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Effect of oxygen desorption on electrical transport in $YBa_2Cu_3O_{7-\delta}$

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Electrical resistivity of polycrystalline $YBa_2Cu_3O_{7-\delta}$ at temperatures between 20 and 900 °C and various O_2 pressures, is correlated with oxygen deficiency δ. The observed strong increase above 400 °C is explained by a model of homogeneous disorder: elastic scattering proportional to δ and electronic density of states depressed as $(\delta_c - \delta)$, where $\delta_c \approx 0.85$. The orthorhombic-to-tetragonal structural transition temperature, which is broadened by intrinsic fluctuations, is shown to be a linear function of δ.

In this paper we address the nature of the sharp upturn in electrical resistivity $\rho(T)$ of $YBa_2Cu_3O_{7-\delta}$ at $T > 400\,°C$ (Fig. 1). We demonstrate that a straightforward model of homogeneous oxygen desorption, characterized by a value of oxygen deficiency δ, can account for this behavior. In our model, as δ increases with temperature, the density of electronic states decreases and the elastic scattering rate caused by oxygen-vacancy disorder increases. Both factors contribute to the increase in $\rho(T)$. Contribution from scattering on phonons appears to be independent of δ in this regime; it is assumed to be determined by the electron-phonon coupling constant and the temperature, as usual. The conductivity extrapolates to zero at $\delta \approx 0.85$, a transition point smeared somewhat by thermal broadening. (At $\delta = 1$, $YBa_2Cu_3O_6$ is semiconducting.[1]) We also found that as a function of temperature, the resistivity shows a change in slope at the orthorhombic-to-tetragonal structural transition $T_{\text{O-T}}$ (Fig. 2). This measurement by resistivity is used to show that $\delta_{\text{O-T}}$ increases as $T_{\text{O-T}}$ is lowered by reducing the oxygen partial pressure in the ambient.

Samples for the present work were dry diamond-saw cut from superconducting ceramic material (midpoint $T_c = 93$ K) in the shape of rectangular bars, which were then reannealed in oxygen at 950 °C and slow cooled. Contacts for 4-probe electrical measurements were attached with a refractory silver cement using silver lead wires. Platinum is not a suitable choice for contacts as it reacts with $YBa_2Cu_3O_7$ above ~650 °C to yield a semiconducting compound, and thus was found to poison the sample. Gold wire may be substituted for silver, although alloying reactions can cause contact failure. The sample was supported in the furnace by cubic zirconia, which was chosen because it was found to be the least-reactive substrate material for deposited superconducting films.[2]

Resistivity is plotted in Fig. 1 for several oxygen partial pressures, established by controlling an argon-oxygen flow mixture in a tube furnace. The temperature was varied by ramping the furnace filament current over a period of 5–10 h, with slower variation employed at low temperatures where equilibration times are longer. Hysteresis in $\rho(T)$ becomes noticeable near 400 °C for pressures below about 0.2 atm where oxygen reaction is too slow and the

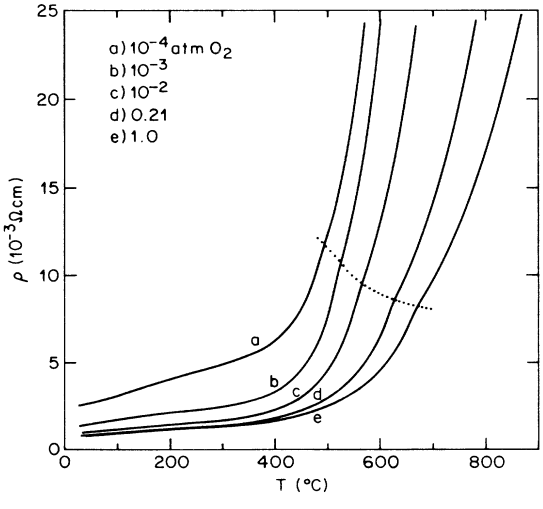

FIG. 1. Temperature dependence of $YBa_2Cu_3O_{7-\delta}$ in various O_2 partial pressures. Dotted curve is the locus of O-T structural transitions.

