The effect of hydrostatic pressure on the elastic behaviour of $GdBa_2Cu_3O_{7-x}$

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Abstract. The pressure dependences of ultrasonic longitudinal and shear waves have been measured in the high-T_c superconductor GdBa$_2$Cu$_3$O$_{7-x}$. The effects of porosity have been taken into account by using wave scattering theory in a porous medium. The pressure dependence $(\partial B/\partial P)_{P=0}$ of the bulk modulus of the non-porous matrix at room temperature has the considerable value of 55. The adiabatic bulk modulus B_0^S measured ultrasonically at atmospheric pressure is much smaller than that $B^T(P)$ determined by x-ray measurements of lattice parameters at high pressure; this discrepancy is due to the large pressure dependence of the bulk modulus. It is suggested that the rather small bulk modulus and its large pressure dependence could be due to a combination of fluctuating copper valence and to the vacant sites in the crystal structure.

1. Introduction

GdBa$_2$Cu$_3$O$_{7-x}$ is one of the orthorhombic, ternary oxide compounds (RBa$_2$Cu$_3$O$_{7-x}$, where R is Y, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb or Lu) which can exhibit high-T_c superconductivity (Hor 1987). Recently the effects of hydrostatic pressure on the velocities of longitudinal and transverse ultrasonic waves propagated in polycrystalline ceramic specimens of the archetypal material YBa$_2$Cu$_3$O$_{7-x}$ have been measured (Al-Kheffaji *et al* 1989, Cankurtaran *et al* 1989). The bulk modulus is rather smaller than expected and the hydrostatic pressure derivative $(\partial B/\partial P)$ of the bulk modulus extremely large. These two effects were attributed to a combination of valence fluctuation of the copper ions (Cankurtaran *et al* 1989) and to the presence of sited vacancies in the rather open, oxygen-deficient, defect perovskite structure (Al-Kheffaji *et al* 1989, Cankurtaran *et al* 1989). From both practical and theoretical viewpoints it is important to know whether a large pressure dependence of the bulk modulus is a general characteristic of the mixed oxide superconductors based on copper. Therefore the elastic behaviour under pressure of GdBa$_2$Cu$_3$O$_{7-x}$, which is isomorphic with YBa$_2$Cu$_3$O$_{7-x}$, has now been studied.

A striking feature of YBa$_2$Cu$_3$O$_{7-x}$ is that the bulk modulus B_0 obtained from ultrasonic wave velocity measurements at atmospheric pressure (Almond *et al* 1987, Al-Kheffaji *et al* 1989, Cankurtaran *et al* 1989) is much smaller than that determined at high

pressure ($>10^9$ Pa) from x-ray measurements of the pressure dependence of the lattice parameters (Fietz *et al* 1987). It has been shown that the discrepancy arises from the large magnitude of $(\partial B/\partial P)$: the bulk modulus is strongly pressure dependent (Cankurtaran *et al* 1989). The present measurements of B_0 and $(\partial B/\partial P)$ for $GdBa_2Cu_3O_{7-x}$ enable a similar direct comparison to be made with the bulk modulus obtained from the compression measured (Ecke *et al* 1988) at high pressures for this material. A similar discrepancy to that observed in $YBa_2Cu_3O_{7-x}$ has been found for $GdBa_2Cu_3O_{7-x}$, which can also be accounted for by the large pressure dependence of the bulk modulus.

2. Experimental techniques

The ceramic specimens of $GdBa_2Cu_3O_{7-x}$ were prepared by reacting weighed proportions of Gd_2O_3, BaO and CuO at 940 °C for 48 h in air. The product was ground into a fine powder, pressed into cylindrical pellets (about 1 cm diameter, 0.6 cm long), sintered at 940 °C in an oxygen flow for 48 h and then cooled slowly to room temperature at about 20 °C per hour. The pressed pellets were lightly polished to produce flat faces parallel to about 10^{-4} rad.

