

Crystal and magnetic structure of LaTiO₃: Evidence for nondegenerate t_{2g} orbitals

M. Cwik,¹ T. Lorenz,¹ J. Baier,¹ R. Müller,¹ G. André,² F. Bourée,² F. Lichtenberg,³ A. Freimuth,¹ R. Schmitz,⁴ E. Müller-Hartmann,⁴ and M. Braden¹

¹*II. Physikalisches Institut, Universität zu Köln, Zùlpicher Str. 77, D-50937 Köln, Germany*

²*Laboratoire Léon Brillouin, CEA/CNRS, F-91191 Gif-sur-Yvette CEDEX, France*

³*Experimentalphysik VI, EKM, Institut für Physik, Universität Augsburg, 86135 Augsburg, Germany*

⁴*Institut für Theoretische Physik, Universität zu Köln, Zùlpicher Str. 77, D-50937 Köln, Germany*

(Received 4 February 2003; published 7 August 2003)

The crystal and magnetic structures of LaTiO₃ have been studied by x-ray and neutron-diffraction techniques using nearly stoichiometric samples. We find a strong structural anomaly near the antiferromagnetic ordering $T_N = 146$ K. In addition, the octahedra in LaTiO₃ exhibit an intrinsic distortion, which implies a splitting of the t_{2g} levels. Our results indicate that LaTiO₃ should be considered as a Jahn-Teller system where the structural distortion and the resulting level splitting are enhanced by the magnetic ordering.

DOI: 10.1103/PhysRevB.68.060401

PACS number(s): 75.30.-m, 61.12.-q, 75.25.+z

LaTiO₃ has been studied already in the seventies and was thought to be a text book example of a Mott insulator with antiferromagnetic order.¹ Ti is in its trivalent state with a single electron in the t_{2g} orbitals of the $3d$ shell. The titanate is hence an electron analog to the cuprates with a single hole in the $3d$ shell. However, the t_{2g} orbitals in the LaTiO₃ are less Jahn-Teller active and therefore, the orbital moment may not be fully quenched in the titanate. The physics of the orbital degree of freedom has recently reattracted attention to this material.^{2,3}

The ordered moment in LaTiO₃ amounts to $0.46 \mu_B$, which is much smaller than the value of $1 \mu_B$ expected for a single electron with quenched orbital moment.⁴ Quantum fluctuations can explain only about 15% reduction in the three-dimensional case. A straightforward explanation could be given in terms of spin-orbit coupling, as an unquenched orbital moment would align antiparallel to the spin moment in the titanate. However, in a recent neutron-scattering experiment, the magnon spin gap was observed at 3.3 meV, and it was argued that the strong interaction of an orbital moment with the crystal lattice implies a much larger value for the spin gap.² An orbital contribution to the ordered moment in LaTiO₃ was hence excluded. On the basis of standard theories, however, even the G -type antiferromagnetic ordering in LaTiO₃ may not be explained without a spin-orbit coupling. Instead, one expects ferromagnetism^{5,6} related with the orbital degeneracy. Under the assumption of a specific structural distortion, Moshizuki and Imada recently presented a successful model for the antiferromagnetic order in LaTiO₃.⁷ However, there is no experimental evidence for such a distortion. The puzzling magnetic properties of LaTiO₃ led Khaliullin and Maekawa to suggest a novel theoretical description for RE TiO₃ with RE a rare-earth, based on the idea of an orbital liquid. They were able to explain many of the magnetic characteristics of LaTiO₃,³ but the presumed orbital fluctuations have not been observed.⁸ Therefore, magnetism in LaTiO₃ still remains an open issue.

We have reanalyzed the crystal and magnetic structures of LaTiO₃ by x-ray and by neutron-diffraction samples with almost perfect stoichiometry. First, we find a clear structural

anomaly at the Néel ordering and second, the shape of the octahedra in this compound is not ideal but distorted. From these observations, we conclude that LaTiO₃ has to be considered as a soft Jahn-Teller system, thereby explaining many of its unusual magnetic properties.

