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Magnetic-field dependence of the specific heat of $YBa_2Cu_3O_7$

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Specific-heat measurements on $YBa_2Cu_3O_7$ in magnetic fields to 7 T have shown the presence of Schottky anomalies with the field and temperature dependence expected for a fixed concentration of Cu^{2+} magnetic moments. The field-dependent part of the specific heat also includes a temperature-proportional contribution that is approximately proportional to field. These results are qualitatively different from those reported recently from another laboratory.

Early measurements in this laboratory of the specific heat (C) of $YBa_2Cu_3O_7$ (YBCO) in magnetic fields (H) showed the presence of both a Schottky anomaly and an approximately linear-in-H increase in $\gamma^*(H)$, the coefficient of the "linear term" in C.[1] In the model proposed to explain these results, the Schottky anomaly arises from a low concentration (n_2) of Cu^{2+} magnetic moments that are also responsible for the zero-field "upturn" in C/T. The importance of n_2 is related to its negative correlation with certain superconducting-state properties such as $\Delta C(T_c)$. These correlations were based on measurements on a number of large polycrystalline samples that had been made by seven different research groups. They show that the strong sample-to-sample variation in parameters derived from specific-heat data are associated with corresponding variations in the volume fraction of superconductivity. The Cu^{2+} moments are associated with the nonsuperconducting material, and n_2 measures its amount.[8–11] Both n_2 and $d\gamma^*/dH$ played important roles in estimating the values of parameters characteristic of the "ideal" fully superconducting state, and the normal-state density of electron states.[10–12] In a few early measurements data were taken in both 3.5 and 7 T, but more recently only 7-T data, which give the most accurate values of n_2 and $d\gamma^*/dH$, have been taken.

Recent specific-heat measurements by Sanchez *et al.*[13] suggest a substantially different model for the H dependence of C and the parameter n_2. These measurements, which were made on a 68-mg polycrystalline sample, confirm the occurrence of both the Schottky anomalies and the linear-in-H increase in $\gamma^*(H)$, but in addition to the usual H dependence of a Schottky anomaly there is an H-proportional amplitude factor, i.e., the effective value of n_2 is proportional to H. This led Sanchez *et al.* to suggest that this contribution to C "originates from the vortex cores"—a model very different from that in which n_2 measures a fixed concentration of Cu^{2+} moments that are associated with nonsuperconducting regions of the sample. The stronger field dependence of the Schottky contribution associated with the H-proportional prefactor is partially offset by a substantially smaller value of $d\gamma^*/dH$ to leave an overall H dependence of C similar in magnitude to that observed in this laboratory.

The differences between our earlier work and that of Sanchez *et al.* are important for understanding the properties of YBCO much more generally, and have led us to make measurements with greater attention to the effect of the intermediate fields that are important for testing the two models. For $H=0$ and 7 T the results are consistent with those obtained earlier. For all fields they are consistent with the model proposed earlier, and not with the H dependence reported by Sanchez *et al.* Our data do not fit their model; their data do not fit ours. There is no obvious explanation of this discrepancy, which is well outside the apparent experimental uncertainties. It may be, in part, either another manifestation of the well-known sample dependence of YBCO properties or related to differences in the way the magnetic fields were applied. This paper is intended, in part, to define the discrepancy and to call attention to the need for its resolution.

The sample was polycrystalline, 30 g in mass, prepared from stoichiometric quantities of Y_2O_3, BaO_2, and CuO and fired three times at 950 °C with intermediate grindings and compaction before the final firing. The first two firings were in air, and the last in O_2; during the final cooling the sample was held at 650 °C for 12 h, and at 350 °C for 72 h. The sample consisted of randomly oriented crystallites with a median size of the order of 10 μm; no impurity phases were detectable by x-ray analysis; the density was 72% of the theoretical; high-temperature (100–300 K) susceptibility measurements gave the total concentration of Cu^{2+} moments, $n=0.0082$ moles Cu^{2+}/mole YBCO; an entropy-conserving construction on the specific-heat anomaly at T_c gave $T_c=91.5$ K and $\Delta C(T_c)/T_c=49$ mJ/mole K^2, which corresponds[8–11] to 63% superconductivity. For each measurement in a magnetic field the sample was cooled from above T_c in the field. The specific heat was measured by a heat pulse technique that would have detected contributions with associated time constants of up to several minutes.