The quality of the ultrasonic signal varied substantially from specimen to specimen and that giving the best pulse echo train was chosen for the ultrasonic wave velocity measurements as a function of pressure. The density of this sample was 5549 kg m^{-3}. The theoretical x-ray density has been taken as 7138 kg m^{-3}. Hence the porosity n was 0.22. The pores were irregularly shaped, having dimensions of about 5 μm.

Ultrasonic wave velocity measurements were made by the single-ended pulse echo overlap technique at a carrier frequency of 10 MHz. Quartz transducers (X cut for longitudinal, Y cut for shear) were used to excite and detect the ultrasonic waves. Hydrostatic pressures of up to about 1.5×10^8 Pa were applied in a piston-and-cylinder apparatus using silicone oil as the pressure transmitting medium, the pressure being measured by a precalibrated manganin resistance gauge. Pressure experiments were made at room temperature; Dow Resin (276-V9) was used to bond the quartz transducers to the specimen. Ceramic specimens take up the silicone oil when subjected to pressure. By weighing before and after cycling under pressure it was shown that 97% of the pore volume had become filled with oil: the pores must be interconnected.

3. Experimental results

The velocities of longitudinal (V_L) and shear (V_S) ultrasonic waves propagated at room temperature in ceramic $GdBa_2Cu_3O_{7-x}$ of porosity n equal to 0.22 are given in table 1. These velocities are somewhat smaller than but consistent with those ($V_L = 4.4 \pm 0.2 \times 10^3$ m s^{-1}, $V_S = 2.6 \pm 0.1 \times 10^3$ m s^{-1}) measured by the ultrasonic pulse echo technique in a specimen having a lower porosity ($n = 0.16$) (Brown *et al* 1988). The effect of increasing porosity in a porous ceramic is to decrease the measured ultrasonic wave velocity. Application of wave scattering theory to correct for the influence of porosity (see below, equations (2) and (3)) leads to ultrasonic wave velocities of V_L equal to 4710 m s^{-1} and V_S to 2700 m s^{-1} for the non-porous $GdBa_2Cu_3O_{7-x}$ matrix.

Table 1. The elastic properties of polycrystalline $GdBa_2Cu_3O_{7-x}$ at 295 K. The raw experimental data for the porous ceramic (porosity $n = 0.22$) are given in the first column. Data for the non-porous matrix obtained by applying the equations (2) and (3) developed from wave scattering theory are given in the second column.

	Raw data	Non-porous matrix
Ultrasonic wave velocity (m s^{-1})		
longitudinal V_L	3955	4710
shear V_S	2306	2700
Density ρ (kg m^{-3})	5549	7138
Bulk modulus B_0 (GPa)	47.5	89
C_{11} (GPa)	86.8	158
C_{44} (GPa)	29.5	52
Poisson ratio σ	0.242	0.255
$(\partial C_{11}/P)_{P=0}$	22	56
$(\partial C_{44}/\partial P)_{P=0}$	1.5	0.8
$(\partial B/\partial P)_{P=0}$	20	55

This small-grained polycrystalline ceramic can be treated as if it were an isotropic material having two independent elastic stiffness constants:

$$C_{11} = \rho V_L^2 \qquad C_{44} = \rho V_S^2. \tag{1}$$

These elastic moduli, the adiabatic bulk modulus B_0^S and the Poisson ratio σ for the specimen as measured and for the non-porous matrix are given in table 1.

