Superconductivity in the La–Ca–Co–O system at 227 K?

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(Submitted 8 October 1990)
Pis'ma Zh. Eksp. Teor. Fiz. **52**, No. 9, 1096–1099 (10 November 1990)

A transition to the diamagnetic state, which is linked with the onset of high-T_c superconductivity with $T_c = 227$ K, has been observed in samples of nominal composition $LaCa_2Co_3O_{6+y}$. At lower temperatures the compound undergoes a transition to the ferromagnetic state with a Curie temperature $\Theta = 174$ K. The Meissner effect, diamagnetic screening, suppression of diamagnetism by the magnetic field, flux capture, and flux creep have been observed in the diamagnetic region ($\Theta < T < T_c$).

During the years after the discovery of high-T_c superconductivity by Bednorz and Müller[1] considerable progress has been achieved in raising the critical temperature of the newly discovered superconductors[2–6] and in the understanding of the basic laws governing this phenomenon. The high-T_c superconductors that have so far been discovered nonetheless contain copper and oxygen as the basic chemical elements, and their basic structure is comprised of the CuO_2 planes, whose presence accounts for the conductivity and for the possible superconductivity mechanisms. A copper-free superconducting compound $Ba_{1-x}K_xBiO_3$ has a maximum T_c of nearly 30 K and lies halfway between the low-temperature and the high-T_c superconductors. While the role of oxygen in high-T_c superconducting compounds is now being clarified (specifically, holes which account for the conductivity are formed in the $2p$ oxygen band as a result of doping), the role of the $3d$ element is largely unclear. The search for high-T_c superconducting compounds in copper-free metal oxides is accordingly of crucial importance.

Honig *et al.*[7] have recently reported the observation of superconductivity at $T_c = 70$ K in La_2NiO_4 and $La_{1.8}Sr_{0.2}NiO_4$ single crystals.[7] We measured an electrical resistance in La_2NiO_4 doped with alkali metals, which can be interpreted as evidence of the onset of high-T_c superconductivity.[8] The results obtained for nickelates have not been reliably confirmed, however, by other research groups[9,10] and require further study.

We have recently been involved in synthesizing cobalt-containing oxide compounds and analyzing their properties. This is the first paper, to the best of our knowledge, to report the observation of high-T_c superconductivity in cobalt-containing metal oxides.

The samples were synthesized by the standard ceramic technology from a mixture of La_2O_3 and Co_3O_4 oxides and $CaCO_3$, $BaCO_3$, or $SrCO_3$ carbonates. To homogenize the samples, we sintered them three times at temperatures of 900–1000 °C in air; we then ground the samples and compressed them. After synthesis the samples were rapidly cooled. The samples of nominal compositions $LaCa_2Co_3O_{6+y}$, $LaSr_2Co_3O_{6+y}$, and $LaBa_2Co_3O_{6+y}$ were synthesized. The main results were obtained from the first compound, while the initial data for the other compounds will be published separately. The $LaCa_2Co_3O_{6+y}$ sample is, according to the initial x-ray data, essentially a single-phase sample, whose structure is different from the 1–2–3 structure of the copper-containing superconducting compounds. We studied the temperature dependence of the magnetic susceptibility of $LaCa_2Co_3O_{6+y}$ in various magnetic fields by the Faraday relative method. As the standards we used Ge and KCl single crystals. The error in determining the absolute value of the susceptibility is $\leqslant 5\%$, and the relative error for small fields is indicated in the figures; in the remaining cases this error is lower than that of the experimental points. In all the cases the susceptibility was defined as $\chi = M/H$, where M is the magnetic moment and H is the magnetic field.