Parameters characterizing $C(H,T)$ were derived from data for $H=0$, 1, 3, 5, and 7 T in the range 0.35–10 K. For both $H=0$ and 1 T, the contribution form the Cu^{2+} moments is much broader than a Schottky function, and only the high-temperature tail falls in this temperature range. For those data, the sum of the Cu^{2+} contribution, the linear term, and the lattice contribution is best represented by

$$C=\sum A_{-n}T^{-n}+\gamma^*(H)T+B_3T^3+B_5T^5 \ . \quad (1)$$

The higher applied fields shift the specific-heat anomaly associated with the Cu^{2+} moments into the temperature range of the measurements, and also sharpen it, making the Schottky function a better approximation, and

$$C=n_2C_{\rm Sch}\left[\frac{g\mu_BH}{k_BT}\right]+\left[\gamma^*(0)+\frac{Hd\gamma^*}{dH}\right]T +B_3T^3+B_5T^5 \ , \quad (2)$$

in which the linear H dependence of $\gamma^*(H)$ has been assumed, is a useful representation. In addition to the terms in Eqs. (1) and (2), a hyperfine contribution of the form $D_{-2}(H/T)^2$ is expected for the copper nuclear magnetic moments. In 7 T the Cu^{2+} Schottky anomaly is well separated from the hyperfine contribution, the latter is a significant part of C at the lowest temperatures, and analysis of the data gives $D_{-2}=0.0057$ mJ K/T mole with an uncertainty of about 10%. Since the hyperfine contribution was determined less accurately in other fields, the 7-T result was used to correct *all* the data for that contribution before further analysis. (Consistent with earlier measurements the value of D_{-2} is less than that expected for the full Cu nuclear magnetic dipole contribution, $D_{-2}=0.0096$ mJ K/T^2 mole. Presumably the difference is a consequence of long nuclear relaxation times in parts of the sample.)

A number of different analyses of the data gave generally consistent values of the various parameters. Several of these are described here, and the results are summarized in Table I. To ensure that the fits were not unduly influenced by the higher-temperature data, they were obtained by procedures that minimized the *fractional* deviations in C. The analyses of the 0- and 1-T data with Eq. (1), both of which are designated "analysis I" in Table I, required, respectively, 5 and 6 negative-exponent terms to give good fits to the data to 0.35 K, but essentially the same values of $\gamma^*(H)$, B_3, and B_5 were obtained with fewer terms and appropriate low-temperature cutoffs to the data. In analysis II, the 3-, 5-, and 7-T data were combined with the zero-field data (from which the upturn had been subtracted) and fitted by Eq. (2) with g, n_2, $\gamma^*(0)$, $d\gamma^*/dH$, B_3, and B_5 taken as adjustable parameters to obtain the values that best represented *all* the data. The value obtained for g, 2.10, is consistent with that obtained in other analyses and is reasonable for Cu^{2+} moments but the fit is not very sensitive to the value of g: an otherwise similar fit with g fixed at 2.00 gave essentially the same values of the other parameters and the same rms deviation. The quality of the fit is illustrated in Fig. 1 where $n_2C_{\rm Sch}/T+Hd\gamma^*/dH$ derived for 3 and 7 T is compared with the experimental data from which the other contributions have been subtracted. Although the contribution of the Cu^{2+} moments to C is much sharper in 3 T than in the lower fields, its broadening relative to both the Schottky curve and the 7-T data is apparent. Analysis III was similar to analysis II except that g was fixed at 2.10 and n_2 was allowed to take

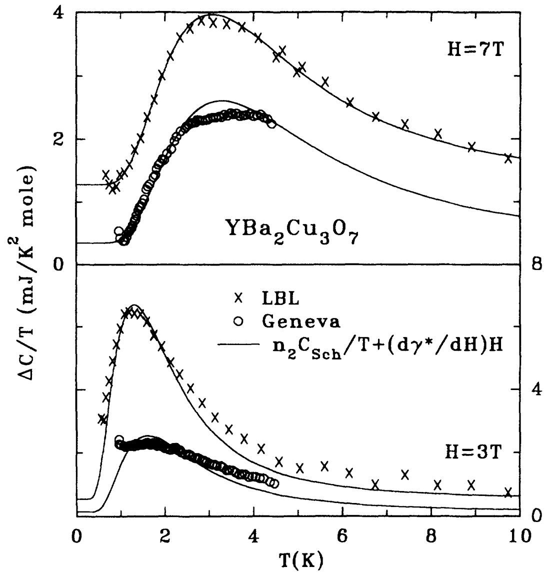

FIG. 1. Comparisons of the Lawrence Berkeley Laboratory (LBL) and Geneva data for 3 and 7 T. In both cases the curves represent the reported fitting expressions for the H-dependent part of C, $\Delta C=n_2C_{\rm Sch}+H(d\gamma^*/dH)T$; and the discrete symbols the experimental data corrected for other contributions.

