The evolution of the structural and magnetic properties of the CMR (colossal-magnetoresistance) compound La$_{0.35}$Pr$_{0.35}$Ca$_{0.30}$MnO$_3$ as the temperature changes from 10 to 293 K is investigated by means of neutron diffraction. It is shown that the changes in the transport and magnetic properties are directly related with the rearrangement of the atomic structure. A phase transition to the metallic state occurs together with simultaneous ferromagnetic ordering of the manganese moments and is accompanied by a jump in volume. The static distortions of the oxygen octahedra which are observed to occur prior to the magnetic phase transition and which are practically absent at room temperature and in the FM phase attest to the orbital ordering of oxygen atoms on the bonds, with freezing-in of the Jahn–Teller modes. © 1998 American Institute of Physics.

PACS numbers: 75.70.Pa, 72.60.+g, 61.12.Ld

The perovskites La$_{1-x}$A$_x$MnO$_3$, where A = Ca, Sr, and Ba, have been under intensive study in recent years, since the discovery of negative colossal magnetoresistance (CMR) in them at the beginning of the 1990s. Depending on the doping level, temperature, or magnetic field strength, these crystals are found in two basic states — antiferromagnetic or paramagnetic insulator or ferromagnetic metal with ordered magnetic moments of manganese. Numerous investigations (see, for example, the reviews Refs. 2 and 3) have shown that the insulator–metal and paramagnet–ferromagnet transitions are interrelated and the transition temperatures $T_{I-M}$ and $T_c$ are close or equal to each other. Both the properties of the metallic phase and this interrelationship are ordinarily described on the basis of the “double exchange” model, which was introduced at the beginning of the 1950s. However, recently discovered features of the phase transitions
occurring in CMR compounds and the ground state of these compounds have shown that the complete picture cannot be described solely by this model; it is necessary to enlist the interaction of electrons with the crystal lattice.

It is well known that, just as external fields, complete or partial substitution of rare-earth elements with a short ionic radius for La makes it possible to change the charge and magnetic state of a CMR compound. Of special interest are compositions in which lanthanum is replaced by praseodymium, since the narrow-gap CMR compounds obtained in so doing possess a rich phase diagram, as is shown, for example, by detailed neutron diffraction investigations of the magnetic states of $Pr_{1-x}Ca_xMnO_3$ (Ref. 5) and precise structural investigations of the compositions $La–Pr_{1–x}(Ca–Sr–Ba)_xMnO_3$ (Ref. 6).

In the present letter we report new experimental data obtained for the CMR compound $La_{0.35}Pr_{0.35}Ca_{0.30}MnO_3$ (referred to below as LPCM) mainly by neutron diffraction. This composition is of interest because of its unusual transport properties, manifested in the dependence of the resistivity at liquid-helium temperatures on the time and on the method of cooling. In the compound $(La_{0.25}Pr_{0.75})_{0.7}Ca_{0.30}MnO_3$ a “giant” isotope effect is also observed — complete suppression of a transition to the ferromagnetic metallic phase accompanying the substitution of $^{16}O$ for $^{18}O$ (Ref. 8), indicating the important role of lattice dynamics in this transition.

An experimental sample with the composition $(La_{0.3}Pr_{0.3})_{0.7}Ca_{0.3}MnO_3$ was prepared in the form of a powder by means of the so-called “paper synthesis.” For this, an aqueous solution of a mixture of La, Pr, Ca, and Mn nitrates taken in the required ratios was deposited on ash-free paper filters, which were dried (120 °C) and then burned. The oxide products thus obtained was roasted in air at 700 °C for 2 h. The final heat treatment consisted of annealing pressed tablets in air at 1200 °C for 12 h. The tablets obtained were ground into a powder prior to the neutron diffraction experiment. Preliminary x-ray analysis showed the sample to be uniform and orthorhombic.

Figure 1 shows the electrical resistivity of a ceramic sample of LPCM, measured by the standard four-contact method, versus temperature. At a temperature $T_c ≈ 175 K$ a transition occurs to a metallic state with a small hysteresis. We note that the comparatively small decrease in the resistivity with a further decrease of temperature (only a

![FIG. 1. Electrical resistivity of the ceramic $La_{0.35}Pr_{0.35}Ca_{0.30}MnO_3$ as a function of temperature.](image)

10 May 1998 Balagurov et al.