

Thermodynamics of the (lanthanum + strontium + copper + oxygen) high- T_c superconductors

I. Heat capacities of SrCuO_2 , Sr_2CuO_3 , and $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$

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The subambient heat capacities of three $(\text{SrO})_x(\text{CuO})_y$ inter-oxide samples with $x = y = 1$; $x = 2$, $y = 1$; and $x = 1$, $y = 2$, were measured as a part of an investigation into the chemical thermodynamics of the high- T_c superconducting system (lanthanum + strontium + copper + oxygen). No anomalous contribution to the heat capacity was observed over the experimental region. The heat capacity of the $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ phase was derived from that of the mixed phase of nominal composition $x = 1$, $y = 2$. All samples exhibit a Debye-like behavior at low temperatures with finite linear electronic terms. Thermophysical properties at selected temperatures are presented and compared for the three compounds. The values of S_m° at 298.15 K for the three compounds $\text{Sr}_{1/2}\text{Cu}_{1/2}\text{O}$, $\text{Sr}_{2/3}\text{Cu}_{1/3}\text{O}$, and $\text{Sr}_{14/38}\text{Cu}_{24/38}\text{O}_{41/38}$ were: $5.828 \cdot R$, $5.953 \cdot R$, and $6.032 \cdot R$, respectively.

1. Introduction

The system (lanthanum + strontium + copper + oxygen) shows an unusual array of electric and magnetic properties, of which the most remarkable is the superconductivity of the Sr-doped La_2CuO_4 phase. We have measured the subambient heat capacities of three (strontium + copper + oxygen) samples as a part of a thorough investigation into the thermochemistry and the thermophysics of the system. The superambient chemical-thermodynamic properties of the same samples investigated by solid-state electrochemical technique and by thermogravimetric analysis are the subject of a separate report.⁽¹⁾ Several stable $\text{Sr}_x\text{Cu}_y\text{O}_z$ phases, in addition to CuO and SrO , were identified in this system.^(2–4) The exact stoichiometry of these phases is believed to be Sr_2CuO_3 , SrCuO_2 , and $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$.^(3,4) Earlier reports suggested that the composition SrCu_2O_3 might also be a distinct inter-oxide

compound,^(5,6) however, more recent reports^(3,4,7) rule out this composition as a distinct phase.

CuO is an antiferromagnetic insulator which assumes a monoclinic structure at subambient temperatures. The heat capacity of CuO has been reported by several authors.⁽⁸⁻¹²⁾ Antiferromagnetic disordering was observed by neutron diffraction^(13,14) at $T_N = 230$ K and is associated with two transitions, at about 213 K and 230 K, in the heat-capacity values.⁽⁶⁻⁸⁾

The heat capacity of SrO was measured by Anderson⁽¹⁵⁾ and later by Gmelin⁽¹⁶⁾ whose values were used in this report for all calculations involving that heat capacity. No excess contributions, other than that of the lattice, are identifiable in the heat-capacity values for this compound.

This report is the first in a series of papers regarding the thermochemistry of the system (lanthanum + strontium + copper + oxygen). The heat capacity of samples of the nominal compositions Sr_2CuO_3 , SrCuO_2 , and $\text{SrCu}_2\text{O}_{4.5-14}$ are reported here. The first two samples are believed to be single-phase compounds Sr_2CuO_3 and SrCuO_2 , while the third sample consists mainly of the oxygen-rich phase $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ plus some CuO as a distinct phase. The heat capacities and derived thermophysical properties of several superconducting Sr-doped La_2CuO_4 samples ($\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$) and of La_2CuO_4 will be the subject of subsequent papers in the series.^(17,18)

2. Experimental

The oxide samples were prepared by a conventional ceramic mixing technique using high-purity starting powders of SrCO_3 and CuO. The thoroughly mixed powders with proper ratios of Cu to Sr were pressed into pellets and sintered in air at 1193 K for 7 d, with daily regrinding and re-pressing. The formation of a single-phase compound was confirmed by X-ray powder diffraction analysis for Sr_2CuO_3 and SrCuO_2 . The sample with $x = 1$ and $y = 2$ was found to consist of at least two phases, of which one is the oxygen rich phase $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ and the other is excess CuO. Excess free CuO still remained after sintering the sample for 30 d in air from 1073 K to 1193 K. Thermogravimetric analysis⁽¹⁹⁾ supported the $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ composition of the compound proposed earlier by McCarron *et al.*,⁽⁷⁾ Siegrist *et al.*,⁽²⁰⁾ and Roth *et al.*⁽⁴⁾ The excess copper is believed to be in the form of CuO, and the mass ratio between these two phases is calculated to be 91.54/8.46.

