Thermopower of an untwinned $YBa_2Cu_3O_{7-\delta}$ crystal

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The thermopower and resistivity of a fully loaded and a partially unloaded crystal of $YBa_2Cu_3O_{7-\delta}$ (Y123) have been measured along the *a* and *b* axes. The temperature dependence of the *a*-axis thermopower in the fully loaded crystal is similar to that observed previously in crystalline and polycrystalline Y123, and rather smaller than is found in other high-T_c cuprates. The thermopower along the *b* axis, which is affected more strongly by the chains, shows substantial variation between the present and previous data, and we ascribe this to chain disorder. In the unloaded crystal there is a nearly temperature-independent shift to larger thermopower along the *a* axis, while the *b*-axis thermopower shows in addition an altered temperature dependence.

I. INTRODUCTION

The *a*-*b* plane thermoelectric power in the normal state of the majority of the copper oxide superconductors shows a simple, though unusual, dependence on temperature and on the hole density in the CuO_2 planes.[1–4] The thermopower is linear in temperature, with a slope, which is nearly the same (approximately -3×10^{-8} V/K^2) for most of the high-T_c cuprates and depends only weakly on the doping level. The extrapolated zero-temperature intercept is much more strongly dependent on the hole concentration, with the large positive value at low concentration (on the underdoped side of the maximum T_c) falling to near zero when the transition temperature approaches 0 K on the overdoped side. This very simple pattern leads to the situation that at any given temperature the *a*-*b* plane thermopower varies approximately linearly with the doping level. The relatively high conductivity in the plane as compared to that along the *c* axis ensures that even in polycrystalline materials a measurement of the thermopower yields essentially the *a*-*b* plane value,[1,2] and as a consequence the thermopower has developed as a convenient empirical indicator of the hole concentration.[5]

There does not yet exist a consensus concerning the explanation of the temperature and doping dependence of the thermopower. Its simplicity and almost universal occurrence in the cuprate superconductors suggests that it is related in a very general way to the electronic structure in the normal state of these materials, and that it may provide a test for any proposed model (provided that the thermopower within the model can be predicted). It has been suggested that the doping dependence can be understood within a conventional Fermi-liquid model and is related to the common electron dispersion found in the entire class of high-T_c cuprates.[6] On the other hand the *temperature* dependence is not easily reconciled with a conventional Fermi-liquid model unless there is a very strong energy dependence in the quasiparticle density of states within 100 K of the Fermi level, as, for example, might be supplied by a very strong electron-phonon interaction.[7] It is worthwhile noting that the pattern does not depend strongly on the atomic species maintaining the separation of the CuO_2 planes, nor even on the number of adjacent CuO_2 planes within one unit cell.

The most notable exception to the pattern described above is $YBa_2Cu_3O_{7-\delta}$ (Y123), in which conduction by CuO chains running along the *b* axis confuses the results.[8–11] The situation is further complicated by oxygen vacancies in the chains, which will almost certainly affect the *b*-axis thermopower. Nonetheless, Y123 is an attractive material to use as the prototype high-T_c cuprate, for it can be prepared in the form of relatively pure single crystals, and the optimum level of doping is achieved when the oxygen concentration is very near the stoichiometric value ($\delta=0.0$). It is thus essential to understand the thermopower in this material and to identify its similarities to and differences from the other high-T_c materials.

There have been a number of attempts to determine and model the thermopower of Y123, but to date these show no evidence of converging onto a common result, let alone a common model. It is clear that no real progress can be made until the *a*- and *b*-axis thermopowers are measured separately with reproducible results. The two measurements in the literature,[10,11] which separate the thermopower in the two directions, show little agreement. In both measurements the crystals were said to be fully loaded, as is indeed indicated by their high transition temperatures, but there were acknowledged imperfections (twinning and/or possible contamination with gold) in both cases. Both measurements yielded an *a*-axis thermopower, which fell monotonically with temperature above 100 K, but in neither case was the result linear in temperature as is found in most of the other cuprate superconductors. The average rates of fall above 150 K were of the order of -1×10^{-8} V/K^2 (Ref. 11) and -0.2×10^{-8} V/K^2 (Ref. 10), rather smaller than the slope of the linear dependence in other superconducting cuprates. In one measurement[10] the thermopower was positive over most of the reported temperature range, falling to zero near 300 K, consistent with the empirical rule for an optimally doped material,[5] while in the other[11] it was negative at all temperatures except for a peak, which develops only below 150 K. The *b*-axis thermopower shows even less agreement between the two measurements, being negative and approximately independent of temperature in one case[10] and positive with a complex temperature dependence and again a broad peak above T_c in the other.[11] It is interesting to note that similar peaks have been observed in Y123, since the very first measurements[8,12] on polycrystalline materials, and they have also been seen in Tl2201,[5] but they are not a universal feature in any of the cuprate superconductors.