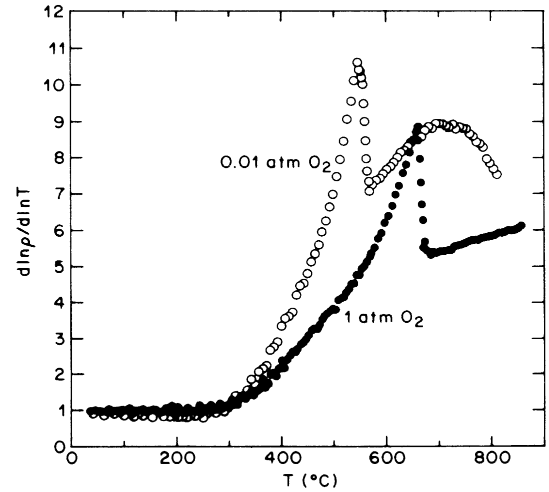

FIG. 2. Temperature dependence of the resistivity logarithmic derivative.

system is not in equilibrium. Figure 2 shows the logarithmic derivative $(T/\rho)d\rho/dT$ (absolute T) as a function of temperature for several atmospheres. The slope is unity for temperatures below about 300 °C. As noted by previous work,[3,4] at lower temperatures the resistivity is essentially linear: $\rho(T)=\rho(0)+\alpha T$, where $\rho(0)$ is an extrapolated residual resistivity, 70 $\mu\Omega$ cm after annealing in pure O_2. Above $\sim 300\,^\circ\mathrm{C}$ one finds thermally activated departure from the linear law caused by oxygen desorption,[5-7] with $(\rho-\alpha T)$ following an Arrhenius temperature dependence, $\propto \exp[(0.7\text{ eV})/k_B T]$. The break in slope at higher temperature,[2] a point which varies with oxygen pressure,[4,8,9] corresponds closely with the temperature of the orthorhombic-to-tetragonal structural transition $T_{\text{O-T}}$ found by x ray[7,10] and neutron diffraction studies.[11,12] The width of the transition, defined by the interval between extrema in the $d\rho/dT$ curve at $T_{\text{O-T}}$, is $\lesssim 15\,^\circ\mathrm{C}$. The transition temperature and the width are slightly sample dependent. There is no hysteresis associated with the transition when the temperature is swept slowly enough ($\lesssim 5\,^\circ\mathrm{C\,min}^{-1}$) to allow temperature and oxygen equilibration. This is characteristic of a second-order phase transition and was confirmed in a separate study of polycrystalline thin-film samples[2] where oxygen equilibration times are below 1 sec. The locus of $T_{\text{O-T}}$ points gives the phase boundary determined from the resistivity as shown in Fig. 1. At $T_{\text{O-T}}$ the resistivity is 4 times larger than the extrapolated value $\alpha T_{\text{O-T}}$, illustrating that the disordering caused by oxygen desorption is large and influences all Cu—O planes, i.e., it is much larger than the 33% maximum increase which would occur if transport along only the central chain of the $YBa_2Cu_3O_7$ structure was disrupted. Because of this, microscopic anisotropy will be ignored in modeling this behavior.

In principle, the resistivity can be expressed in terms of two scattering rates: elastic scattering by quasistatic oxygen-vacancy disorder, treated adiabatically here as far as transport is concerned, and inelastic scattering by lattice vibrations—phonons and possibly tunneling states.[13] At high temperature the total electron scattering rate is given by

$$\tau^{-1}=\langle v_F\rangle l_d^{-1}+2\pi\hbar^{-1}\lambda k_B T\ , \tag{1}$$

where v_F is the Fermi velocity, l_d the defect mean free path, taken to be a function of δ only, and in the phonon term λ is a coupling constant which is proportional to the density of states $N(E_F)$.[14] Two additional inelastic mechanisms have recently been suggested to explain the linear temperature dependence of τ^{-1}, namely, electron-electron scattering[15] and scattering by tunneling states.[13] We will assume that these inelastic contributions, if important, can be included in an effective λ which is proportional to $N(E_F)$. The resistivity in 3D is written as

$$\rho^{-1}(T)=(\tfrac{1}{3})e^2N(E_F)\langle v_F^2\rangle\tau+\rho_s^{-1}\ , \tag{2}$$

where, for completeness, a second term ρ_s^{-1} is included to phenomenologically account for resistivity saturation as ρ approaches the Ioffe-Regel limit of $l_d\sim a_0$.[4] The apparent absence of saturation in the linear portion of the data in Fig. 1 indicate that ρ_s^{-1} is sufficiently small compared to the first term that it may be dropped in the present analysis. As a result of $\lambda\propto N(E_F)$, the inelastic scattering term in ρ should vary as $\langle v_F^2\rangle^{-1}$, explicitly independent of the density of states, a point made previously by Allen.[16]