The sub-ambient heat capacities of the three (strontium + copper) oxides were measured in a new adiabatic calorimetric cryostat (laboratory designated Mark XIII),^(21,22) an improved version of the Mark X cryostat which was previously described together with relevant operating technique⁽²³⁾ and which itself is an improved version (by addition of a guard shield surrounding the adiabatic shield)⁽²⁴⁾ of the Mark II cryostat. Acquisition of results was computer assisted. After being programmed for a series of determinations, the computer recorded: (a), the drift reading of the calorimeter temperature over a suitable period before and after each energy-input period; and (b), the current and potential of the heater and the duration of the heating period. Information on the initial, final, and mean temperatures, the

energy input, and the resistance of the heater, together with the apparent heat capacity of the system were also recorded over the temperature range 5.3 K to 350 K. The same gold-plated oxygen-free high-conductivity (OFHC) copper calorimeter (laboratory designation W-99) was used for all three samples. The calorimeter had a mass of 10.21 g and an internal volume of 11 cm³. The temperature of the calorimeter was measured with a Leeds & Northrup platinum capsule-type resistance thermometer in an entrant well. The (thermometer + heater) assembly had a mass of about 6 g. The thermometer was calibrated by the U.S. National Bureau of Standards against IPTS-48 and was considered to reproduce thermodynamic temperatures within 0.03 K from 5 K to 380 K.

Samples having masses 30.82 g of SrCuO₂, 23.74 g of Sr₂CuO₃, and 26.36 g of SrCu₂O_{4.5/14} were used for the calorimetry. To facilitate rapid thermal equilibration about 3 kPa at 300 K of helium gas was introduced into the calorimeter vessel after evacuation for each experiment. The calorimeter was then sealed, placed in the cryostat, and cooled. The heat capacity of the (empty calorimeter + thermometer) assembly represented about 50 per cent of the total heat capacity over the entire experimental temperature range for SrCuO₂ and Sr₂CuO₃ experiments, and about 40 per cent of the total heat capacity for the SrCu₂O_{4.5/14} experiment over the same temperatures. The experimental standard deviations in these measurements between 7 K and 25 K decrease gradually from about 4 per cent to 0.1 per cent at 25 K and remain no larger than that value at higher temperatures.

3. Results and discussion

The three compounds Sr_{1/2}Cu_{1/2}O, Sr_{2/3}Cu_{1/3}O, and Sr_{14/38}Cu_{24/38}O_{41/38} as defined in table 1 are hereafter designated, for the convenience of the discussion, as I, II, and III, respectively. The actual stoichiometry of the third sample was Sr₁₄Cu₂₈O₄₅, which is equivalent to (Sr₁₄Cu₂₄O₄₁ + 4CuO). Thus the molar heat capacity of III, *i.e.* (Sr₁₄Cu₂₄O₄₁)/38, was derived from that of the mixed-phase Sr₁₄Cu₂₈O₄₅ sample by subtracting the heat capacity of the excess CuO from the experimental results. The experimental molar heat capacities of the samples SrCuO₂, Sr₂CuO₃, and Sr₁₄Cu₂₈O₄₅ are presented in table 2. These results are plotted in figure 1 for (x + y) = 1. Similarly presented thermophysical properties at selected temperatures are given in table 3. The experimental heat capacities were extrapolated

TABLE 1. Sample masses *m* and molar masses *M*

Formula ^a	<i>m</i> /g	Designation	<i>M</i> /(g·mol ⁻¹)
CuO	—	—	79.545
SrO	—	—	103.619
Sr _{1/2} Cu _{1/2} O	30.82	I	91.583
Sr _{2/3} Cu _{1/3} O	23.74	II	95.595
Sr _{14/38} Cu _{24/38} O _{41/38}	26.39	III	89.678

^a Sr_xCu_yO_z with (x + y) = 1.