The effects of hydrostatic pressure P on longitudinal and shear ultrasonic wave velocities for $GdBa_2Cu_3O_{7-x}$ at room temperature are shown in figure 1. These velocities show the unusual feature of a non-linear pressure dependence, although the non-linearity of ultrasonic velocities and elastic stiffnesses is not so pronounced as found (Al-Kheffaji *et al* 1989, Cankurtaran *et al* 1989) for $YBa_2Cu_3O_{7-x}$. The pressure dependences of the longitudinal C_{11} and shear C_{44} moduli and the bulk modulus B_0^S obtained directly from the experimental data are plotted in figure 2; each can be fitted by a polynomial of the form $(a_0 + a_1P + a_2P^2)$. The coefficients (a_0, a_1, a_2), which provide a measure of the vibrational anharmonicity, are given in table 2. Previously it was found for $YBa_2Cu_3O_{7-x}$ that hysteresis effects occur on pressure cycling for dense samples but not in those of higher porosity (Al-Kheffaji *et al* 1989). This porous $GdBa_2Cu_3O_{7-x}$ does not show hysteresis effects during pressure cycling (figure 1).

4. Discussion

For a theoretical understanding of the physical nature of the interatomic binding forces in these high-T_c superconductors the most useful quantities are the elastic moduli and their pressure derivatives for the non-porous matrix. Solution of the wave equations for propagation in an oil-saturated porous medium with a uniform distribution of interconnected pores has been found to give the following expressions for bulk and shear moduli (Cankurtaran *et al* 1989):

$$B^m = B^n + [n/(1-n)](3B^m + 4\mu^n)(B^n - B^w)/(3B^w + 4\mu^n) \tag{2}$$

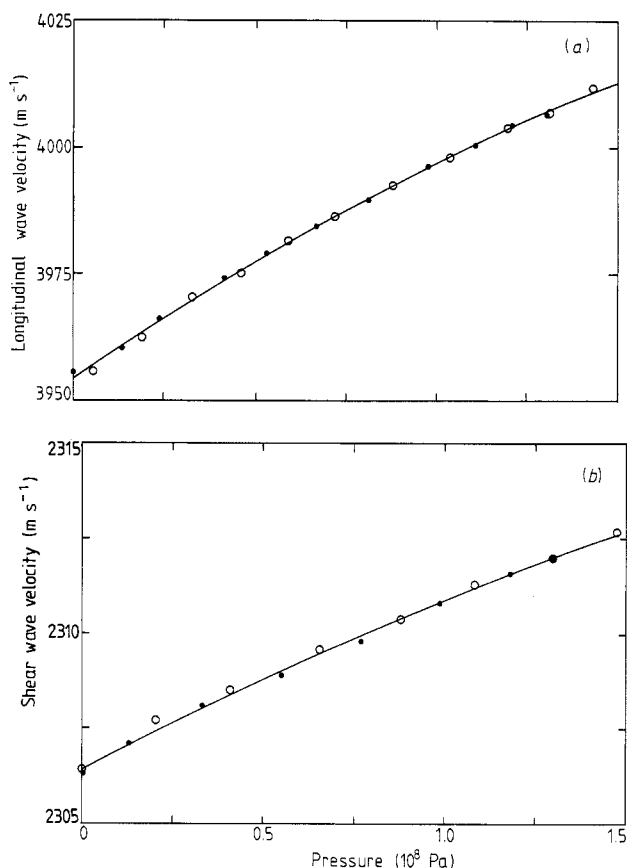$$\mu^m = \mu^n + [n/(1-n)][9B^n\mu^n + 8(\mu^n)^2 + 6\mu^m(B^n + 2\mu^n)]/(9B^n + 8\mu^n). \tag{3}$$

Figure 1. The hydrostatic pressure dependence of the velocity of (*a*) longitudinal and (*b*) shear ultrasonic waves propagated in $GdBa_2Cu_3O_{7-x}$ at 295 K. The open circles correspond to velocity measurements made with increasing pressure and the full circles to data obtained as the pressure was decreased. The full curve is the best fit curve.