Recent neutron diffraction measurements[11,12] have shown that oxygen stoichiometry disorder is confined to the central (001) Cu—O plane in the $YBa_2Cu_3O_{7-\delta}$ structure. Thermal activation depletes the oxygens at $[0\,\tfrac{1}{2}\,0]$ sites while simultaneously increasing occupancy of normally vacant $[\tfrac{1}{2}\,0\,0]$ sites, with unequal occupancies below $T_{\text{O-T}}$ and equal above. Hence, the $YBa_2Cu_2O_7$ lattice transforms by thermal activation into a disordered variant of the hypothetical $YBa_2Cu_3O_8$ structure treated theoretically by Herman, Kasowski, and Hsu,[17] but with $\gtrsim \tfrac{1}{2}$ of the oxygen in the central plane missing. We expect uniform disorder in equilibrium at high temperature, in contrast to studies of partially oxygen-depleted samples prepared by either rapid quenching[6] or getter annealing,[18] where partial ordering of the oxygen vacancies may occur.[18]

Band-structure calculations show that the Cu—O valence bands in $YBa_2Cu_3O_7$ are about 8 eV wide[19] with three bands crossing the Fermi level.[17,20,21] In the hypothetical $YBa_2Cu_3O_8$ structure[17] octahedral oxygen coordination about the central Cu gives rise to an additional band while elimination of the central Cu—O chain in the YBa_2CuO_6 structure removes a band.[17,19] The relative position of the Fermi level appears changed very little, as might be expected since oxygen stoichiometry affects only the Cu—O bands. Although intermediate cases containing oxygen defects are not treated by band-structure theory, one could speculate by way of interpolation that the Fermi velocity is insensitive to stoichiometry since the bands near the Fermi level involved in transport have similar shape in each of the cases treated. Because of thermal broadening, details finer than 0.1 eV in band structure are smeared out. A reasonable assumption then is that inelastic contributions to τ^{-1} will be independent of disorder, as a first approximation, and will vary linearly with temperature. Consequently, the first elastic term in Eq. (1) is the main cause of the large increases in ρ observed in Fig. 1, contributing a term in ρ proportional to $[\langle v_F\rangle N(E_F)]^{-1}$.

Since the $YBa_2Cu_3O_6$ structure is a semiconductor, the limiting cases are for $N(E_F)$ to be maximum at $\delta=0$ and vanish at $\delta\approx 1$. We will assume a linear interpolation model for the depression of $N(E_F)$ associated with static structural disorder, $N(E_F)\propto(1-\delta)$. Although this is simplistic, we presently lack the carrier density information which is needed if we are to account for localization and interaction effects correctly.[22] In addition, since resistivity scales with defect concentration and the vacancy concentration varies as δ, it follows that $l_d^{-1}\propto\delta$ is a reasonable assumption. Combining these factors gives for the static disorder a term in the resistivity proportional to $\delta/(1-\delta)$. Hence, the total resistivity in the region $T\gtrsim 300\,^\circ\mathrm{C}$ is modeled by