TABLE 2. Molar heat capacities of SrCuO₂, Sr₂CuO₃, and Sr₁₄Cu₂₈O₄₅ ($R = 8.3144 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)

I: SrCuO ₂									
$\{M(\text{SrCuO}_2) = 183.165 \text{ g} \cdot \text{mol}^{-1}\}$									
Series I		Series II		41.933	1.253	107.574	5.396	213.259	9.030
6.037	0.004 ^a	6.084	0.001 ^a	44.751	1.438	112.379	5.638	219.428	9.165
6.852	0.006	7.156	0.008	47.759	1.644	117.397	5.881	225.586	9.289
7.424	0.010	8.184	0.013	50.779	1.860	122.623	6.122	231.754	9.415
7.950	0.012	9.332	0.021	54.063	2.095	127.876	6.352	237.925	9.524
8.117	0.013	10.485	0.026	57.533	2.343	133.127	6.572	244.109	9.650
8.582	0.017	11.673	0.035	61.025	2.585	138.383	6.789	250.310	9.758
9.502	0.022	12.831	0.045	64.531	2.823	143.662	6.994	256.485	9.867
10.336	0.025	14.032	0.058			148.947	7.191	262.652	9.956
11.176	0.031	15.264	0.075	Series III		154.241	7.381	268.841	10.052
12.019	0.038	16.501	0.095	51.578	1.916	159.548	7.564	275.049	10.137
12.996	0.047	17.910	0.121	55.203	2.519 ^a	164.857	7.741	281.245	10.224
14.089	0.059	19.465	0.154	58.402	2.404			287.421	10.309
15.181	0.073	21.044	0.196	61.629	2.612 ^a	Series IV		293.627	10.386
16.282	0.091	22.624	0.247	65.095	2.860	152.271	7.313	299.827	10.458
17.394	0.112	24.238	0.299	68.832	3.107	158.010	7.509	306.041	10.528
18.525	0.134	24.388	0.307	72.599	3.356	164.116	7.715	312.248	10.596
19.787	0.162	26.127	0.374	76.575	3.624	170.230	7.908	318.435	10.676
21.161	0.200	28.010	0.458	80.768	3.875 ^a	176.358	8.084	324.662	10.758
22.534	0.244	30.029	0.555	84.980	4.161	182.493	8.257	330.851	10.840
23.929	0.289	32.190	0.669	89.221	4.414	188.639	8.425	337.041	10.916
25.462	0.346	34.373	0.792	93.484	4.653	194.784	8.589	343.271	10.965
		36.752	0.932	97.997	4.894	200.932	8.740		
		39.326	1.088	102.780	5.147	207.085	8.892		
II: Sr ₂ CuO ₃									
$\{M(\text{Sr}_2\text{CuO}_3) = 286.784 \text{ g} \cdot \text{mol}^{-1}\}$									
Series I		22.337	0.297	59.096	3.627	149.709	11.215	238.609	14.780
5.972	0.002 ^a	23.721	0.359	62.311	3.974	155.001	11.508	244.790	14.946
6.169	0.007	25.119	0.429	65.539	4.309	160.325	11.778	250.941	15.118
6.744	0.010	26.532	0.509	68.961	4.668	165.641	12.043	257.177	15.280
7.402	0.009 ^a	27.953	0.597	72.566	5.044	170.944	12.314	263.370	15.424
7.464	0.014	29.389	0.694	76.183	5.420	176.252	12.582	269.525	15.563
7.725	0.015	31.099	0.821	79.920	5.807	181.555	12.823	275.724	15.716
8.152	0.022 ^a	33.043	0.976	83.837	6.204	186.885	13.062	281.917	15.858
8.951	0.020	34.992	1.141	87.751	6.582	192.208	13.291	288.133	16.000
9.934	0.025	37.100	1.326	91.858	6.963			294.314	16.133
10.795	0.031	39.353	1.532	96.230	7.346	Series III		300.496	16.268
11.665	0.038	41.619	1.745	100.613	7.724	177.608	12.732 ^a	306.702	16.380
12.546	0.048	44.076	1.984	104.999	8.092	183.161	12.895	312.905	16.486
13.407	0.060	46.750	2.260	109.583	8.460	189.279	13.164	319.131	16.567
14.251	0.073	49.446	2.551	114.384	8.836	195.394	13.423	325.352	16.622
15.246	0.090	52.327	2.860	119.231	9.202	201.619	13.651	331.583	16.693
16.374	0.110	55.402	3.197	124.057	9.558	207.841	13.874	337.833	16.787
17.486	0.134	58.502	3.553	128.870	9.901	213.936	14.081	343.033	16.905
18.589	0.163			133.924	10.243	220.077	14.276	347.240	16.911 ^a
19.707	0.197	Series II		139.190	10.584	226.247	14.433		
20.958	0.242	55.954	3.266	144.463	10.917	232.393	14.598		