Samples of LaTiO₃ were prepared following the standard solid-state reaction; however, the last process was performed in a floating-zone image furnace. This procedure gave large single crystals with small mosaic spread. Since twinning would induce severe problems in any single-crystal diffraction experiment, we crushed parts of these single crystals in order to perform powder-diffraction studies. Special care was given to the stoichiometry of these samples. LaTiO₃ has the tendency to incorporate La and Ti vacancies which are frequently denoted by an excess of oxygen in the formula LaTiO_{3+ δ} . By adjusting the ratio of TiO and TiO₂ in the starting materials,⁹ one may vary the final oxygen content of the samples. Stoichiometry was verified by thermogravimetric analyzes and by determining the Néel temperature in a superconducting quantum interference device magnetometer. For the stoichiometric sample studied here, we obtain $T_N = 146$ K, amongst the highest values reported so far for LaTiO₃. The temperature dependence of the lattice parameters was determined on a Siemens D5000 x-ray diffractometer using Cu-K α radiation. Powder neutron-diffraction experiments were performed at the Orphée reactor in Saclay, using the high-resolution diffractometer 3T.2 ($\lambda = 1.2$ Å) and the high-flux diffractometer G4.1 ($\lambda = 2.4$ Å).

At room temperature, LaTiO₃ exhibits the crystal structure of GdFeO₃ type (space group $Pbnm$) (see Fig. 1). This structure arises from the ideal perovskite (space group $Pm\bar{3}m$) by tilting the TiO₆ octahedron around a $[110]_c$ axis (subscript c denotes the notation with respect to the cubic perovskite lattice), followed by a rotation around the c axis (or $[001]_c$ axis). One may note that while tilt distortions are opposite for any neighboring pair of octahedra, octahedra neighboring along the c axis rotate in the same sense.

Figure 2 shows the temperature dependence of the orthorhombic lattice parameters and that of the crystal volume. There are clear anisotropic anomalies near the antiferromag-

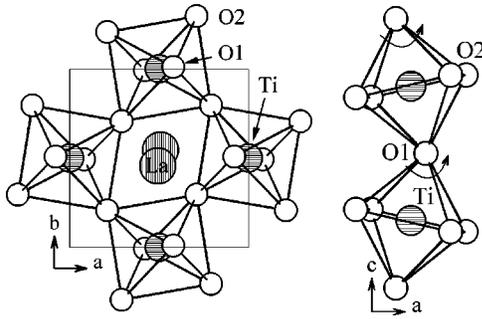


FIG. 1. Crystal structure of LaTiO_3 in space group $Pbnm$, O_2 denotes the oxygen in the a, b planes and O_1 the apical one. The left part shows four octahedra connected in the a, b plane, the right part a pair of neighboring octahedra along c .

netic ordering. Upon passing into the ordered state, the lattice elongates along a and shrinks along b , whereas for the c direction and for the lattice volume, no anomalous changes can be resolved. Anomalies in the thermal expansion have also been observed independently in a capacitance dilatometer experiment.¹⁰

The anomalous temperature dependence of the a and b lattice parameters is not restricted to a temperature range close to T_N (see Fig. 3). In particular, the a parameter, which is almost constant between 200–500 K, deviates from a normal thermal expansion over a large temperature interval. Here, it is instructive to analyze the orthorhombic splitting. The lattice in $Pbnm$ results from that of an ideal cubic perovskite (denoted by subscript c) by setting $a = \sqrt{2}a_c$, $b = \sqrt{2}a_c$, and $c = 2a_c$. Considering a rigid tilt of the ideal octahedron, one obtains the nonequalities $c \neq (1/\sqrt{2})(a+b)$ due to the rotation and the tilt, and $a \neq b$ due to the tilt distortion only. However, tilting of an ideal octahedron around the b axis would lead to $b > a$, whereas LaTiO_3 exhibits just the opposite behavior below about 650 K. The sign of the orthorhombic distortion, $\epsilon = (b-a)/(a+b)$, already indicates that the octahedron shape in LaTiO_3 is not ideal.

We have determined the crystal structure on our almost stoichiometric sample using high-resolution neutron diffraction. The results are given in Table I. The splitting in the Ti-O-bond distances is small, though not negligible. There is,

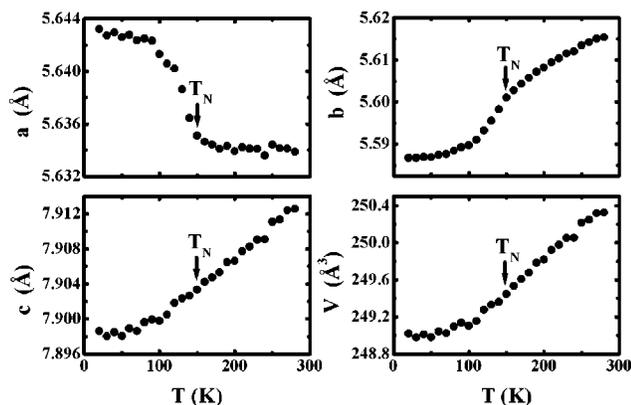


FIG. 2. Temperature dependence of the orthorhombic lattice constants and of the lattice volume, obtained by x-ray diffraction.