TABLE I. Parameters derived from specific-heat data in the 0.35–10 K range. n_2 is in moles Cu^{2+}/mole YBCO; other quantities are in units of mJ, K, T, and moles YBCO.

Analysis	Data included	% rms Deviation	g	10^3n_2	$\gamma^*(0)$	$\gamma^*(1\ T)$	$d\gamma^*/dH$	B_3	10^4B_5
I	$H=0$	0.5			4.88			0.297	7.4
I	$H=1$ T	0.6				5.10		0.295	7.5
II	$H=0,3,5,7$ T	2.1	2.10	2.6	4.90		0.187	0.302	7.5
III	$H=0,3,5,7$ T	2.4		2.6,2.6,2.4 [a]	4.87		0.189	0.306	7.2

[a] The three values of n_2 from analysis III are for $H=3$, 5, and 7 T, respectively.

different values for each H, to obtain independent values of n_2 for 3, 5, and 7 T.

The values of n_2 obtained in the different analyses are all in satisfactory agreement: they show no obvious dependence on H. The good agreement between the values derived in analyses II and III, in which n_2 was constrained to the same value in all fields in the first case but free to vary in the second, is particularly noteworthy in this respect. The values of both n_2 and $\gamma^*(H)$ derived in the various analyses are also compared in Fig. 2. In the upper part of that figure the solid line represents the single value of n_2 derived from analysis II; the ×'s represent the values of n_2 derived for $H=0$ in analysis I (note comment above) and for $H=3$, 5, and 7 T in analysis III. In the lower part of the figure the solid line represents both $\gamma^*(0)$ and $d\gamma^*/dH$ derived from the data for 0, 3, 5, and 7 T in analysis II; the ×'s represent the values of $\gamma^*(0)$ and $\gamma^*(1\text{ T})$ derived in analysis I. We conclude that the data are well represented by an n_2 that is independent of H, and a $\gamma^*(H)$ that is linear in H.

Sanchez *et al.* measured the specific heat of YBCO in fields of 0, 0.2, 0.5, 1, 3, 7, and 14 T, and reported values of parameters derived from the data in the 1–10-K range. With respect to certain of the major features, their analysis was the same as analysis III: it was based on Eq. (2); the data for *all* fields were fit simultaneously with $\gamma^*(0)$, $d\gamma^*/dH$, and B_3 independent of H; n_2 was determined independently for each H. There were, however, several differences: the T^5 term in the lattice heat capacity was found to be unnecessary and was omitted; the full value of the hyperfine specific heat was assumed to be correct and subtracted from all $H\neq0$ data; $C_{\text{Sch}}(H+H_0)$ was used in place of $C_{\text{Sch}}(H)$, with H_0 a parameter taken to be independent of H and determined by the fit as $H_0=0.9$ T. The effect of H_0 is to shift the Schottky anomaly, without broadening it, and in particular to give a finite contribution of $H=0$ that is intended to represent the zero-field upturn, and which is required for any estimate of n_2.

The most striking discrepancy between our results and those of the Geneva group is in the H dependence of n_2; whereas we find n_2 independent of H, they find n_2 approximately proportional to H. The very different results of essentially identical analyses are illustrated in Fig. 2(b). A second discrepancy is the substantial difference in the values of $d\gamma^*/dH$, which are represented in Fig. 2(a) by the slopes of the solid and dashed lines, for the Lawrence Berkeley Laboratory (LBL) and Geneva data, respectively. To extend the comparison to the actual experimental data, we have read the points ($T\leq4.5$ K) from Fig. 3 of Ref. 13 and compared both the 3- and 7-T data with ours in Fig. 1, where the data and the derived fitting expressions have been plotted in the same way as the LBL results. (It should be noted that the curves in Fig. 3 of Ref. 13 are "guides to the eyes," not the fitting expressions.) For 7 T, the two values of n_2 are essentially the same, and the data are consistent with Schottky anomalies with the same amplitude; for 3 T for which the two values of n_2 are substantially different, the data are consistent with that difference. These comparisons suggest that the discrepancy—the H proportionality of n_2 in one case,