The experimental results are shown in Figs. 1 and 2. In weak magnetic fields the susceptibility is nearly independent of the temperature at high temperatures. Below about 240 K the value of χ increases rapidly because of the ferromagnetic fluctuations. Below 227 K, however, the magnetic susceptibility decreases gradually and a transition to the diamagnetic state occurs. This effect increases as the measuring magnetic field is lowered. For the lowest fields the diamagnetism and the nature of the tempera-

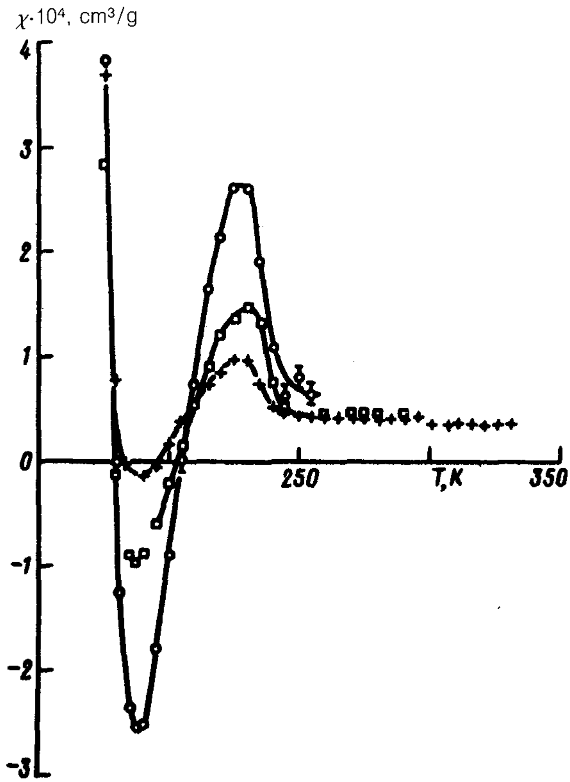

FIG. 1. Temperature dependence of the magnetic susceptibility of $LaCa_2Co_3O_{6+y}$ in various magnetic fields. ○—$H = 0.1$ kOe, □—$H = 0.21$ kOe, +—$H = 0.39$ kOe. The experimental points are connected for convenience.

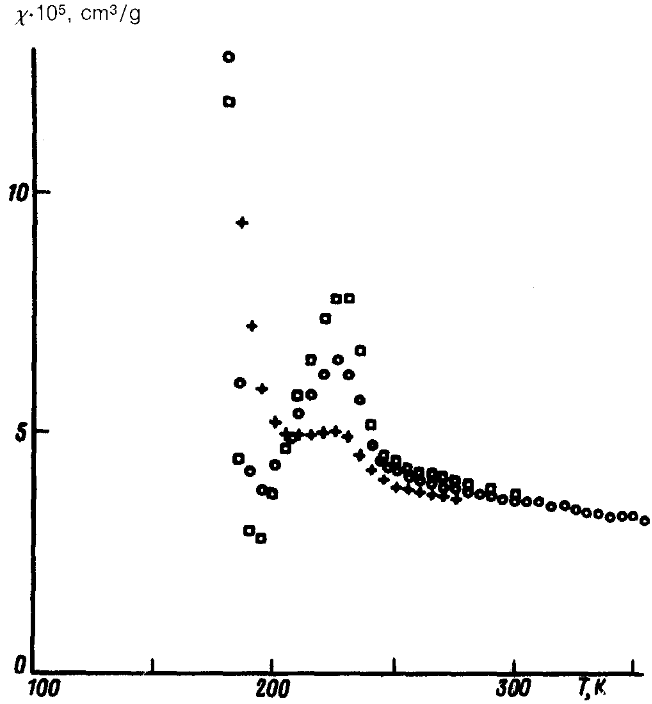

FIG. 2. Temperature dependence of the magnetic susceptibility of $LaCa_2Co_3O_{6+y}$ in strong fields. □—$H = 0.76$ kOe, O—$H = 1.15$ kOe, +—$H = 3.83$ kOe.

ture dependence are virtually independent of the manner in which the sample is cooled (with or without the field). The maximum diamagnetic susceptibility observed by us (about 3×10^{-4} cm^3/g) is too high for any transition to a state with a Langevin diamagnetism. Consequently, the only explanation of this transition, in our view, is the occurrence of high-T_c susceptibility with $T_c = 227$ K.