TABLE 2—continued

		III: Sr ₁₄ Cu ₂₈ O ₄₅							
		{M(Sr ₁₄ Cu ₂₈ O ₄₅) = 3725.94 g·mol ⁻¹ }							
Series I		33.281	18.728	14.913	2.515	64.907	60.907	181.584	172.674
5.729	0.051 ^a	34.861	19.789 ^a	15.588	2.834	68.058	65.002	187.707	176.792
6.381	0.185	36.455	24.583 ^a	16.306	3.305	71.390	69.376	193.847	180.586
6.978	0.286	38.116	26.851 ^a	17.054	3.707	74.896	73.982	199.999	184.377
7.873	0.463 ^a	40.003	24.979 ^a	17.836	4.114	78.545	78.714	206.144	188.138
8.556	0.628	41.932	29.696	18.681	4.650	82.374	83.516	212.278	191.851
9.412	0.745	43.874	32.289	19.807	5.385	86.412	88.430	218.421	195.124
10.017	2.874 ^a	45.962	35.115	21.194	6.461	90.686	93.408	224.594	198.215
11.201	1.271	48.155	38.170	22.593	7.608	95.179	98.422	230.767	200.907
11.376	1.022 ^a	50.453	41.323	24.006	8.807	99.923	103.651	236.938	203.579
12.984	1.704	52.863	44.857 ^a	25.279	9.967	104.841	108.918	243.122	206.233
13.897	2.031	55.410	47.996 ^a	26.442	11.089	109.815	114.000	249.292	209.147
14.908	2.531	58.090	51.328 ^a	27.666	12.348	114.832	118.893	255.460	211.755
15.891	3.939 ^a	60.947	51.298 ^a	28.950	13.761	119.849	123.538	261.637	214.502
16.782	3.322 ^a	63.822	64.512 ^a	30.294	15.307	125.027	128.267	267.833	216.969
17.581	4.524 ^a	66.867	63.436 ^a	31.703	16.961	130.382	133.217	274.019	219.501
18.370	4.719 ^a			33.187	18.633	135.767	138.051	280.199	221.938
19.234	5.428 ^a			34.741	20.472	141.151	142.699	286.394	224.263
20.148	5.419 ^a	Series II		36.680	22.955	146.520	147.235	292.583	226.366
21.049	7.544 ^a	5.811	0.116	38.979	25.879	151.909	151.464	298.768	228.553
22.146	4.874 ^a	6.883	0.274	41.274	28.829	157.605	155.860	304.949	230.583
23.255	7.834 ^a	7.449	0.410	43.588	31.883	163.599	160.396	311.140	232.818
24.218	9.268 ^a	8.158	0.578			169.607	164.606	317.315	235.162
25.334	10.020	9.017	0.689	Series III		175.633	168.645	323.475	237.336
26.516	11.164	9.907	0.867	51.591	42.913	181.653	172.721	329.652	239.472
27.743	12.427	10.891	1.168	53.722	45.871	187.678	176.747	335.865	241.299
29.034	13.691 ^a	11.978	1.418	56.321	49.474			342.082	243.147
30.381	15.410	13.864	1.679 ^a	59.063	53.274	Series IV		347.294	244.818
31.791	17.056	14.276	2.190	61.927	57.045	175.644	168.710		