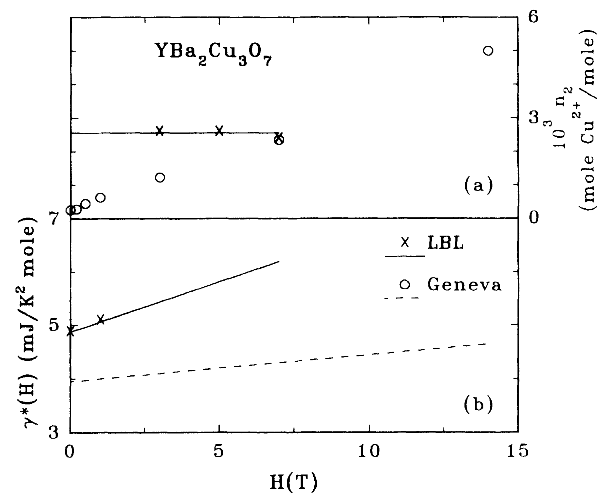

FIG. 2. Comparisons of the LBL and Geneva values of $\gamma^*(H)$ and n_2. The discrete symbols (× for LBL, ○ for Geneva) represent values that apply to data for a single field: the lines (solid for LBL, dashed for Geneva) represent the result of fits to data for a number of fields.

and the H independence in the other, and the different values of $d\gamma^*/dH$—is inherent in the data, and not an artifact of the analysis.

Several additional points relevant to possible sample differences, to the data analyses or to the models deserve attention:

(i) The magnitude and temperature dependence of the lattice specific heats of the two samples are substantially different: 0.44 T^3 mJ/K mole for the Geneva sample; $0.30\,T^3+7.3\times10^{-4}\,T^5$ mJ/K mole for the LBL sample.

(ii) The $n_2(H)C_{\text{Sch}}(H+H_0)$ term in the fitting expression used by Sanchez *et al.* provides only a very rough approximation to the corresponding contribution to C for $H\leq1$ T. It deviates from the zero-field upturn by as much as 50%, but in that case an independent estimate of n_2 based on our correlation of n_2 with the magnitude of the upturn at 1 K gives essentially the same value. Since that correlation is based primarily on 7-T data for n_2, this comparison underlines the striking difference in H dependence between the samples on which the correlation was based and that studied by Sanchez *et al.*—for their sample, the zero-field upturn is 10 times smaller relative to the 7-T Schottky anomaly.

(iii) The zero-field value of n_2 for the Geneva sample, 2.5×10^{-4} moles Cu^{2+}/mole YBCO, is unusually small—10 times smaller than the value for the sample studied in this work; smaller than all but one of the more than 20 values we have obtained for other samples, many of which were prepared in other laboratories; and smaller than almost all values that can be estimated from other published work. The larger value of n_2 for our sample facilitates accurate measurements of the H dependence of that contribution to C, but raises the question of whether the observed H dependence might not depend on n_2, and differ from that of the Geneva sample because n_2 is larger. Evidence against that possibility is offered by two other samples with n_2 smaller by factors of 3 and 10 (for the latter, n_2 is similar to the $H=0$ value for the Geneva sample) that show H dependences similar to that reported here–similar values of $d\gamma^*/dH$ and Schottky anomalies in 7 T consistent with the correlation with the zero-field upturns. The comparison in Fig. 2(b) also rules out a resolution of the discrepancy on the basis of two contributions to n_2, one proportional to H, and one independent of H.

(iv) A model in which the Schottky anomalies are associated with the vortex cores does not account for the zero-field upturn. In addition, Schottky anomalies associated with the vortex cores might be expected to be broadened by increasing H, whereas the opposite is the case.

In conclusion, there is a significant qualitative difference between the field dependence of the specific heat of YBCO as reported here and as reported by Sanchez *et al.* The difference seems to be inherent in the data, and not simply an artifact of the analyses. Certain other parameters are also different for the two samples, but there is no obvious indication that they are related to, or explain the difference in field dependence.

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[1]These features were reported in Refs. 2–5, and were also described in two review articles, Refs. 6 and 7. In the earliest papers the Schottky anomalies were attributed to impurity phases, but later it was recognized that Cu^{2+} moments contributing to the Schottky anomalies were also located on the YBCO lattice (see subsequent description and references in the text).

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