Specific heat of a high-T_c perovskite superconductor YBa₂Cu₃O₈₋δ

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Heat capacity determinations reveal sensitively the character of a transformation in solids and are not affected by minor amounts of impurity phases. Previous studies of high-T_c superconductors report either small[1,2] or no[3-5] jumps in the heat capacity at the superconducting transition temperature T_c. We communicate here the main finding from our specific heat measurements on a perovskite superconductor YBa₂Cu₃O₈₋δ in which conductivity measurements indicate a transition temperature near 92 K. A full report with tables of data will be published subsequently.

The sample was prepared by mixing stoichiometric amounts of Y₂O₃, BaO, and CuO so as to yield a 1:2:3 ratio of metals. The nominal composition corresponds to $\delta = 1.5$. Starting materials were checked by x-ray powder diffraction. There was evidence that the BaO may have reacted with atmospheric water to form the hydrated hydroxide, and the diffraction pattern of the product contained four very weak reflections which could not be indexed on the cell described by Lepage et al.[6] The powder diffraction pattern of the final product is in excellent agreement with the pattern described by Cava et al.[7] with $a = 3.8202(3)$ Å, $b = 3.8885(3)$ Å, and $c = 11.684(1)$ Å.

The starting materials were mixed, heated at 10 °C min⁻¹ to 910 °C, held at that temperature for 12 h, and cooled at 5 °C min⁻¹ to 750 °C and then 10 °C min⁻¹ to room temperature. The product was ground, pressed into pellets and sintered at 930 °C with the same heating and cooling rates as in the first heat.

The resistance of one of the pellets was measured using four-terminal connections, with a thermocouple attached to the pellet. The resistance dropped by about two orders of magnitude at approximately 92 K; there was a small residual resistance of unknown origin below this temperature.

The specific heat C_p was measured from 5.3 to 345 K by adiabatic calorimetry in the Mark XIII adiabatic cyrostat, which is an upgraded version of the Mark X cryostat already described.[8] It was necessary to crush the sample to a coarse powder for loading into the calorimeter. Unsmoothed values of the specific heat are shown as a function of temperature in the vicinity of the transition in Fig. 1. Between about 90 and 92 K, which can be considered the width of the transition, the heat capacity drops by about 1% before resuming its increase. By extrapolation of the curves below and above this range, the drop in specific heat ΔC at 91 K, the center of the

transition, is (5.9 ± 1.0) mJ K⁻¹ g⁻¹ which amounts to 3.1% of the total C_p. The drop is equivalent to 3.9 J K⁻¹ mol⁻¹ based upon a molar mass of 658.2 g mol⁻¹ for the nominal compositions $\delta = 1.5$. Throughout this paper, "mole" means a mole of the formula unit.

The decrease in specific heat ΔC at T_c can be compared with the value calculated from the Rutgers' formula[9]

$$\Delta C = V T_c \mu_0 \left(\frac{dH_c}{dT}\right)^2 .$$

Using $V = 0.154$ cm³ g⁻¹ for the specific volume,[16] setting $H_c = H_{c2}/(\sqrt{2}\,\kappa)$ and using the parameters,[7] $dH_{c2}/dT = -13\,kOE$ K⁻¹ $= -1.0\times10^{-6}$ A m⁻¹ K⁻¹, the Ginzburg–Landau constant $\kappa = 62$ and $\mu_0 = 4\Pi\times10^{-7}$ J A⁻² m⁻¹, we find a calculated value of $\Delta C = 2.4$ mJ K⁻¹ g⁻¹, which is less than half the measured value, showing that although the parameters used in this calculation may be modified in the light of new data,[10] the superconducting volume must be of the same order of magnitude as the sample volume.

The electronic heat capacity coefficient determined from our measurements using the weak coupling, isotropic gap BCS theory[11] is $\gamma_{BCS} = \Delta C/(1.43\,T_c) = 30 \pm 5$ mJ K⁻² mol⁻¹. This result may be compared with the values 14 ± 3 mJ K⁻² mol⁻¹ for La₁.₈₅Sr₀.₁₅CuO₄ obtained by Dunlap et al., and 23 ± 4 mJ K⁻² mol⁻¹ for
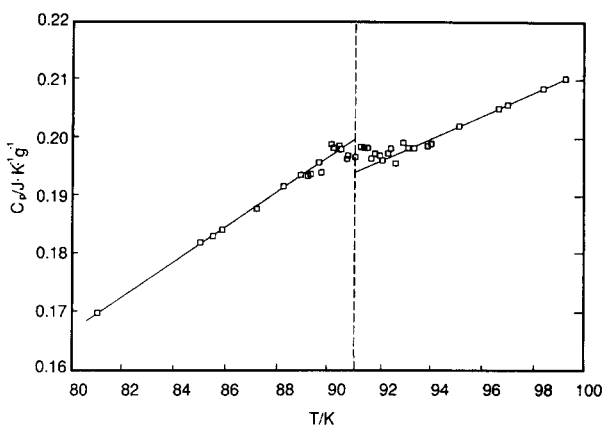
FIG. 1. Specific heat C_p vs temperature for YBa₂Cu₃O₈₋δ in the vicinity of the transition.