^a Not used in the evaluation of thermophysical properties.

to $T \rightarrow 0$ by means of $C_{p,m}/T$ against T^2 plots (figure 2). The thermophysical properties at 15 K were calculated from these plots by fitting the experimental values as $C_{p,m} = \gamma T + \alpha T^3$ with $\gamma = 1.262 \cdot 10^{-4} \cdot R \cdot K^{-1}$, $C_{p,m}$, $6.583 \cdot 10^{-5} \cdot R \cdot K^{-1}$, and $3.390 \cdot 10^{-4} \cdot R \cdot K^{-1}$, and $\alpha = 1.01 \cdot 10^{-5} \cdot R \cdot K^{-3}$, $8.19 \cdot 10^{-6} \cdot R \cdot K^{-3}$, and $1.615 \cdot 10^{-5} \cdot R \cdot K^{-3}$ for I, II, and III, respectively. Thus the molar entropies and molar enthalpies were $0.013 \cdot R$ and $0.142 \cdot R \cdot K$, $0.019 \cdot R$ and $0.178 \cdot R \cdot K$, and $0.023 \cdot R$ and $0.242 \cdot R \cdot K$ at 15 K for I, II, and III, respectively. The corresponding values at 298.15 K — which were calculated by means of the FITAB2 program^(2,5) — were $5.828 \cdot R$ and $931.15 \cdot R \cdot K$, $5.953 \cdot R$ and $959.03 \cdot R \cdot K$, and $6.032 \cdot R$ and $952.13 \cdot R \cdot K$, for the three inter-oxide compounds.

The linear electronic contributions to the heat capacities were obtained from the intercepts of the abscissæ in these $C_{p,m}$ against T^2 plots (the coefficients γ in figure 2). It is evident from this figure that the linear electronic contribution for III is larger than that of the other two phases. Since the linear (electronic) term in the molar heat