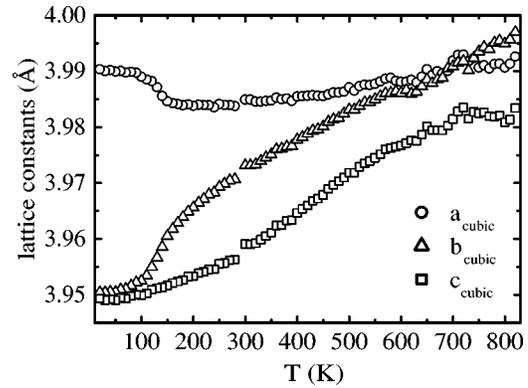


FIG. 3. Temperature dependence of the orthorhombic lattice constants scaled to the cubic perovskite lattice (x-ray results).

however, a large splitting in the O_2 - O_2 edge lengths of the octahedron basal plane, which had escaped attention previously. At 8 K, the edges along a and b differ by about 4%. This distortion is comparable in its strength to that observed for the Ti-O-bond distances in YTiO_3 , which is considered

TABLE I. Results of the neutron high-resolution powder-diffraction studies at different temperatures, the two right columns present data from Refs. 12 and 11, respectively. Lattice constants are given in Å and thermal parameters in Å².

	LaTiO ₃ , $T_N=150$ K		LaTiO ₃	YTiO ₃	
	293	155	Temperature (K)	298	293
a	5.6336(1)	5.6353(1)	5.6435(1)	5.6247(1)	5.316(2)
b	5.6156(1)	5.6021(1)	5.5885(1)	5.6071(1)	5.679(2)
c	7.9145(2)	7.9057(2)	7.9006(2)	7.9175(1)	7.611(3)
Ti-O ₂	2.057(1)	2.054(1)	2.053(1)	2.044(1)	2.077(4)
Ti-O ₁	2.031(1)	2.032(1)	2.032(1)	2.032(1)	2.016(4)
Ti-O ₁	2.0298(4)	2.0273(1)	2.0280(4)	2.028(1)	2.023(2)
O ₂ -O ₂	2.935(2)	2.938(2)	2.944(2)	2.924	2.908(5)
O ₂ -O ₂	2.845(2)	2.840(2)	2.832(2)	2.839	2.881(5)
x_{RE}	0.9916(3)	0.9930(3)	0.9930(3)	0.9929(3)	0.9793(1)
y_{RE}	0.0457(2)	0.0482(2)	0.0491(2)	0.0428(1)	0.0729(1)
z_{RE}	0.25	0.25	0.25	0.25	0.25
x_{O1}	0.0799(3)	0.0799(3)	0.0813(3)	0.0781(3)	0.121(1)
y_{O1}	0.4913(3)	0.4939(3)	0.4940(3)	0.4904(3)	0.458(1)
z_{O1}	0.25	0.25	0.25	0.25	0.25
x_{O2}	0.7096(3)	0.7087(3)	0.7092(3)	0.7104(2)	0.691(1)
y_{O2}	0.2941(3)	0.2946(3)	0.2943(3)	0.2914(2)	0.310(1)
z_{O2}	0.0417(1)	0.0421(1)	0.0428(1)	0.0412(1)	0.058(1)
U_{La}	0.0062(2)	0.0052(2)	0.0013(2)	0.0162(3)	0.0055(4)
U_{Ti}	0.0036(4)	0.0047(4)	0.0008(4)	0.0104(5)	0.0042(6)
U_{O1}	0.0075(3)	0.0066(3)	0.0040(3)	0.0174(4)	0.006(3)
U_{O2}	0.0069(2)	0.0064(2)	0.0034(2)	0.0183(3)	0.007(2)
Θ (°)	12.88(5)	12.86(5)	13.11(5)	11.26(4)	19.9(2)
Φ (°)	9.53(1)	9.69(1)	9.60(1)	8.08(1)	13.33(4)