It is natural to propose a two-band model to describe these results, with a plane-related, quasi-two-dimensional band conducting on a cylindrical Fermi surface and a chain-related quasi-one-dimensional band with a Fermi surface approximated by two parallel sheets. We note that band-structure calculations suggest that this model is an oversimplification, for the Fermi surface (and even more strongly the band mass) of the plane-related band in Y123 shows a significant anisotropy as regards the *a* and *b* directions, and even the chain-related sheets show nonzero velocity in the *a* direction.[13–15] Nonetheless within this very simple model one might expect to be able to separate the two contributions to the thermopower, provided only that *a*- and *b*-axis-resolved measurements are available. Such a resolution into "plane" and "chain" contributions has been reported for one set of the results on Y123.[11]

Conductivity measurements on untwinned Y123 crystals show very clearly that the conductivity along the chain direction has an extra contribution when compared to the *a*-axis conductivity. Furthermore, the extra contribution, which many authors associate with conduction on the chains, has a distinctly different temperature dependence than the linear form, which is found along the *a* axis and in the *a*-*b* plane of the other cuprate superconductors.[16] Below we report thermopower and resistivity measurements on a high-quality untwinned Y123 crystal, both fully loaded with oxygen ($\delta=0.05$) and partially unloaded ($\delta=0.3$).

II. EXPERIMENTAL DETAILS

Single crystals of Y123, prepared and detwinned by techniques described elsewhere,[17,18] were supplied by Quantum Innovations Inc. The crystal was of approximate dimensions $1\times1\times0.08$ mm and was initially loaded to $\delta=0.05$. After performance of a set of resistivity and thermopower measurements it was unloaded to $\delta=0.3$ ($T_c=70$ K) by annealing it in an oxygen environment ($P=1$ atm) at a temperature of 650°C for a period of 24 h, followed by a liquid-nitrogen quench, and the thermopower measurements were repeated.

The thermopower was measured using a setup similar to that described by Vasudeva Rao *et al.*[19] The Montgomery technique[20] was used for the resistivity measurements. Care was taken to apply a correction for the systematic error resulting from a missing corner (containing about 5% of the area of the crystal). The required correction was determined empirically by cutting the real shape of the crystal from isotropic two-dimensional conductors, attaching leads at the positions actually used in our measurements, and determining the parameter H (as defined in Ref. 20). The process was then repeated on figures derived from the crystal by applying different scaling factors in the two directions to simulate an anisotropic resistivity, thus determining the *shape-corrected* parameter H as a function of the ratio (l_1/l_2).

III. RESULTS

In Fig. 1 we show the resistivity and thermopower in the two directions in the basal plane, for a fully loaded ($\delta=0.05$) crystal. It can be seen that the resistivity along the *a* axis extrapolates to zero at about 10 K, suggesting that the normal-state resistivity would show superlinear temperature dependence at low temperatures. The absolute value of the resistivity is comparable to the lowest in the literature, and the ratio ρ_a/ρ_b, near 1.6 at room temperature, lies in the ranges quoted by many groups.[16,21]

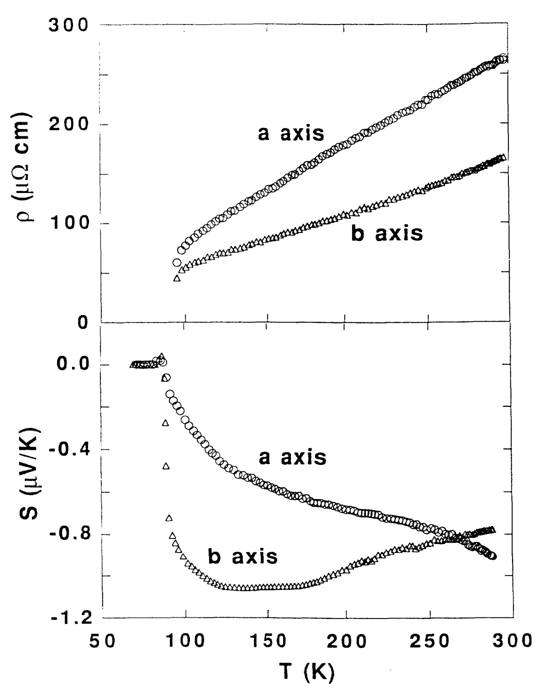

FIG. 1. Temperature dependence of the direction-resolved (a) resistivity and (b) thermopower for a fully loaded detwinned crystal of Y123.

The stronger curvature in the b-axis data implies an approximately quadratic temperature dependence in the chain resistivity, in agreement with recent results on good untwinned crystals.[16]

Turning to a comparison with previously published thermopower results, compared to our results in Fig. 2, we note that the a-axis thermopower lies directly between the two curves found in the literature, confirming that Y123 does not show the simple temperature-linear behavior common to the majority of cuprate superconductors. The average slope above 150 K is near -0.2×10^{-8} V/K^2, a factor of 10 less than the common value but similar to that found by Lowe, Regan, and Howson.[10] The differences in the absolute magnitudes between the various measurements are, however, relatively small on the scale of the thermopower more common in the high-T_c materials, and they probably result from small differences (±0.02) in the oxygen stoichiometry.