$$\rho(T,\delta)=\alpha T+\rho_0\frac{\delta}{\delta_c-\delta}\ , \tag{3}$$

where ρ_0 is a scaling resistivity of similar magnitude as the saturation resistivity, and $\delta_c \approx 1$. It is expected that α is given by the slope below 300 °C for data taken at atmospheric pressure of O_2, which for the sample of Fig. 1 is 2.5 $\mu\Omega\,\text{cm}\,\text{K}^{-1}$. In Fig. 3 this model is tested by plotting resistivity against $\delta/(1-\delta)$, where $\delta(T)$ is taken from published thermogravimetric data.[5-7] We observe a nearly linear dependence, as predicted by this model. For the isotherm curve, obtained by interpolating curves at different pressures, we chose 550 °C so as to present a wide variation in δ over the available range in oxygen pressure. It is immediately evident that structure in the $\rho(T)$ data at the O-T transition is suppressed when data are plotted in this manner; for the 550 °C isotherm data, the structural transition takes place at $\delta/(1-\delta)=0.67$. Extrapolation to the ordinate axis gives $\rho = 1.86$ mΩ cm, which is in good agreement with the expected value $\alpha T = 2.06$ mΩ cm at $T = 550\,°\text{C}$. The slope of the curve gives $\rho_0 = 11.4$ mΩ cm. An isobar also shown in Fig. 3 demonstrates that the αT term has little effect at high temperatures. The small variations in the curve are most likely systematic computation errors. This result shows that resistivity is dominated by oxygen defect density and is only weakly sensitive to the change in lattice symmetry at $T_{\text{O-T}}$. Published thermogravimetric data for δ show a peak in the slope near $T_{\text{O-T}}$,[5,6] although the precision is not as good as in resistivity to clearly define a break in the slope. Since in resistivity two factors involving δ are combined, the effect at $T_{\text{O-T}}$ is more pronounced.

The region $\delta \rightarrow 1$, where $N(E_F) \rightarrow 0$, is examined further in Fig. 4, which is a plot of the defect contribution $\sigma_d = (\rho - \alpha T)^{-1}$, against $(1-\delta)/\delta$ for two isobar curves. Systematic errors are about 10% in the orthorhombic phase region, shown as dotted curves. The solid portion of the curves corresponds to the tetragonal phase, and extrapolate to zero conductivity at a critical value $\delta_c \approx 0.85$. This extrapolation procedure is somewhat imprecise as it neglects the small thermally activated conductivity of the semiconducting phase.[1] Taken together, Figs. 3 and 4 show that the depression of $N(E_F)$ varies as $(\delta_c - \delta)$ to within 10% accuracy over the range $0.2 < \delta < 1$. It would appear that the depression is a consequence of strong disorder, since $\hbar \langle v_F \rangle l_d^{-1} > kT$ and, moreover, theoretical band-structure calculations predict a much weaker 10% decrease in $N(E_F)$.[17] This smooth, monotonic dependence on δ at high temperature is different from the low-temperature behavior of oxygen deficient samples, where resistivity and superconducting T_c can show plateau structure as functions of δ.[3,18,23] A quantitative estimate of the upper limit of oxygen deficiency at low temperatures can be made using the residual resistivity $\rho(0)$ mentioned earlier. From Eq. (3) and the value of ρ_0 found from Fig. 3, the residual disorder at low temperature is equivalent to having 0.6% of the oxygens randomly removed from the central chain. This is taken as an upper limit, since other forms of disorder are present.[24,25]

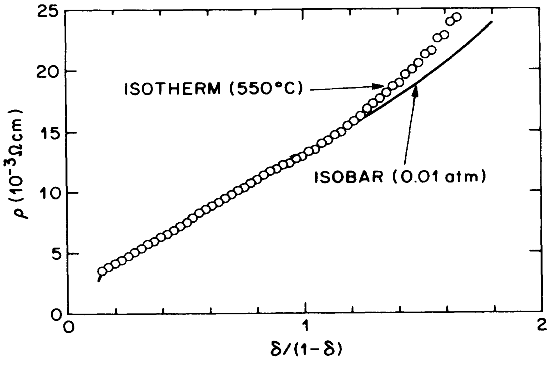

FIG. 3. Resistivity vs disorder function $\delta/(1-\delta)$, computed for an isotherm and an isobar. Solid curves: orthorhombic phase; dotted curves: tetragonal phase.

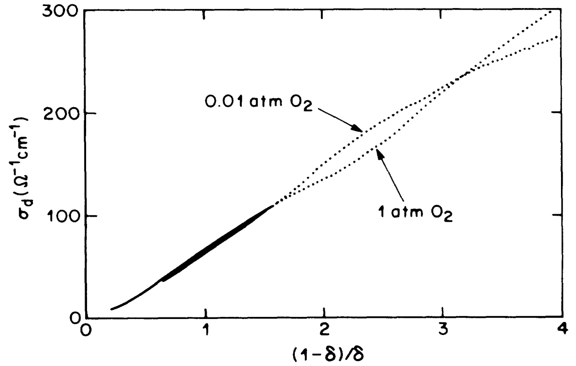

FIG. 4. Defect conductivity, defined as $\sigma_d - (\rho - \alpha T)^{-1}$, plotted against model function $(1-\delta)/\delta$.