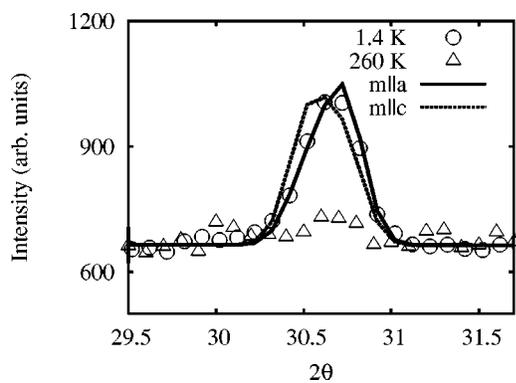


FIG. 4. Part of the neutron-diffraction pattern for different temperatures; the two lines correspond to Rietveld fits with the antiferromagnetic component either along a or c .

as being orbitally ordered.¹ In LaTiO_3 , the octahedron elongation perpendicular to the tilt axis overcompensates the shortening of a through a rigid tilt. The negative sign of the orthorhombic strain in LaTiO_3 is hence caused by the elongation of the octahedron along a . Interestingly, this effect is found to be strengthened at the antiferromagnetic transition; the behavior of the $O2-O2$ -bond distances accounts for the anisotropic anomalies: an elongation along a and a shrinking along b . Comparing our results with those of Refs. 11,12, one recognizes that the splitting in Ti-O-bond lengths, the splitting in the $O2-O2$ edges as well as the anomalies near T_N are less pronounced in the samples of Refs. 11,12. Nonstoichiometry seems to significantly reduce the long-range distortion of the TiO_6 octahedron. This was confirmed by our own studies on samples with excess oxygen, which revealed a continuous reduction of the orthorhombic strain and the anomalies around T_N .

Meijer *et al.* performed neutron-diffraction studies on single crystals in order to determine the magnetic structure.⁴ According to the symmetry of the GdFeO_3 structure,^{4,13} a G -type antiferromagnetic order may be associated with a weak ferromagnetic moment. However, Meijer *et al.* could not distinguish between the following two configurations due to twinning: either a G -type moment along a and ferromagnetism along c or a G -type moment along c and ferromagnetism along a . Using the high-flux diffractometer data, we get evidence that the ordered antiferromagnetic moment points along the a direction (see Fig. 4), although some underlying weak nuclear reflection complicates the analysis. Constraining the crystal structure to the high-resolution results given in Table I, we find a low-temperature ordered moment of $0.57(5) \mu_B$ slightly higher than previous studies.

The crystal structure within the RETiO_3 series is determined through the ionic radius of the RE. A smaller radius implies increasing tilt and rotation distortions. In Fig. 5(a) we plot the orthorhombic splitting against the square of the tilt angle. There is a clear deviation from the proportionality expected in the Landau theory,¹⁴ which we attribute to the anomalous stretching of the octahedron basal plane. Without this anomalous elongation, one would expect an orthorhombic splitting in LaTiO_3 to be three times larger and of positive sign. The anomalous octahedron elongation at the mag-

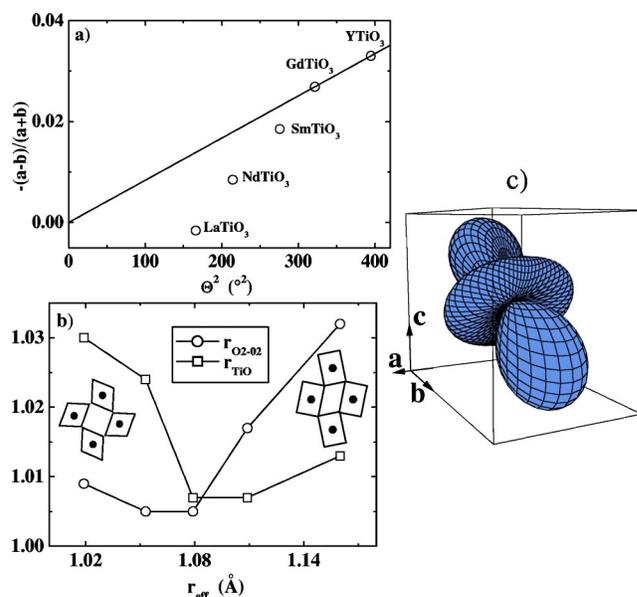


FIG. 5. (a) Plot of the orthorhombic distortion against the square of the tilt angle for different RETiO_3 . (b) Plot of the two prominent distortions of the TiO_6 octahedron against the ionic radius of the rare earth (RE) in RETiO_3 . Left scale denotes the ratio of the longest to the shortest TiO-bond length, right scale the ratio of the $O2-O2$ basal plane edge lengths. Except our LaTiO_3 , data were taken from Ref. 11. The insets in (b) show a drawing of the two different octahedron distortion schemes. (c) Shape of the t_{2g} orbital in LaTiO_3 , which is lowered in energy due to the distortion of the octahedron (axes correspond to the $Pbnm$ lattice).

