Thermal Expansion in (La$_{0.62}$Pb$_{0.38}$)MnO$_3$: Possible Evidence for a Coupling Between Elastic and Magnetic Exchange Forces

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Received August 7, 1972

Using single-crystal, automated diffractometer techniques, the linear coefficient of thermal expansion has been determined for La$_{0.62}$Pb$_{0.38}$MnO$_3$ from 298 to 627 K. The linear coefficient of thermal expansion is observed to undergo a change from $7.2 \times 10^{-5}$ Å/K for $T<T_c$ to $10.8 \times 10^{-5}$ Å/K for $T>T_c$. It is concluded that while the rhombohedral distortion in the (La, Pb)MnO$_3$ system can be understood qualitatively on the basis of ionic size and polarizability considerations alone, the quantitative systematics of the distortion parameters and the change in the linear thermal expansion coefficient at $T_c$ indicate a significant coupling between the elastic and magnetic exchange forces.

Introduction

Recently, single crystals of the perovskite, La$_{1-x}$Pb$_x$MnO$_3$ (0.26 $\leq x \leq$ 0.44) have been synthesized and characterized (1). Subsequently a variety of magnetic and electrical studies have been conducted on these materials (2–4). While the magnetic and electrical properties have been investigated extensively, the systematics of the crystal chemistry of these materials have not been given adequate consideration. The generation of more data on the crystal chemistry of these materials is important, if for no other reason than that the unusual behavior in the temperature-dependent changes of the magnetic properties might be related to temperature-dependent changes in the crystal chemical parameters.

It was observed that the rather rapid drop in magnetization, $\sigma_M$, of the La$_{1-x}$Pb$_x$MnO$_3$ samples as $T$ approached $T_c$ could not be explained within the existing theoretical framework of the double-exchange mechanism (2, 5). A search for evidence of a biquadratic exchange term, resulting from a lattice distortion and which could explain the rapid drop in $\sigma_M$ as $T\rightarrow T_c$, did not prove to be fruitful (4). A subsequent study of the effects of local spin excitations at high temperatures, near $T_c$ has led to a rationalization of the rapid drop in $\sigma_M$ as $T\rightarrow T_c$ (5). While the importance of the local spin excitations should not be minimized, it is still an open question as to whether temperature-dependent lattice distortion (and/or associated lattice strain) might not also account for the rapid drop in $\sigma_M$ as $T\rightarrow T_c$. Indeed, the determination of a linear dependence of the lattice constant, $a_0$, and the rhombohedral angle, $\alpha_R$, on temperature for La$_{0.62}$Pb$_{0.38}$MnO$_3$ (4) is rather surprising in view of the rather strong coupling between the elastic and magnetic exchange forces expected in these materials (6). This is doubly disconcerting since the expected change in this coupling at $T_c$ (6) would have provided a natural mechanism for the rapid drop in the magnetization near $T_c$.

Because of the highly-twinned nature of single crystals of La$_{0.68}$Pb$_{0.32}$MnO$_3$ and the difficulties associated with preferred orientation and line broadening in X-ray powder diffractometry, it is possible that changes in $\partial a_0/\partial T$ may have been masked in the earlier search for a temperature-dependent lattice distortion in La$_{0.62}$Pb$_{0.38}$MnO$_3$ in which powder diffractometry was employed (4). Inhomogeneities in sample temperature, due to its large size, may also have obscured any subtle changes in the lattice parameters. Due to the availability in our laboratories of a high-temperature, single-crystal X-ray furnace with low temperature gradients at the sample and an automated diffractometer (7), we have deter-
minded the temperature dependence of \( d\{100\} \) for a single-crystal specimen of \( \text{La}_{0.68}\text{Pb}_{0.38}\text{MnO}_3 \) from 298 to 627 K.