The b-axis thermopower again lies between the two curves found in the literature. In no case is there a linear temperature dependence, and the order of the previous two results is opposite to that found along the a axis. Again the differences are relatively small on the scale of the thermopowers in most of the high-T_c cuprates. The most common vacancies and impurities in this material lie predominantly in the chains, and we ascribe the differences to scattering by those defects. It is widely recognized that the thermopower is a particularly sensitive probe of the details of carrier scattering.

In order to relate the differences noted above to the oxygen stoichiometry, we have unloaded the crystal and repeated the thermopower measurements, with the results

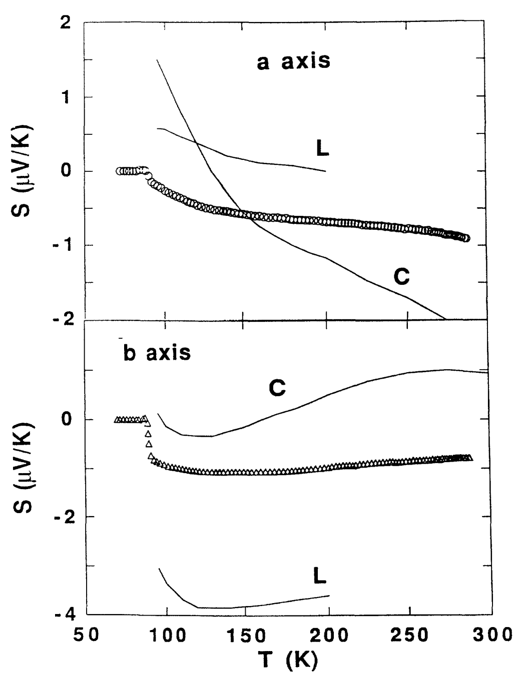

FIG. 2. A comparison between the present results, and the thermopowers determined in two previous studies (C. Cohn *et al.*, Ref. 11 and L. Lowe, Regan, and Howson, Ref. 10).

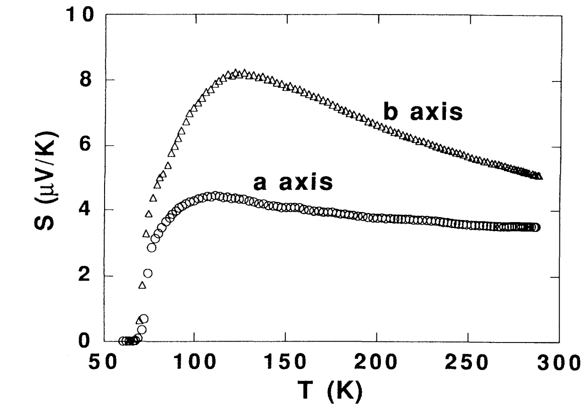

FIG. 3. Temperature dependences of the thermopowers along the two axes for the crystal unloaded to $\delta=0.3$.

in Fig. 3. Note that in this case the resistivities along the two axes could not be determined, for the c-axis resistivity[22] of this unloaded crystal prevents even this thin crystal from being approximated by a two-dimensional limit, and the Montgomery method failed to yield reliable results. The thermopower shows a similar temperature dependence to the fully loaded data, and the difference is primarily a shift of the baseline. It is interesting to note that a- and b-axis thermopowers show similar increases and that the trend conforms to the relation between S (290 K) and hole doping as proposed by Obertelli, Cooper, and Tallon.[5] It is perhaps fortunate that the temperature at which Obertelli, Cooper, and Tallon chose to establish their relationship was 290 K, for at any temperature differing from that value by more than about 50 K the temperature dependence of Y123 would have made it an exception.

The entire set of data on single crystals, including both the two previously published results and the present work, then show a consistent picture as regards the a-axis thermopower. The temperature derivative is substantially smaller but of the same sign as in the pattern described in the Introduction, and the dependence on the hole concentration is typical of that in all the cuprate superconductors. The calculated band structure for Y123 has been shown to predict the observed temperature dependence,[23] but we are not aware of any corresponding prediction for the other cuprates.

IV. CONCLUSIONS

We have measured the thermopower of a single crystal of Y123, both in a fully loaded state and with a reduced oxygen concentration. The results provide a framework in which to understand the differences between the two previous attempts to perform such single-crystal measurements, clearly identifying the major cause of the differences in the a-axis values as relating to their oxygen concentration. The b-axis thermopower, on the other hand, is strongly dependent on disorder (oxygen vacancies and impurities) on the chains, due to the contribution of chain conduction along this axis.

The a-axis thermopower almost surely contains a predominantly plane contribution, and it differs in detail from the plane thermopower in the other high-T_c cuprates. The similar temperature dependencies shown by the fully loaded and unloaded crystals, in which the chain is substantially disrupted by oxygen vacancies, argues that the chain has little direct effect on the thermopower in this direction. Y123 then forms a real exception to the pattern described in the Introduction, for it has a substantially weaker temperature dependence than the rest of the high-T_c cuprates. Nonetheless it shows a simple shift in the thermopower with hole concentration, accompanied by at most a small change in its temperature dependence, in common with the overall pattern. We suggest that the temperature dependence is determined by details of the Fermi surface, while the shift has an as yet unidentified universal source.

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