209	m	3.077	vw
1	1	0	2.719	s	2.653	s
			2.639	s		
0	0	5	2.313	m		
1	1	3			2.150	w
0	2	0	1.936	w		
2	0	0			1.857	w
1	1	6	1.574	s	1.532	w
2	2	0	1.360	w	1.329	vw
			$R=0.08\%$		$R=0.45\%$	

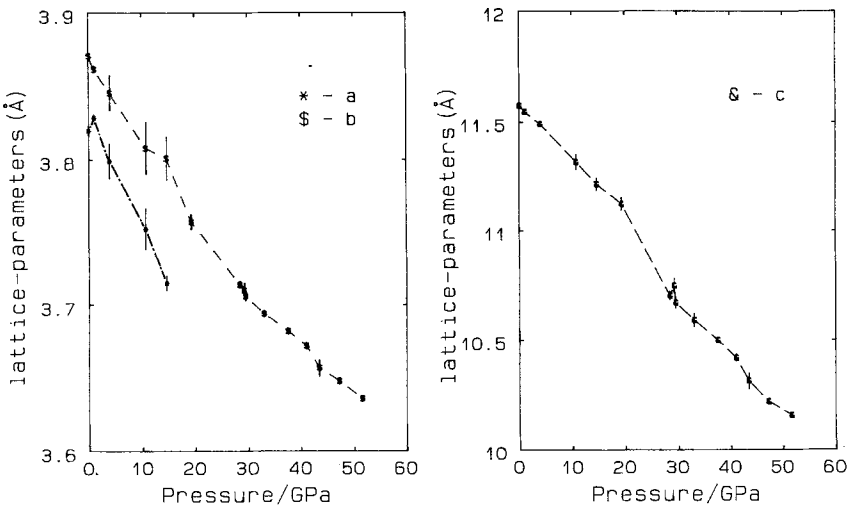

Fig. 3. Lattice parameters for $EuBa_2Cu_3O_{9-\delta}$ as obtained from the observed d-values and indexing shown in Fig. 2

Table 3. Lattice parameters for $RBa_2Cu_3O_{9-\delta}$ at ambient pressure

	a(Å)	b(Å)	c(Å)	V(Å^3)
$YBa_2Cu_3O_{9-\delta}$	3.842 (5)	3.891 (5)	11.76 (2)	175.8 (4)
$EuBa_2Cu_3O_{9-\delta}$	3.820 (3)	3.871 (2)	11.576 (5)	171.2 (2)
$HoBa_2Cu_3O_{9-\delta}$	3.842 (5)	3.888 (3)	11.68 (1)	174.6 (3)

sured intensities are not very meaningful. At ambient pressure the lattice parameters thus obtained (by a least-squares fit) as shown in Table 3 are in fair agreement with those measured earlier [1]. The lines 003/100, 110/103/013, 200/020/006 and 123/213/116 are not distinguished, but as seen from Fig. 2 the 003/010 are observed as separate peaks above a pressure of around 15 GPa, likewise for the 110/103 above around 20 GPa and 116/123 above 28 GPa.

The orthorhombic phase is consistent with the data for pressures up to about 20 GPa for all the materials examined. Figure 3 shows the lattice parameters for $EuBa_2Cu_3O_{9-\delta}$ as function of pressure. At around 20 GPa the splitting of the 110 and 103 peaks becomes measurable, the best fit is obtained for the tetragonal phase, which phase is consistent with the data up to the maximum pressure. The volume change is shown in Fig. 4 in which the points are the measured values, whilst the continuous curves are least-squares fits to the measured points of the two-parameter Murnaghan equation of state:

$$P=(B_0/B_0')\,[(V_0/V)^{B_0'}-1]$$

B_0 is the isothermal bulk modulus, B_0' its pressure derivative at ambient temperature and pressure, V_0 and V the volume at ambient pressure and at P. From these fits, the bulk moduli are obtained as shown in Table 4.

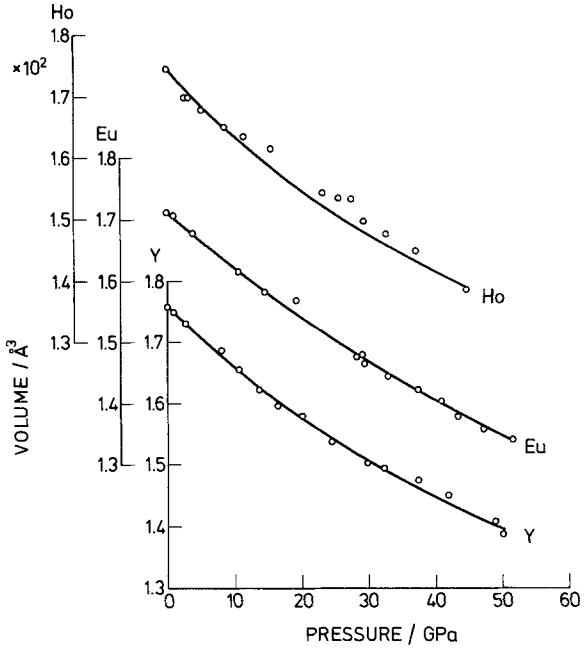

Fig. 4. Volume as a function of pressure for the three compounds studied. The points are the measured values and the lines are the fits to the two-parameter Murnaghan equation

Table 4. Bulk modulus and its pressure derivative for $RBa_2Cu_3O_{9-\delta}$

	B_0(GPa)	B_0'
$YBa_2Cu_3O_{9-\delta}$	157 (5)	2.9 (4)
$EuBa_2Cu_3O_{9-\delta}$	176 (6)	1.4 (3)
$HoBa_2Cu_3O_{9-\delta}$	167 (13)	1.2 (7)

Discussion

It has been shown that the different high temperature superconductors $RBa_2Cu_3O_{9-\delta}$, with R substituted by Y, Eu or Ho have qualitatively similar behaviour

also at high pressure. The transition pressure for the transition from the orthorhombic to the tetragonal phase is at about 20 GPa, and takes place without a measurable volume change. It was also found that the transition is without hysteresis and the original orthorhombic phase is recovered after the pressure is released.

The effect of pressure on the electrical resistance and the superconducting transistion temperature has been determined up to 2 GPa [2, 3] with the result that the transistion temperature increases with increasing pressure. No measurement of the transition temperature in the pressure range used here is available, but a comparison with our structural studies would be of interest, since the tetragonal phase obtained at high temperature or for low oxygen content apparently is not superconducting.

The transition orthorhombic to tetragonal phase observed for changes in temperature seems to indicate some connection with the high pressure transition. It would be interesting to investigate the new superconductors at high pressure for elevated temperature.

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