Here the superscripts n and m denote the measured moduli in an oil-saturated medium and those of the non-porous matrix respectively. Measurement of the bulk modulus B^w of the silicone oil has shown that it is only 1.0 GPa, so that its influence is small. The bulk $B^m(P)$ and shear $\mu^m \equiv (C_{44}^m(P))$ corresponding to the matrix of $GdBa_2Cu_3O_{7-x}$ determined using equations (2) and (3) from the experimental results for $B^n(P)$ and $C_{44}^n(P)$ (figure 2) are plotted in figure 3. Comparison between the elastic moduli as measured on the porous ceramic and those of the non-porous matrix shows that the porosity does reduce the moduli considerably in the case of this highly porous material ($n = 0.22$). The bulk modulus of the non-porous matrix of $GdBa_2Cu_3O_{7-x}$ is rather larger than that of $YBa_2Cu_3O_{7-x}$, for which B^m is 65 GPa (Cankurtaran *et al* 1989), suggesting that the interatomic binding forces are stronger in the gadolinium compound.

The hydrostatic pressure derivative $(\partial B^m/\partial P)_{P=0} (= 55)$ of the matrix is much greater than that $(\partial B^n/\partial P)_{P=0} (= 20)$ for the porous ceramic and similar to that (85) found for $YBa_2Cu_3O_{7-x}$. Thus the effect of porosity is to reduce $(\partial B/\partial P)$ as well as B_0; comparisons between results obtained both here and in earlier work (Al-Kheffaji *et al* 1989, Cankurtaran *et al* 1989) on $YBa_2Cu_3O_{7-x}$ samples covering a wide range of porosities show that this is a general and consistent feature of these ceramic materials.
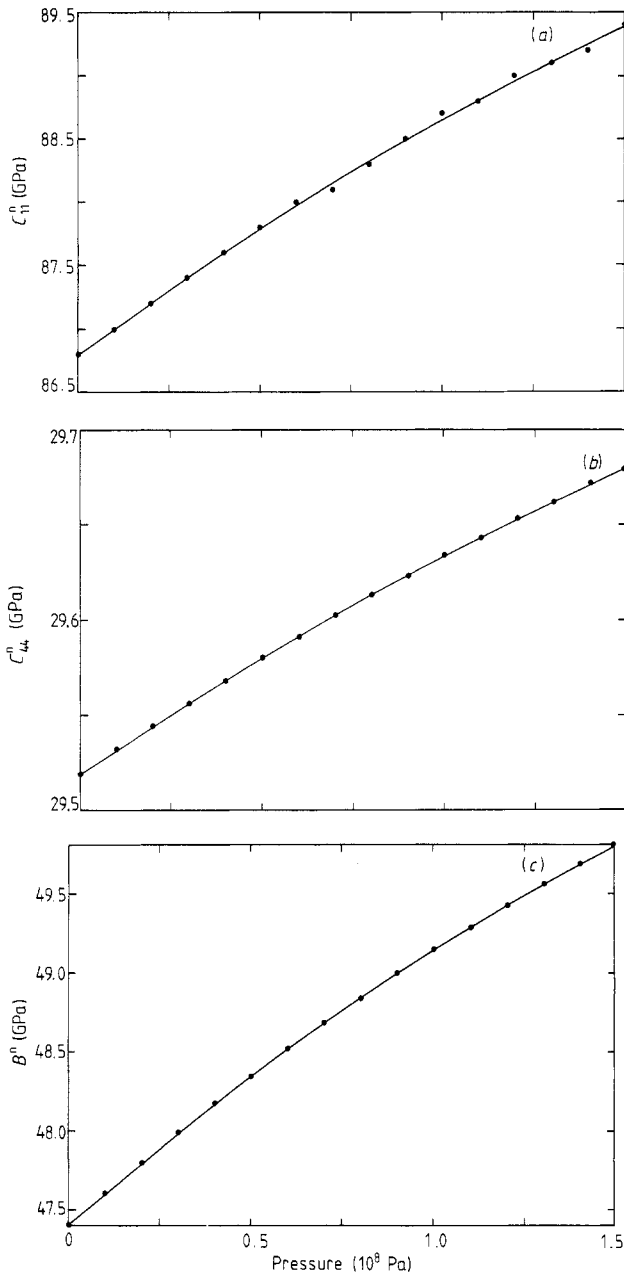
Figure 2. Experimental data for (*a*) C_{11}^{n}, (*b*) the shear modulus C_{44}^{n} and (*c*) the bulk modulus B^{n} of GdBa₂Cu₃O₇₋ₓ at 295 K.