$[La_{0.925}Ca_{0.075}]_2 CuO_4$ obtained by Kitazawa et al.,[2] based upon similar measurements and the same formula. Cava et al. obtained a revised value $\gamma = 18 - 24$ mJ K^{-2} mol^{-1} for material similar to ours, based upon magnetic susceptibility measurements.[7,10]

From the slope of the plot of C_p/T vs T^2 at low temperatures, a Debye temperature of $\Theta_D = 145\ n^{1/3}$ is obtained, where n is the number of atoms in the primitive unit cell[2]; for the nominal stoichiometry $n = 12.5$, and so $\Theta_D = 336$ K. At 342 K, $C_p = 35.92\ R$, which is less than the upper limit of $37.5\ R$ for this value of n.

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A rotationally resolved LIF study of the N₂⁺ products of the thermal energy Penning ionization reaction: Ne*(³P₂)+N₂

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We report the results of a rotationally resolved laser-induced fluorescence (LIF) study of the N₂⁺ products of the Penning ionization, Ne*(³P₂) + N₂. Considerable rotational excitation is observed; the rotational distributions cannot be characterized by a single Boltzmann temperature, indicating a dynamical origin of the nascent distributions. The distributions are similar in character for each vibrational level. This work represents one of the first applications of supersonic beam technology to reveal rotational subtleties in the dynamics of reactive atom–diatom systems. The results also add important new information to the few examples of rotationally resolved Penning ionization.

In previous work on the Penning ionization of diatomics by rare gas metastable atoms,[1] little attention has been given to the rotational distributions of the diatom.[2–4] This is understandable in light of the generally held mechanistic view that Penning ionization occurs via a long-range interaction with little torque exerted on the collision partners at the instant of ionization.

Product rotational distributions, however, can be a sensitive probe of the dynamics of a reactive encounter. To explore the dynamics of Penning ionization on a finer scale, we have carried out a product rotationally resolved investigation of the system

$$Ne^*(^3P_2) + N_2(X\,^1\Sigma_g)$$
$$\rightarrow Ne(^1S_0) + N_2^+ (X\,^2\Sigma_g, v = 0\text{–}3) + e^-,$$
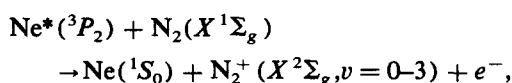
for which $\Delta H = -1.04$ eV. The experiment was performed at a collision energy of 70 meV using LIF detection of the B–X system of N₂⁺; N₂⁺ ($v = 4$) is accessible via the collision energy. Both rotational and vibrational product distributions were measured.[5] The experiments were conducted in a single collision ion–molecule apparatus[6] modified to include a pulsed, supersonic expansion as the neutral source. The initial N₂ rotational distribution was measured by two-photon LIF[7,8] and was characterized by a Boltzmann temperature of 8 K. The metastable source produces over 90% Ne*(³P₂).[9]

The observed N₂⁺ rotational populations show several components. The populations for $2 \leqslant N \leqslant 21$ can be well fit by two-component Boltzmann distributions having a low temperature of 50 K ± 10 K and a high temperature ranging from 220 to 490 K ± 50 K (Fig. 1). The cold:hot component branching ratio is 62% ± 5%:38% ± 5% in $v = 0$ and decreases with vibrational level.

Several mechanisms may account for the multiple temperatures of the observed rotational distributions. Since the highest rotational level observed ($N = 24$) corresponds to an energy of 150 meV while the initial kinetic energy is only 70 meV, a fraction of the reaction exothermicity must be partitioned into excitation of the hot rotational component. The present system may be similar to the Ne* + HBr system. Ionization occurs at short range in this case, and the HBr⁺ (A) rotational distributions are determined by an im-