**Experimental**

The crystal used in the present study was from the same parent batch as those described in the earlier characterization study (I). It was established in that study that compositional variations among crystals from the same batch are small; therefore the crystal used in the present study was not subjected to a chemical analysis. As reported previously (I), the La and Pb contents were determined using X-ray fluorescence and are accurate to \( \pm 0.2 \) weight percent. The total Mn content was determined oxidimetrically, employing the bismuthate method. The Mn\(^{4+}\) content was determined using excess ferrous ammonium sulfate as a reducing agent and then back-titrating with \( \text{KMnO}_4 \) solution. The oxygen content was not determined, and the experimental weight percentages were converted into the formulae of Table I assuming a stoichiometric oxygen content. The slight discrepancies between the Pb\(^{2+}\) and Mn\(^{4+}\) contents are within the experimental error of the analytical techniques.

Cleavage fragments from single crystals were first examined using the Weissenberg method. The photographs showed reflections occurring as resolved doublets, being consistent with a twinned trigonal phase having pseudo-cubic symmetry. No reflections were observed which would result in doubling of the primitive, cubic perovskite cell edge, however. A cleavage fragment mounted on the \( a \) axis was then placed in a silica capillary and mounted within the furnace on the single-crystal diffractometer (Weissenberg geometry). Reflections were analyzed by utilizing \( \text{CuK}_\alpha \) radiation, a scintillation counter, and a flat-crystal graphite monochromator. The reflection (131) (indexed with a doubled cell edge) and its symmetry equivalents were detected, thus verifying that the cell edge of the trigonal phase is double that of primitive, cubic perovskite.

High-temperature results were obtained by monitoring the reflections (006), (064), and (046). The twinning results in exact superposition of twin-related \{00l\} reflections, and doubling of all \{0kl\} reflections. The individual components of these doublets are not resolvable, however. For the determination of peak profiles and integrated intensities, scans across each peak were made for all three reflections, while 2\( \theta \) was measured only for (006). Measurements were made at a given temperature only after establishing that equilibrium had been reached. After a change in temperature, intensity was monitored for time periods up to 15 hr. No variation in intensity with time, at constant temperature, was detected. Changes in intensity and 2\( \theta \) were therefore immediate and reversible as a function of temperature.

**Results**

In Fig. 1 the temperature dependence of 2\( \theta \) (600) is shown. Unlike the findings of the previous study (4), in which the linear coefficient of thermal expansion was found to be constant from 297 to 450 K, we observed a definite change in the linear coefficient of thermal expansion at 343 \( \pm 5 \) K.

The linear coefficient of thermal expansion below 343 K as determined by least-squares fit of a

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mn(^{4+}) (percent)(^b)</th>
<th>( a_R ) (( \AA ))</th>
<th>( a_R )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{La}<em>{0.74}\text{Pb}</em>{0.26}\text{MnO}_3 )</td>
<td>31 7.80 ± 0.01</td>
<td>90°28'</td>
<td></td>
</tr>
<tr>
<td>( \text{La}<em>{0.62}\text{Pb}</em>{0.38}\text{MnO}_3 )</td>
<td>31 7.815 ± 0.004</td>
<td>90°24'</td>
<td></td>
</tr>
<tr>
<td>( \text{La}<em>{0.69}\text{Pb}</em>{0.31}\text{MnO}_3 )</td>
<td>36 7.80 ± 0.02</td>
<td>90°23'</td>
<td></td>
</tr>
<tr>
<td>( \text{La}<em>{0.60}\text{Pb}</em>{0.40}\text{MnO}_3 )</td>
<td>38 7.80 ± 0.01</td>
<td>90°23'</td>
<td></td>
</tr>
<tr>
<td>( \text{La}<em>{0.55}\text{Pb}</em>{0.45}\text{MnO}_3 )</td>
<td>44 7.776 ± 0.005</td>
<td>90°19'</td>
<td></td>
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</tbody>
</table>

\(^a\) Adopted from (I).

\(^b\) Per cent of total Mn that is present as Mn\(^{4+}\).