The adiabatic bulk modulus B_0^{S} (equal to B^{m} at $P = 0$) of the non-porous matrix GdBa₂Cu₃O₇₋ₓ determined ultrasonically is 89 GPa at atmospheric pressure. This is much smaller than the isothermal bulk modulus $B^{T}(P)$ (155 GPa) determined from x-ray diffraction measurements of high-pressure-dependence of the lattice parameters (Ecke *et al* 1988). Hence GdBa₂Cu₃O₇₋ₓ behaves in a similar way to YBa₂Cu₃O₇₋ₓ,

Table 2. (*a*) Parameters used to fit the hydrostatic pressure dependences of shear and bulk moduli of GdBa$_2$Cu$_3$O$_{7-x}$ to the form $a_0 + a_1P + a_2P^2$ or both the porous ceramic and the non-porous matrix (obtained using equations (2) and (3) developed using wave propagation theory) data. (*b*) The bulk modulus and its first and second pressure derivatives.

(*a*)	C_{11}	C_{44}	B_0	B_0^m	$(C_{44}^m)_0$
a_0 (GPa)	86.8	29.5	47.4	89.0	52.0
a_1	21.3	1.3	20.1	55	0.8
a_2 ($\times 10^{-7}$Pa^{-1})	−0.27	−0.014	−0.28	−0.72	−0.0016

(*b*)	Porous specimen	Non-porous matrix
B (GPa)	47.4	89
$(\partial B/\partial P)_{P=0}$	20.1	55
$(\partial^2 B/\partial P^2)_{P=0}$	−56 (GPa^{-1})	−144 (GPa^{-1})

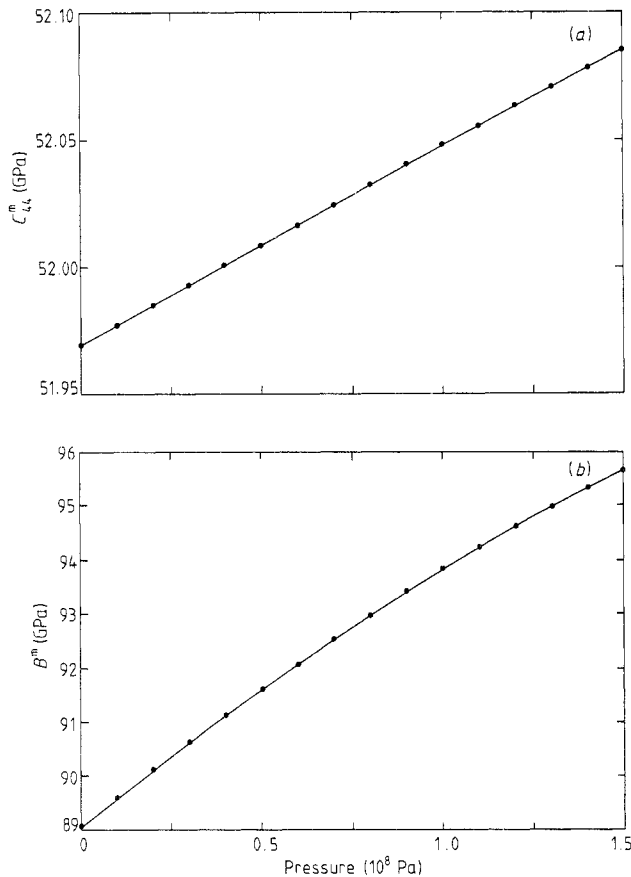**Figure 3.** The (*a*) shear C_{44}^m and (*b*) bulk moduli B^m of the non-porous matrix of GdBa$_2$Cu$_3$O$_{7-x}$ obtained by application of the solutions (2) and (3) of wave scattering theory to the raw experimental data for the porous ceramic given in figure 2.