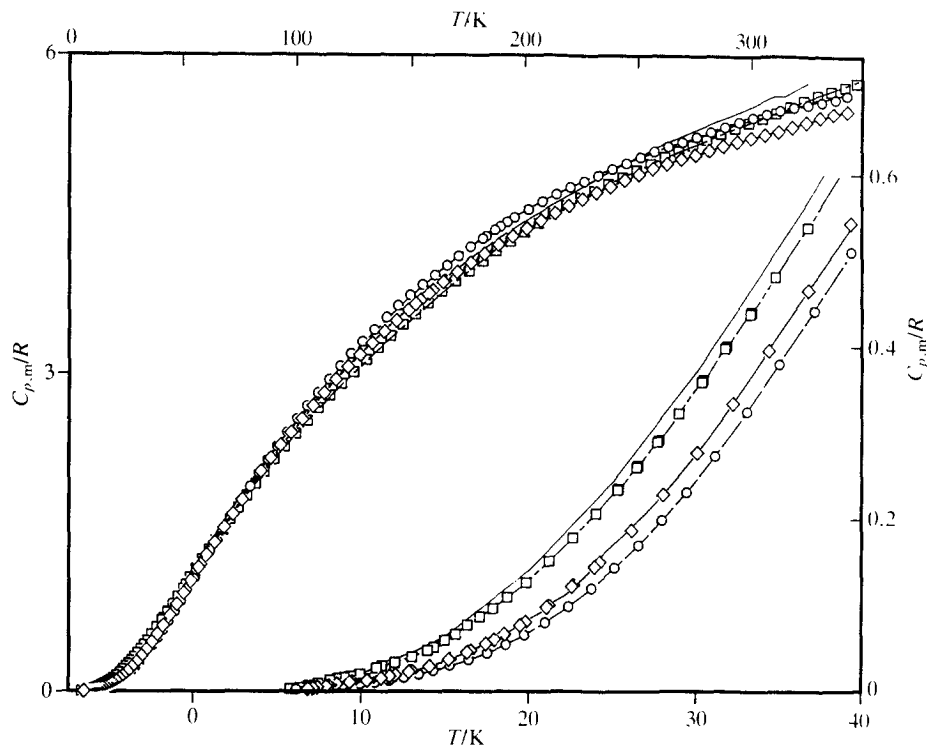


FIGURE 1. Experimental molar heat capacities of \diamond , I: $\text{Sr}_{1/2}\text{Cu}_{1/2}\text{O}$; \circ , II: $\text{Sr}_{2/3}\text{Cu}_{1/3}\text{O}$; \square , III: $\text{Sr}_{14/42}\text{Cu}_{28/42}\text{O}_{45/42}$. —, Calculated for $\text{Sr}_{14/38}\text{Cu}_{24/38}\text{O}_{41/38}$.

capacity is directly proportional to the density of the electronic states at the Fermi level divided by the Fermi temperature, $C_{\text{el.,m}} = R\pi^2 T/2T_{\text{F}}$, we conclude that this ratio is larger for the oxygen-rich phase III. This conclusion is reaffirmed by the electrical conductivity at higher temperatures which is found to be $9.41 \cdot 10^{-5} \cdot \Omega^{-1} \cdot \text{cm}^{-1}$ for I, $5.33 \cdot 10^{-4} \cdot \Omega^{-1} \cdot \text{cm}^{-1}$ for II, and $8.21 \cdot 10^{-3} \cdot \Omega^{-1} \cdot \text{cm}^{-1}$ for the mixed-phase sample III.

No excess contribution is observed in the heat capacities of these samples. The magnetic orderings that were observed in CuO ,^(8,11) are not present in these compounds. Nor is an anomaly observed even in the mixed-phase sample. The lack of experimental evidence for magnetic anomalies in a sample that apparently contains excess CuO is disturbing. The measured sample contains almost 10 mass per cent of CuO . Therefore, at the transition temperature about 10 per cent of the total heat capacity should be of CuO origin. The magnetic transitions in CuO correspond to about 10 per cent of the total heat capacity at the transition temperatures.⁽¹⁰⁾ Thus the magnetic anomalies should produce a deviation of about 1 per cent from a smooth curve at the transition temperatures — well within the experimental precision of these experiments — but no deviations from the smooth

TABLE 3. Thermodynamic properties at selected temperatures for phases I, II, and III