**TABLE I**

**LATTICE PARAMETERS AND Mn\(^{4+}\) CONTENT OF (La, Pb)MnO\(_3\)**

![Fig. 1. Temperature dependence of 2\( \theta \) for the (600) diffraction peak for \( \text{La}_{0.68}\text{Pb}_{0.38}\text{MnO}_3 \). 2\( \theta \) values are for CuK\(_\alpha\) radiation. Open and closed circles indicate increasing and decreasing \( T \), respectively.](image-url)
straight line to the data is $7.2 \times 10^{-5}$ Å/K; and above 343 K, it is $10.8 \times 10^{-5}$ Å/K. In arriving at these values, we have neglected the small deviations of $\alpha_R$ from 90°. In addition, the peak profiles and integrated intensities of the reflections 006, 046, and 064, as determined over the same temperature interval, showed no nonlinear behavior or change in slope.

**Discussion**

These results indicate that there is no first-order phase transition in La$_{0.62}$Pb$_{0.38}$MnO$_3$ up to 627 K and are, therefore, in qualitative agreement with the earlier study (4). The present study extends the temperature range in which there is no first-order phase transition by 100% over the earlier study. On the other hand, there is a significant change in the coefficient of thermal expansion which was not detected in the earlier study. The fact that the change in the thermal expansion coefficient occurs at $T_C$ is significant and permits a qualitatively different conclusion than that reached in (4) concerning the existence of a coupling between the elastic and exchange forces. It is also of interest in this regard that the coefficient of thermal expansion is significantly greater for $T > T_C$ than for $T < T_C$. The volume coefficient of thermal expansion of Fe$_3$O$_4$ exhibits a similar behavior (8); double-exchange interactions are also believed to be important in Fe$_3$O$_4$. It is possible that the change in thermal expansion coefficient is also accompanied by a change in the distortion. The rhombohedral angle for the primitive cell is 60°42' (9) and it is possible that the change in thermal expansion coefficient also corresponds to a change in $\alpha_R$ to the “ideal” rhombohedral angle of 60°.

In the previous studies (1, 4), little or no attention was devoted to the crystal chemistry of La$_{1-x}$Pb$_x$MnO$_3$ phases. However, to gain further insight into the possibility of coupling between the elastic and exchange forces, it is necessary to determine whether the rhombohedral distortions, i.e., the rhombohedral distortion from cubic symmetry and the deviation of $\alpha_R$ from 60°, are determined primarily by cation-size effects or if they are determined by cooperative distortions due to magnetic exchange interactions (6). A similar question has been raised in an earlier study of the system LaMn$_{1-x}$Mn$_x$O$_{3+y}$ (10). While the systematics of crystal symmetry versus ionic size and polarizability have been developed for A$^{3+}$B$^{3+}$O$_3$ and A$^{2+}$B$^{4+}$O$_3$ perovskites, there are some doubts about these correlations in mixed (A$^{3+}$, A$^{3+}$) (B$^{4+}$, B$^{4+}$)O$_3$ perovskites (11); and a conclusion of the origin of the rhombohedral distortion in the (La, Pb)MnO$_3$ system cannot be reached without some caution. An unambiguous conclusion can be reached, nonetheless, by considering the crystal chemical systematics of systems having similar magnetic and electrical properties, namely, (La, Ca)MnO$_3$, (La, Sr)MnO$_3$ and (La, Ba)MnO$_3$ (6). The (La, Pb)- (1), (La, Ba)- (12), and (La, Sr)MnO$_3$ (12, 13) systems exhibit rhombohedral distortions, whereas La$_{1-x}$Ca$_x$MnO$_3$ goes directly from orthorhombic symmetry at $x = 0$ to the cubic symmetry at $x \approx 0.15$ (12). The important difference between the Sr- and Ba-substituted perovskites, on the one hand, and Ca-substituted perovskites, on the other, lies in the larger ionic radii of the Ba$^{2+}$ (1.60 Å) and Sr$^{2+}$ (1.44 Å) ions than that of the Ca$^{2+}$ (1.35 Å) ion (14); there are also important differences in the polarizabilities of the Ba$^{2+}$ (1.69 x 10^{-24} cm$^3$) and Sr$^{2+}$ (0.90 x 10^{-24} cm$^3$) ions vis-à-vis the Ca$^{2+}$ (0.69 x 10^{-24} cm$^3$) ion (15). We conclude, therefore, that the rhombohedral distortions in (La, Ba)MnO$_3$ and (La, Sr)MnO$_3$ relative to the cubic symmetry of (La, Ca)MnO$_3$ are due to size and polarizability effects. Pb$^{2+}$ has an ionic radius of 1.49 Å (14) which is intermediate to the radii of Sr and Ba; the polarizability of Pb$^{2+}$ (3.6 x 10^{-24} cm$^3$) (15) is considerably larger than those of either Ca$^{2+}$, Sr$^{2+}$ or Ba$^{2+}$. Consequently, the rhombohedral symmetry of (La, Pb)MnO$_3$ appears to be in agreement with crystal chemical systematics based on ionic size and polarizability effects alone. It is also noteworthy that the (PbTiO$_3$)$_{1-x}$-(LaMnO$_3$)$_x$ system is also rhombohedral at $x > 0.30$ (16). In the above considerations, it is tacitly assumed that different electronic configurations of Pb$^{2+}$ and the heavy alkaline earth elements are not important to the gross structural aspects considered here. While it is true that the Pb$^{2+}$-O$^{2-}$ bonds in many substances are predominantly covalent, there are many isostructural Pb, Ba, and Sr compounds in which the bonding mechanisms are known to be similar and principally ionic in character (17). It has been demonstrated previously (16) that the Mn$^{3+}$ ion suppresses the tendency of the unique combination of large ionic radii and high polarizability of the Pb$^{2+}$ ion to induce ferroelectricity and concomitant structural changes.