netic ordering is, therefore, about an order of magnitude smaller than the total deformation in LaTiO_3 (see Fig. 3 and Table I). In Fig. 5(b) we compare the octahedron deformation in LaTiO_3 with that seen in the RETiO_3 series using the data of MacLean, Ng, and Greedan.¹¹ In LaTiO_3 we find a small variation in the TiO-bond distances, described by $r_{\text{TiO}} = (\text{Ti-O}_{\text{long}})/(\text{Ti-O}_{\text{short}})$, but a strong variation in the basal plane edge lengths described by $r_{O2-O2} = (O2-O2_{\text{long}})/(O2-O2_{\text{short}})$. In contrast, in YTiO_3 , the variation in the Ti-O distances is strong and that in the $O2-O2$ lengths is small, as was recently confirmed.¹⁵ Figure 5(b) shows that these distortions change continuously in the RETiO_3 series. The two distinct deformations of the octahedra imply different orbital ordering schemes. The variation of the Ti-O distances arises from the shift of an $O2$ site towards a Ti site; consequently, the distance to the opposite Ti is elongated and antiferro-orbital-type ordering results, which has been directly observed in YTiO_3 .¹⁶ In contrast, the elongation of the basal planes along a in LaTiO_3 implies ferro-orbital-type ordering. Following Goodenough-Kanamori rules, these orderings imply ferromagnetic and antiferromagnetic coupling, respectively. Most interestingly, the crossover between the two types of structural deformation¹⁷ coincides with the crossover from antiferromagnetic to ferromagnetic ordering¹⁸⁻²⁰ in the RETiO_3 compounds. With decreasing RE ionic radius, NdTiO_3 and SmTiO_3 still exhibit antiferromagnetic order with small T_N ,^{19,20} whereas GdTiO_3 is ferromagnetically ordered. A similar magnetic crossover is seen

in the $\text{La}_{1-x}\text{Y}_x\text{TiO}_3$ series.²¹ This coincidence between the structural and magnetic crossovers clearly documents the relevance of the octahedron deformation for the magnetism in RETiO_3 .

In the following, we analyze the effect of the octahedron basal plane elongation on the t_{2g} -energy levels. Qualitatively, one may argue that the octahedron elongation splits the degenerate xz and yz levels into $(1/\sqrt{2})(xz+yz)$ and $(1/\sqrt{2})(xz-yz)$. In the notation used here, the orbital coordinates refer to the cubic perovskite lattice, i.e., x, y , and z are parallel to the Ti-O bonds. We have calculated the t_{2g} -level splitting within a full Madelung-sum point-charge model, taking into account the second-order covalent contribution. Using the experimentally determined crystal structure, we obtain a sizeable splitting: one level is about 0.24 eV below the two others which remain almost degenerate. The crystal-field splitting is about one order of magnitude stronger than the spin-orbit coupling, and we have to conclude that the t_{2g} orbitals are not degenerate in LaTiO_3 , but the splitting is not sufficiently strong to completely quench the orbital moment. The occupied orbital can be constructed as a linear combination of the three standard t_{2g} orbitals: $0.77[(1/\sqrt{2})|xz+yz\rangle] \pm 0.636|xy\rangle$. The admixture of the xy orbital to $(1/\sqrt{2})|xz+yz\rangle$ alternates in its sign along the c axis and is constant in the (a, b) plane. The occupied orbital is oriented in the orthorhombic b, c plane and has almost the shape of the usual $3z^2 - r^2$ orbital pointing near the cubic $[111]_c$ direction²² (56° angle with the c axis, compared to 54.7° for the $[111]_c$ direction) [see Fig. 5(c)]. The lowered orbital points to the center of one of the octahedron triangles faces which are formed by two $O2$'s and one $O1$. It is interesting to note that the $O2$ - $O1$ distances of this triangle are elongated compared to the average. This means that the TiO_6 octahedron is compressed along the direction of the occupied