T K	$C_{p,m}$ R	$\frac{\Delta_0^T S_m^\circ}{R}$	$\frac{\Delta_0^T H_m^\circ}{R \cdot K}$	$\frac{\Phi_m^\circ}{R}$	T K	$C_{p,m}$ R	$\frac{\Delta_0^T S_m^\circ}{R}$	$\frac{\Delta_0^T H_m^\circ}{R \cdot K}$	$\frac{\Phi_m^\circ}{R}$
I. $Sr_{1.2}Cu_{1.2}O$ { $R = 8.3144 J \cdot K^{-1} \cdot mol^{-1}$, $M(Sr_{1.2}Cu_{1.2}O) = 91.583 g \cdot mol^{-1}$ }									
15	0.035	0.013	0.142	0.004	160	3.790	2.997	292.450	1.168
20	0.085	0.030	0.430	0.008	170	3.949	3.231	331.150	1.283
25	0.164	0.056	1.038	0.015	180	4.095	3.461	371.400	1.398
30	0.277	0.096	2.130	0.025	190	4.231	3.686	413.000	1.512
35	0.414	0.148	3.849	0.039	200	4.358	3.906	455.950	1.627
40	0.565	0.213	6.293	0.056	210	4.478	4.122	500.150	1.740
45	0.727	0.289	9.520	0.078	220	4.589	4.333	545.500	1.853
50	0.903	0.375	13.588	0.103	230	4.691	4.539	591.900	1.965
60	1.255	0.571	24.389	0.164	240	4.785	4.740	639.300	2.077
70	1.595	0.790	38.655	0.238	250	4.874	4.938	687.600	2.188
80	1.921	1.024	56.255	0.322	260	4.957	5.130	736.750	2.297
90	2.226	1.268	77.005	0.413	270	5.035	5.319	786.750	2.405
100	2.505	1.518	100.675	0.511	280	5.106	5.503	837.450	2.513
110	2.761	1.769	127.025	0.614	290	5.170	5.684	888.850	2.619
120	2.998	2.019	155.835	0.720	298.15	5.217	5.828	931.150	2.705
130	3.220	2.268	186.940	0.830	300	5.228	5.860	940.800	2.724
140	3.426	2.514	220.180	0.942	325	5.382	6.285	1073.400	2.982
150	3.616	2.757	255.400	1.054	350	5.497	6.688	1209.700	3.233
II. $Sr_{2.3}Cu_{1.3}O$ { $R = 8.3144 J \cdot K^{-1} \cdot mol^{-1}$, $M(Sr_{2.3}Cu_{1.3}O) = 95.595 g \cdot mol^{-1}$ }									
15	0.028	0.019	0.178	0.007	160	3.925	3.021	298.000	1.159
20	0.069	0.032	0.410	0.012	170	4.095	3.264	338.100	1.275
25	0.141	0.055	0.921	0.018	180	4.251	3.503	379.833	1.392
30	0.246	0.089	1.875	0.027	190	4.396	3.736	423.100	1.510
35	0.380	0.137	3.431	0.039	200	4.529	3.965	467.733	1.627
40	0.531	0.197	5.706	0.055	210	4.649	4.189	513.633	1.743
45	0.692	0.269	8.756	0.075	220	4.756	4.408	560.667	1.860
50	0.870	0.351	12.660	0.098	230	4.853	4.622	608.700	1.975
60	1.237	0.542	23.197	0.156	240	4.941	4.830	657.700	2.090
70	1.596	0.760	37.373	0.226	250	5.027	5.033	707.533	2.203
80	1.938	0.996	55.057	0.308	260	5.110	5.233	758.200	2.316
90	2.260	1.243	76.067	0.398	270	5.193	5.427	809.733	2.428
100	2.559	1.497	100.180	0.495	280	5.273	5.617	862.067	2.538
110	2.834	1.754	127.163	0.598	290	5.350	5.803	915.200	2.648
120	3.089	2.011	156.797	0.705	298.15	5.407	5.953	959.033	2.736
130	3.324	2.268	188.867	0.815	300	5.420	5.987	969.033	2.756
140	3.542	2.522	223.233	0.928	325	5.543	6.427	1106.167	3.021
150	3.741	2.774	259.667	1.043	350	5.687	6.840	1246.233	3.279
III. $Sr_{14.38}Cu_{24.38}O_{41.38}$ { $R = 8.3144 J \cdot K^{-1} \cdot mol^{-1}$, $M(Sr_{14.38}Cu_{24.38}O_{41.38}) = 89.678 g \cdot mol^{-1}$ }									
15	0.064	0.023	0.242	0.007	100	2.522	1.661	106.324	0.597
20	0.140	0.052	0.743	0.014	110	2.766	1.912	132.774	0.705
25	0.242	0.093	1.687	0.026	120	2.996	2.163	161.583	0.817
30	0.371	0.148	3.211	0.041	130	3.216	2.412	192.662	0.930
35	0.515	0.216	5.419	0.061	140	3.424	2.658	225.881	1.044
40	0.669	0.295	8.379	0.086	150	3.616	2.901	261.094	1.160
45	0.830	0.383	12.124	0.114	160	3.792	3.140	298.136	1.276
50	0.999	0.479	16.698	0.145	170	3.960	3.375	336.922	1.393
60	1.329	0.691	28.355	0.218	180	4.123	3.606	377.349	1.509
70	1.649	0.920	43.250	0.302	190	4.273	3.833	419.316	1.626
80	1.961	1.161	61.309	0.394	200	4.414	4.055	462.763	1.742
90	2.255	1.409	82.413	0.493	210	4.544	4.274	507.560	1.857