Further confirmatory evidence for the import-
THERMAL EXPANSION LANTHANUM–LEAD MANGANITE

The presence of size effects can be obtained from the magnetic and electrical properties of (La, Pb)MnO₃ compositions studied so far. First of all, from the electrical properties of this material (2–5), the ionic species present are perhaps best regarded as (1 − x) La³⁺, x Pb²⁺, (1 − 2x) Mn³⁺, and 2x Mn⁴⁺, and x conduction electrons (in a narrow d band perhaps) for x = 0.38.

Using this assemblage of oxidation numbers, the average A cation radius is calculated to be 1.38 Å and the average B cation radius is 0.566 Å (14); these values for the radii definitely place this material in the rhombohedral field of the symmetry versus ionic site systematics developed for 3-3 perovskites (11). The same result is obtained if the ionic species and their concentrations are assumed to be (1 − x) La³⁺, x Pb²⁺, x Mn⁴⁺, and (1 − x)Mn³⁺. Therefore, the distortion of the lattice in the (La, Pb)MnO₃ system from cubic to rhombohedral symmetry is not believed to be due to an ordering of the covalent bonds such that the net ferromagnetic exchange interactions are maximized (6). There is also additional evidence against such considerations based on a localized double-exchange model inasmuch as the Curie temperature of La₁₋ₓPbₓMnO₃ compositions does not go through a maximum at x = 0.3 (18) and is still an increasing function of x at x = 0.44 (2).

However, as shown in Table I the dependence of the rhombohedral angle on the Mn⁴⁺ concentration seems to indicate that magnetic exchange interactions may be controlling the deviation of αₐ from its ideal value of 60°. αₐ is a decreasing function of Mn⁴⁺ concentration, as is also true of the (La, Sr)MnO₃ (11), and LaMnO₃ (8) systems. It is also interesting to note in Table I that there is no correlation of αₐ with the Pb²⁺ concentration. Therefore, we conclude that the question is still open as to the existence of distortion-dependent exchange interactions in La₁₋ₓPbₓMnO₃, where 0.26 < x < 0.44. There is certainly a change in the linear thermal expansion coefficient at T_c; and this result suggests a significant coupling between the elastic and exchange forces. Additional single crystal studies need to be conducted near T_c in order to determine if changes in other crystallographic properties accompany the change in thermal expansion coefficient.

Acknowledgments

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work (B.J.E.) and to the National Science Foundation (D.R.P.).

References