which also shows a large discrepancy between the adiabatic bulk modulus B_0^S at atmospheric pressure (Cankurtaran *et al* 1989) and $B^T(P)$ obtained at high pressures (Fietz *et al* 1987). The isothermal B_0^T is related to the adiabatic bulk modulus B_0^S by

$$B_0^T = B_0^S/(1 + \alpha\gamma^{\text{th}}T) \tag{4}$$

where the thermal Grüneisen parameter γ^{th} is

$$\gamma^{\text{th}} = 3\alpha B_0^S V/C_p \tag{5}$$

If we take the specific heat C_p at constant pressure as $282.2\,\text{J mol}^{-1}\,\text{K}^{-1}$ at 300 K (Heremans *et al* 1988), the linear coefficient α of thermal expansion as $13 \times 10^{-6}\,\text{K}^{-1}$ and B_0^S as 89.0×10^9 Pa, this gives γ^{th} for GdBa₂Cu₃O₇₋ₓ as 1.27. Hence B_0^T is 88.5 GPa. Therefore, although the ultrasonic technique gives adiabatic (S) moduli while the lattice parameter measurements at high pressure gives isothermal (T) moduli, this difference between B_0 and $B(P)$ is not due to this. For YBa₂Cu₃O₇₋ₓ this difference was shown to arise from the large value of $(\partial B/\partial P)$ which leads to a strong pressure dependence of bulk modulus $B(P)$:

$$B(P) = B_0 + (\partial B/\partial P)^T P \tag{6}$$

This is also true for GdBa₂Cu₃O₇₋ₓ. Lattice parameter measurements have been made up to very high pressures (Ecke *et al* 1988); inserting 10^9 Pa as an approximate lower limit of the pressure employed in that work and the values for $(\partial B/\partial P)^T$ and B_0 measured here into equation (6) gives $B(P)$ 144 GPa, agreeing well with the value of $B(P)$ reported (Ecke *et al* 1988) as 155 GPa as a mean over a wide pressure range. It is interesting that the plots of the volume decrease measured by Ecke *et al* (1988) as a function of pressure at 300 K, 150 K and 15 K do not differ much from each other: they obtained $B(P)$ as 155, 160 and 165 ± 15 GPa respectively at these temperatures. That result implies that neither the bulk modulus nor its pressure derivative vary substantially with temperature and may not be dissimilar in the superconducting and normal states.

Valence fluctuation of the copper d electrons may well play a role in the mechanism of high-temperature superconductivity of YBa₂Cu₃O₇₋ₓ and its related compounds. There are two different copper sites in the unit cell of the YBa₂Cu₃O₇₋ₓ structure; these can tentatively be assigned to Cu(2) sites with a dislocated pyramidal next-nearest-neighbour oxygen environment and Cu(1) chain sites with a planar (rhombic) next-nearest-neighbour environment. Recent nuclear magnetic resonance results indicate that there are valence fluctuations of the Cu(1) ions between the ionic states Cu^+ and Cu^{3+} and of the Cu(2) ions between Cu^+ and Cu^{2+} (Riesemeier *et al* 1988). These fluctuations appear to be characteristic of the high-T_c superconductors formed of complex copper oxides and may be involved in the pairing interaction.