Lowering the temperature results in a gradual decrease of the diamagnetism and an abrupt transition to a magnetically ordered state. Figure 3 shows a temperature dependence of the magnetic moment M at various values of the magnetic field. This is a typical dependence for the state with a ferromagnetic moment. An estimate of the ferromagnetic moment from the $M(T)$ curve as $T\rightarrow0$ gives $\mu_f = 0.16\mu_B$ per Co atom. The relatively small value of the magnetic moment allows us to assume the ferromagnetism either has a band structure or that the magnetic structure is a complex, many-sublattice structure.

It should be noted that all the characteristic features of the samples which contain a few weakly linked superconducting regions are seen in the diamagnetic region. Specifically, one can see in this region the Meissner effect, the diamagnetic screening, the nonlinear dependence of the diamagnetic moment on the applied field, the magnetic hysteresis, and the flux creep. Although the amount of the superconducting phase is estimated to be in the neighborhood of several percent, it actually could be higher,

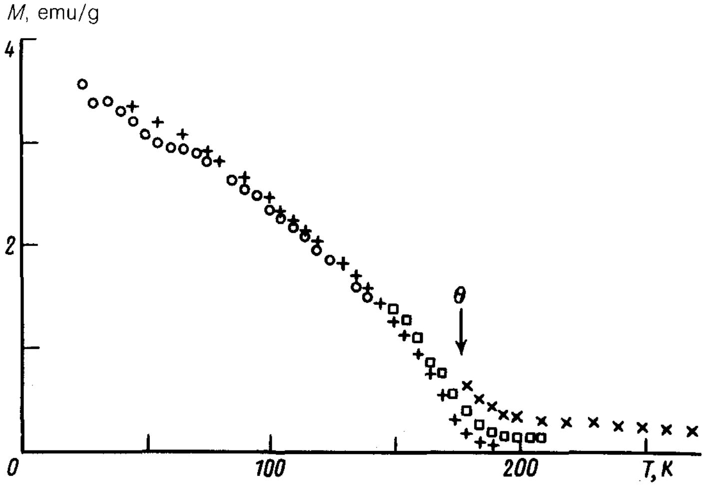

FIG. 3. Temperature dependence of the magnetic moment of an $LaCa_2Co_3O_{6+y}$ sample in the region of the magnetic order. ○—$H = 0.76$ kOe, +—$H = 1.15$ kOe, □—$H = 2.68$ kOe, ×—$H = 5.68$ kOe.

since the measured susceptibility is the result of superposition of the diamagnetic component which increases with decreasing temperature and which has even a more rapidly increasing paramagnetic component.

Whether the phase which becomes a magnetically ordered phase at lower temperatures is responsible for the superconductivity, or whether these are two different phases, at present cannot be answered unambiguously. The similarity to the copper-containing high-T_c superconductors probably suggests that the superconductivity and magnetism are found in different phases which simply differ in the oxygen content. It should also not be ruled out that T_c of $LaCa_2Co_3O_{6+y}$ may be even higher in the case of the best possible oxygen stoichiometry. Experimental studies of this sort are now being carried out.

As can be seen in Fig. 2, the transition to the diamagnetic state vanishes in strong fields. The disappearance of the transition is not caused, however, by the total suppression of superconductivity, since at temperatures in the range 200–225 K the structural feature remains as a kink on the $\chi(T)$ curve. The steadily increasing ferromagnetic component with increasing field (see Fig. 3) "covers" the superconducting region. The value of $(dH_{c2}/dT)_{T_c}$ is roughly estimated to be 1 kOe/K from the temperature displacement of the structural feature on the $\chi(T)$ curve with increasing field.

All the effects mentioned in this paper have been reproduced and the samples were able to withstand multiple thermal cycling without changing their properties.

We wish to thank I. G. Mikhaĭlov and A. Yu. Khramov for technical assistance.

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Translated by S. J. Amoretty