TABLE 3—*continued*

T K	$C_{p,m}$ R	$\Delta_0^I S_m$ R	$\Delta_0^I H_m$ R·K	Φ_m R	T K	$C_{p,m}$ R	$\Delta_0^I S_m$ R	$\Delta_0^I H_m$ R·K	Φ_m R
220	4.668	4.488	553.611	1.972	280	5.320	5.693	854.142	2.643
230	4.788	4.698	600.916	2.086	290	5.404	5.881	907.779	2.751
240	4.907	4.905	649.405	2.199	298.15	5.478	6.032	952.126	2.839
250	5.016	5.107	699.005	2.311	300	5.497	6.066	962.279	2.858
260	5.121	5.306	749.710	2.423	325	5.714	6.512	1101.637	3.123
270	5.222	5.501	801.410	2.533					

curve are observed in the total heat capacity of the measured sample. The cause of the destruction of the magnetic character of CuO in the presence of III is not clear. It should, however, be noted that the composition of these phases is still under discussion in the literature. This report is based upon the best information to date but the possibility of better information which might identify additional phases should not be overlooked.

The molar entropies of the three compounds I, II, and III, which were calculated from the heat capacities, are compared with those calculated from e.m.f. values obtained from solid-state electrochemical studies.⁽¹⁾ These values are presented in

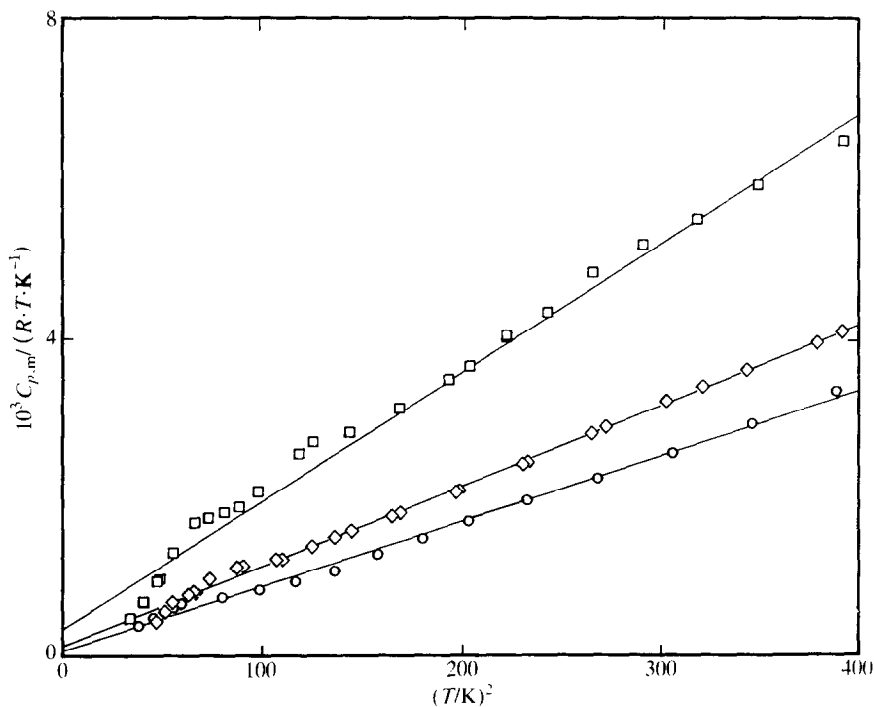


FIGURE 2. $C_{p,m}/T$ against T^2 for \diamond , I; \circ , II; and \square , III.

TABLE 4. Comparison of molar entropies for $(x+y)=1$ at 298.15 K from solid-state electrochemical experiments and from third-law calorimetry

Compound	E.m.f.	S_m/R	Calorimetry
I	5.34 ± 0.5		5.828 ± 0.006
II	5.17 ± 0.5		5.953 ± 0.006
III	5.95 ± 0.5		6.032 ± 0.006

table 4 in terms of $(x+y)=1$ for the three samples. The e.m.f. values were derived from results taken over the temperature range 900 K to 1200 K by extrapolation to 289.15 K using estimated heat capacities, since the superambient heat capacities of these samples are not known yet. Thus the difference between the heat capacities of the inter-oxide compounds and the sum of those of the component oxides was assumed to be negligible at superambient temperatures, and the molar entropies of formation of the compounds from the single oxides are temperature independent. This approximation is an excellent one for compound I for all temperatures and holds for the other two compounds only at superambient temperatures. Further research will be directed towards the determination of the superambient heat capacities of these compounds.

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