Since the higher-valent ions should be smaller than the lower-valent ones, coupling to the lattice can be expected to be strong for longitudinal phonon modes which alter the unit cell volume but not for shear modes. Hence if fluctuating valence is involved in GdBa₂Cu₃O₇₋ₓ, then $(\partial C_{11}/\partial P)_{P=0}$ would be expected to be much larger than $(\partial C_{44}/\partial P)_{P=0}$, and it is (table 1). On this basis the pressure dependence of the bulk modulus $(\partial B/\partial P)_{P=0}$ would also be expected to be large because it quantifies the cubic invariant in equation (7), and a change in volume would affect the valence fluctuation directly. As materials undergo valence instabilities, they tend to undergo substantial volume changes due to size change of the variable valence ion. An iso-structural volume strain is associated with the identical irreducible representation η_0 which is equal to $(\eta_{11} + \eta_{22} + \eta_{33})$ in terms of Lagrangian strain tensor components; there is no symmetry

breaking and volume distortion is not carried by an acoustic wave. The elastic strain energy induced by volume strain alone can be shown to be

$$\varphi = \frac{1}{2!} B_0 \eta_0^2 - \frac{1}{3!} B_0 \frac{\partial B}{\partial P} \eta_0^3 + \frac{1}{4!} \left\{ B_0 \left(\frac{\partial B}{\partial P} \right)^2 + B_0^2 \frac{\partial^2 B}{\partial P^2} \right\} \eta_0^4 + \dots . \quad (7)$$

Experimental measurements of the bulk modulus B_0 (at atmospheric pressure) and its first and second pressure derivatives $(\partial B / \partial P)$ and $(\partial^2 B / \partial P^2)$ can provide a useful indication of volume effects driven by variable valence. The bulk moduli B_0^S of $YBa_2Cu_3O_{7-x}$ and $GdBa_2Cu_3O_{7-x}$ are small (compared for example with that (139.4 GPa) of $BaTiO_3$ (Ishidate and Sasaki 1989)), showing that these materials do have the feature common to intermediate valence materials of being highly compressible.

Recently it has been reported (Kim *et al* 1988) that the longitudinal sound velocity and the bulk modulus are smaller in superconducting compounds than in non-super-conducting compounds in both the La–Sr–Cu–O and Y–Ba–Cu–O systems. The Poisson ratio was also found to be smaller by a factor of two in superconducting $La_{1.85}Sr_{0.15}CuO_4$ than in the non-superconducting compound La_2CuO_4. The compound $YBa_2Cu_3O_{7-x}$ can be either antiferromagnetic or superconducting depending on the oxygen content and in the latter state the Poisson ratio is slightly smaller. As well as the small bulk modulus, a small or even negative Poisson ratio is a characteristic feature of the compounds in intermediate valence state (Boppart *et al* 1981, 1983, Mook and Holtzberg 1981, Hailing *et al* 1984, Yogurtcu *et al* 1985); hence their low values in the super-conducting versions of the compounds can be taken (Kim *et al* 1988) as an indication that valence fluctuation of the Cu 3d electrons might occur in high-temperature super-conductors. The small bulk modulus B_0 found here for $GdBa_2Cu_3O_{7-x}$ (and also for $YBa_2Cu_3O_{7-x}$ (Cankurtaran *et al* 1989)) can be considered to be further evidence for this, although this is counteracted to some extent by the fact that the Poisson ratio is not found to be particularly small.

Now the Gd^{3+} ion (radius = 1.02 Å) is rather larger than the Y^{3+} ion (radius = 0.88 Å). However the volume of the orthorhombic unit cell of $GdBa_2Cu_3O_{7-x}$ (= 178.2 Å^3) is sufficiently larger than that of $YBa_2Cu_3O_{7-x}$ (= 173.3 Å^3) to accommodate the extra ionic volume of Gd^{3+} (4.5 Å^3) over that of Y^{3+} (2.5 Å^3). Hence ion size difference alone of Gd^{3+} and Y^{3+}, and in turn packing density, cannot be the direct source of the difference in bulk moduli of the two materials.