As a final observation, the correlation between $T_{\text{O-T}}$ and oxygen stoichiometry is plotted in Fig. 5, where δ is determined by the oxygen pressure, the independent experimental variable. Each rectangular symbol encloses the interval over which $\rho(T)$ changes slope, taking the full width of the transition region from derivative data like Fig. 2. Transition onsets are taken to be the upper right-hand corners of the symbols. These data show that the oxygen deficiency increases as $T_{\text{O-T}}$ is depressed and it

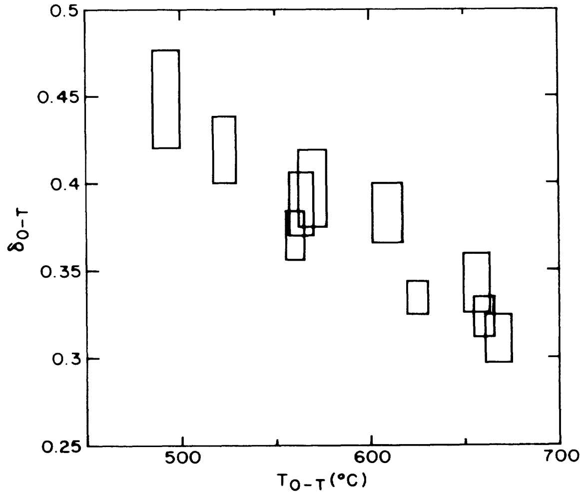

FIG. 5. Dependence of δ on the orthorhombic-tetragonal phase transition temperature determined by resistivity.

can be explained by thermal activation of site occupancy. Just below $T_{\text{O-T}}$, the ratio of oxygen concentrations in the $[\frac{1}{2}00]$ and $[0\frac{1}{2}0]$ site scales with the orthorhombic distortion:[11]

$$c_{[\frac{1}{2}00]}/c_{[0\frac{1}{2}0]}=1-(b-a)(b_0-a_0)^{-1}(1-\delta)^{-1} ,$$

where a and b are the basal lattice parameters and $b_0-a_0=0.06$ Å is the orthorhombic distortion at $\delta=0$. The ratio is assumed also to be activated, given by $\exp[-(b-a)E_{\text{O}}/k_BT]$, where E_{O} is the oxygen atomic deformation potential. Hence, since $(b-a)\ll(b_0-a_0)$ near $T_{\text{O-T}}$, it follows that

$$\delta_{\text{O-T}}=1-\frac{k_BT_{\text{O-T}}}{(b_0-a_0)E_{\text{O}}} . \tag{4}$$

Fitting this expression to the onset region gives $E_{\text{O}}=2.0$ eV Å^{-1} for the oxygen-site deformation potential. In addition to giving a quantitative measure of the Cu—O interaction potential, this result can be used to estimate site occupancy and disorder at temperatures below the range of the experimental data. Referring to Fig. 1, one finds that $\rho(T_{\text{O-T}})$ is higher for lower $T_{\text{O-T}}$, which is also consistent with a larger $\delta_{\text{O-T}}$. The width in δ associated with the O-T transition corresponds to about a 4% inhomogeneity in the occupancy of the $[\frac{1}{2}00]$ and $[0\frac{1}{2}0]$ sites. One can explain the width in terms of statistical fluctuations in the oxygen concentration within the correlation volume ξ^3, where the correlation length ξ diverges at the second-order $T_{\text{O-T}}$ transition, by imposing a cutoff $\xi\lesssim75$ Å. This maximum ξ is close to the ~100 Å defect-microstructure scale observed by electron microscopy[24,25] and is indicative that the phase transition lacks intrinsic sharpness.

In conclusion, the effect of disorder on electrical transport associated with oxygen desorption in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in equilibrium with the ambient O_2 atmosphere at elevated temperature is explained by a straightforward homogeneous-disorder model. The data are consistent with a depression of the electronic density of states proportional to $(\delta_c-\delta)$, where the critical disorder is at $\delta_c\approx0.85$, a disorder-induced electronic elastic scattering rate which is proportional to δ, and a thermal inelastic rate proportional to temperature and independent of δ. The orthorhombic-tetragonal phase transition is broadened intrinsically and is modeled by statistical fluctuations in vacancy concentration. The value of $\delta_{\text{O-T}}$ at the transition increases and the temperature of the transition is lowered by reducing the O_2 partial pressure, as explained by an atomic deformation-potential model.