orbital. Since the occupied orbital is not oriented along one of the bonds, the resulting antiferromagnetic exchange is not expected to be very anisotropic. Assuming the calculated orbital splitting and quantum fluctuations, we obtain an ordered moment of $0.72 \mu_B$. The ordered moment will be further reduced as covalence, will diminish the level splitting, admix orbital contributions, and transfer a part of the spin to the oxygen sites which are not active in the G -type antiferromagnetic ordering. Similar to the proposal by Moshizuki and Imada,⁷ we may thus explain most of the magnetic properties of LaTiO_3 based on the structural distortion observed in the almost stoichiometric compound. The distortion assumed in Ref. 7 does not have the same geometry as the one we find, but is comparable in magnitude.

Since LaTiO_3 exhibits intermediately strong t_{2g} -level splitting, the orbital occupancy, the admixture of an orbital moment, and the resulting antiferromagnetic exchange interaction depend sensitively on the crystal structure. On one side, the system may gain magnetic energy in the ordered phase either by an enhancement of the magnetic interaction parameter or via spin-orbit coupling. On the other side, there will be a loss of elastic energy associated with the additional structural distortion. In the ordered state there should be a trend to increase the orbital ordering in agreement with experiment; according to our calculation the level splitting is enhanced by 6% between 155 and 8 K.

In summary, we have found a sizeable deformation of the TiO_6 octahedron in LaTiO_3 , which causes a relevant splitting in the t_{2g} levels (about 0.24 eV).

We gratefully acknowledge discussions with M. Grüninger, G. Khaliullin, and M. Laad. This work was supported by the Deutsche Forschungsgemeinschaft through the Sonderforschungsbereich 608.

¹M. Imada *et al.* Rev. Mod. Phys. **70**, 1039 (1998).

²B. Keimer *et al.*, Phys. Rev. Lett. **85**, 3946 (2000).

³G. Khaliullin and S. Maekawa, Phys. Rev. Lett. **85**, 3950 (2000).

⁴G.I. Meijer *et al.*, Phys. Rev. B **59**, 11 832 (1999).

⁵T. Mizokawa and A. Fujimori, Phys. Rev. B **54**, 5368 (1996).

⁶T. Mizokawa *et al.*, Phys. Rev. B **60**, 7309 (1999).

⁷M. Moshizuki and M. Imada, J. Phys. Soc. Jpn. **70**, 2872 (2001).

⁸V. Fritsch *et al.*, Phys. Rev. B **65**, 212405 (2002).

⁹F. Lichtenberg *et al.*, Z. Phys. B: Condens. Matter **82**, 211 (1991).

¹⁰D. Bruns and B. Büchner (private communication).

¹¹D.A. MacLean *et al.*, J. Solid State Chem. **30**, 35 (1979).

¹²M. Eitel and J.E. Greedan, J. Less-Common Met. **116**, 95 (1986).

¹³E. F. Bertaut, in *Magnetism III*, edited by G.T. Rado and H. Suhl (Academic Press, New York, 1963), p. 149.

¹⁴A. D. Bruce and R. A. Cowley, *Structural Phase Transitions* (Taylor and Francis, London, 1981).

¹⁵J.R. Hester *et al.*, Acta Crystallogr., Sect. B: Struct. Sci. **53**, 739 (1997).

¹⁶J. Akimitsu *et al.*, J. Phys. Soc. Jpn. **70**, 3475 (2001).

¹⁷Caution has to be taken concerning the stoichiometry of the compounds studied in Ref. 11. Also, the early magnetic study (Ref. 18) did not observe the antiferromagnetism in NdTiO_3 and SmTiO_3 ; structural data on these samples indicate a smoother crossover.

¹⁸J.E. Greedan, J. Less-Common Met. **111**, 335 (1985).

¹⁹G. Amow and J.E. Greedan, J. Solid State Chem. **121**, 443 (1996).

²⁰G. Amow *et al.*, J. Solid State Chem. **141**, 262 (1998).

²¹Y. Okimoto *et al.*, Phys. Rev. B **51**, 9581 (1995).

²²In a rotated coordinate system, the orbital can be described by $3z^2 - (1.1x^2 + 0.9y^2 + 0.8z^2)$.