Like those of $YBa_2Cu_3O_{7-x}$ (Al-Kheffaji *et al* 1989, Cankurtaran *et al* 1989), the pressure derivatives of C_{11} and the bulk modulus are very large for $GdBa_2Cu_3O_{7-x}$. For these materials $(\partial B / \partial P)_{P=0}$ is about an order of magnitude larger than that of most crystalline solids. Even for a highly compressible solid such as the molecular crystal orthorhombic sulphur which is made of S_8 rings weakly bound to each other by van der Waals forces, $(\partial B / \partial P)_{P=0}$ is only 12 (Saunders *et al* 1986). Pertinently, the pressure derivative $(\partial B / \partial P)$ of the bulk modulus of the perovskite $BaTiO_3$ is only 7.44 (Ishidate and Sasaki 1989). The large $(\partial B / \partial P)$ found for $YBa_2Cu_3O_{7-x}$ and $GdBa_2Cu_3O_{7-x}$ shows that the cubic term in the elastic energy with respect to volume strain η_0 (equation (7)) is large. The non-linearities of the bulk and shear moduli with pressure (figure 3) show that the coefficients of the quartic term in η_0 are also large. Application of pressure induces the intermediate valence compound of the type $Sm_xY_{1-x}S$ towards the fully trivalent state (Hailing *et al* 1984, Yogurtcu *et al* 1985). $(\partial B / \partial P)$ is positive and quite large (14.4 for monocrystalline $Sm_{0.58}Y_{0.42}S$) (Hailing *et al* 1984).

In a similar vein, the volume changes under pressure as measured by the bulk modulus and its derivatives found for $YBa_2Cu_3O_{7-x}$ and $GdBa_2Cu_3O_{7-x}$ are consistent

with the possibility of an intermediate valence state being associated with the Cu 3d electrons, and with the fact that application of pressure tends to force the materials towards a higher valence state with a reduced ion size. If the appearance of super-conductivity is linked with a pairing interaction involving the copper valence state, then dT_c/dP would be expected to be positive because pressure would tend to stabilise the superconducting state.

There is, however, another possible explanation for the small bulk modulus and large $(\partial B/\partial P)$ of $YBa_2Cu_3O_{7-x}$ (Al-Kheffaji *et al* 1989, Cankurtaran *et al* 1989) and its isomorphs. These materials have very low anion/cation ratios for perovskite-like compounds (being O_{7-x} rather than the O_9 in $A_3B_3O_9$). In these defect compounds the copper atoms are not coordinated by complete octahedral oxygen cages as in the ABO_3 perovskite structure, but have a four-fold square–planar or four-fold square–pyramid coordination in an open structure. For a series of vacancy compounds in which the number of empty cation sites progressively increases from zero, the bulk modulus reduces markedly as the number of vacant sites increases: HgTe ($B = 46.2$ GPa), $Hg_5In_2\square Te_8$ ($B = 38.9$ GPa), $Hg_3In_2\square Te_6$ ($B = 32$ GPa), $HgIn_2\square Te_4$ ($B = 29.9$ GPa) (Saunders and Seddon 1976). Those vacancy compounds also have somewhat enhanced values of $(\partial B/\partial P)$ (Hailing *et al* 1982); such compounds are easy to compress and rapid densification under pressure enhances the interatomic repulsive forces, leading to a large $(\partial B/\partial P)$. Since there are vacant oxygen sites in the $YBa_2Cu_3O_{7-x}$ structure, their presence should cause diminution of B_0 and enhancement of $(\partial B/\partial P)$. However, comparison with the magnitudes of the effects found with those which occur in the $HgTe$–In_2Te_3 series, which contain much larger proportions of empty anion sites (one empty anion site in four for $HgIn_2\square Te_4$) than the number of empty oxygen sites in $YBa_2Cu_3O_{7-x}$ and $GdBa_2Cu_3O_{7-x}$, indicates that the vacancy effects cannot be nearly large enough to account completely for the small B_0 and the very large $(\partial B/\partial P)$ of these high-T_c superconductors. This leaves room for a substantial contribution from an intermediate valence effect in the copper 3d electrons in both $GdBa_2Cu_3O_{7-x}$ and $YBa_2Cu_3O_{7-x}$.

Acknowledgments

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