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[1] A. Santoro, S. Miraglia, F. Beech, S. A. Sunshine, D. W. Murphy, L. F. Schneemeyer, and J. V. Waszczak, Mater. Res. Bull. **22**, 1007 (1987).

[2] M. Gurvitch and A. T. Fiory, Appl. Phys. Lett. **51**, 1027 (1987).

[3] R. J. Cava, B. Batlogg, R. B. van Dover, D. W. Murphy, S. Sunshine, T. Siegrist, J. P. Remeika, E. A. Rietman, S. Zahurak, and G. P. Espinosa, Phys. Rev. Lett. **58**, 1676 (1987).

[4] M. Gurvitch and A. T. Fiory, in *Proceedings of the International Workshop on Novel Mechanisms of Superconductivity, Berkeley, California, 1987,* edited by S. A. Wolf and V. Z. Kresin (Plenum, New York, 1987).

[5] P. Stobel, J. J. Capponi, C. Chaillout, M. Marezio, and J. L. Tholence, Nature (London) **327**, 306 (1987).

[6] K. Kishio, J. Shimoyama, T. Hasegawa, K. Kitazawa, and K. Fueki, Jpn. J. Appl. Phys. **26**, L1228 (1987).

[7] P. K. Gallagher, Advan. Ceram. Mater. **2**, 632 (1987). P. K. Gallagher, H. M. O'Bryan, S. A. Sunshine, and D. W. Murphy, Mater. Res. Bull. **22**, 995 (1987).

[8] P. P. Freitas and T. S. Plaskett, Phys. Rev. B. **36**, 5723 (1987).

[9] G. S. Grader, P. K. Gallagher, and E. M. Gyorgy, Appl. Phys. Lett. **51**, 1115 (1987).

[10] I. K. Schuller, D. G. Hinks, M. A. Beno, D. W. Capone II, L. Soderholm, J.-P. Locquet, Y. Bruynseraede, C. U. Segre, and K. Zhang, Solid State Commun. **63**, 385 (1987).

[11] J. D. Jorgensen, M. A. Beno, D. G. Hinks, L. Soderholm, K. J. Volin, R. L. Hitterman, J. D. Grace, I. K. Schuller, C. U. Segre, K. Zhang, and M. S. Kleefisch, Phys. Rev. B **36**, 3608 (1987).

[12] A. W. Hewat, J. J. Capponi, C. Chaillout, M. Marezio, and E. A. Hewat, Nature (London) (to be published).

[13] E. Abrahams and C. M. Varma (unpublished).

[14] W. L. McMillan, Phys. Rev. **167**, 331 (1968).

[15] P. A. Lee and N. Read, Phys. Rev. Lett. **58**, 2691 (1987).

[16] P. B. Allen, Phys. Rev. Lett. **37**, 1638 (1976).

[17] F. Herman, R. v. Kasowski, and W. Y. Hsu, this issue, Phys. Rev. B **36**, 6904 (1987).

[18] R. J. Cava, B. Batlogg, C. H. Chen, R. A. Rietman, S. M. Zahurak, and D. Werder, Phys. Rev. B **36**, 5719 (1987).

[19] W. Weber and L. F. Mattheiss (private communication).

[20] L. F. Mattheiss and D. R. Hamann, Solid State Commun. **63**, 395 (1987).

[21] S. Massidda, J. Yu, A. J. Freeman, and D. D. Koelling, Phys. Lett. A **122**, 198 (1987).

[22] P. Lee and T. V. Ramakrishnan, Rev. Mod. Phys. **57**, 287 (1985).

[23] J. M. Tarascon, W. R. McKinnon, L. H. Greene, G. W. Hull, and E. M. Vogel, Phys. Rev. B **36**, 216 (1987).

[24] S. Nakahara, T. Boone, M. F. Yan, G. J. Fisanick, and D. W. Johnson, Jr., J. Appl. Phys. (to be published).

[25] A. Ourmazd, J. A. Rentschler, J. C. H. Spence, M. O'Keefe, R. J. Graham, D. W. Johnson, Jr., and W. W. Rhodes, Nature (London) **327**, 308 (1987).