

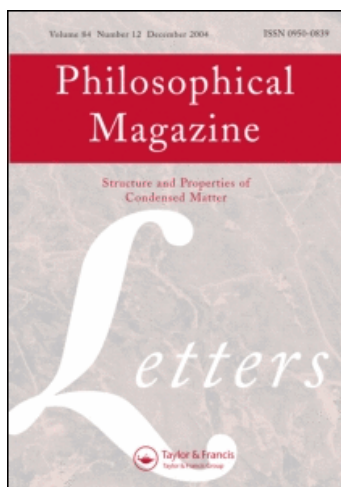
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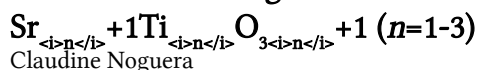


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Theoretical investigation of the Ruddlesden–Popper compounds $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ ($n = 1 - 3$)

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ABSTRACT

We have performed a theoretical study of the atomic and electronic structure of the four compounds Sr_2TiO_4 , $\text{Sr}_3\text{Ti}_2\text{O}_7$, $\text{Sr}_4\text{Ti}_3\text{O}_{10}$ and SrTiO_3 , by a total-energy semiempirical Hartree–Fock method. We show that the intercalation of SrO layers in the perovskite structure of SrTiO_3 induces lattice distortions and modifications of the electronic structure, which are mainly localized close to the stoichiometry defect. They include a contraction of the SrO–TiO₂ interplanar distance, a rumpling of the adjacent layers and an increase in the ionicity of the Sr–O bond. As the index n increases, the compounds $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ become more and more unstable with respect to phase dissociation and we predict a limit of stability for $n \approx 3$.

§ 1. INTRODUCTION

Controlling non-stoichiometry in oxides is a constant challenge, since it induces noticeable modifications of the atomic as well as of the electronic and magnetic properties. This is especially true in ternary oxides $\text{A}_n\text{B}_m\text{O}_p$, where both non-stoichiometric oxygen-to-cation and A-cation-to-B-cation ratios may be found. SrTiO_3 is a good example of a ternary oxide whose properties depend strongly upon its stoichiometry. When fully stoichiometric, it is a small-gap insulator while, upon reduction, it becomes semiconducting, and superconducting upon doping (Schooley *et al.* 1964). Its very important dielectric properties are also strongly dependent upon preparation procedures as well as upon its dimensionality (Nakamura *et al.* 1995).

Of special interest is the part of its phase diagram where the strontium-to-titanium ratio exceeds unity. It has been shown that excess strontium is not accommodated by a large concentration of point defects but rather by the formation of crystallographic shear structures of SrO and TiO₂. The so-called Ruddlesden–Popper (1957, 1958) structures of nominal composition $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ are ordered compounds of the K_2NiF_4 type, which display sequences of one SrO layer intercalated between n SrTiO_3 perovskite layers in the (001) direction. The end members of the family are SrO ($n = 0$) and SrTiO_3 ($n = \infty$). The most easily synthesized compounds are Sr_2TiO_4 ($n = 2$) and $\text{Sr}_3\text{Ti}_2\text{O}_7$ ($n = 3$), but observations of ordered phases (Ruddlesden and Popper 1958) or lamellae (Tilley 1977) of $\text{Sr}_4\text{Ti}_3\text{O}_{10}$ ($n = 4$) have also been reported.

The $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ compounds contain inequivalent oxygen and strontium sites, depending upon whether they belong to the perovskite units or the additional SrO layer. This has been shown, for example, by site-selective laser spectroscopy, on Eu^{3+} -doped Sr_2TiO_4 and $\text{Sr}_3\text{Ti}_2\text{O}_7$, in which the Eu^{3+} ions occupy strontium sites (Cockroft *et al.* 1991). The strength and the range of the perturbation induced by these stoichiometry defects on the atomic and electronic structure of these compounds are still open issues. In other compounds exhibiting similar intergrowth structures, it has been shown that gradual changes in the electronic and magnetic properties take place as the order n of the Ruddlesden–Popper compound increases and as the dimensionality changes from two to three (Michel and Raveau 1984, Rao and Thomas 1985, Rao *et al.* 1988).

A renewal of interest in these questions has taken place recently in relation to the fabrication of thin SrTiO_3 films as substrates for high- T_c superconductors, in for example superconducting field-effect transistors. The stoichiometry of the oxide has direct implications on the dielectric constant and breakdown field of the film. It has been found, using different preparation methods, that the stoichiometry can be represented by the chemical formula $(\text{SrTiO}_3)_n\text{SrO}$ (Michikami and Asahi 1991, Hirano *et al.* 1992, Nakamura *et al.* 1995), with the excess SrO layers being at random positions.

We have undertaken a theoretical study of the three compounds Sr_2TiO_4 , $\text{Sr}_3\text{Ti}_2\text{O}_7$ and $\text{Sr}_4\text{Ti}_3\text{O}_{10}$, and we have compared their properties to those of their parent oxide SrTiO_3 . We have focused our attention on the local atomic arrangement around the added SrO layers, and on the charge redistribution associated with this defect. We have also obtained tentative results on the stability of these compounds with respect to phase separation.

§ 2. METHOD

The method used relies on the self-consistent resolution of the Hartree–Fock equations for the valence electrons in a linear-combination-of-atomic-orbitals and complete-neglect-of-differential-overlap approximation. Details concerning the construction of the Hamiltonian matrix can be found elsewhere (Goniakowski *et al.* 1993). In the present case, the basis set includes the 2s and 2p orbitals for oxygen, 5s and 5p orbitals for strontium, and 4s and 3d orbitals for titanium. The parameters required to calculate the matrix elements and the total energy have been taken from a previous study of SrO and TiO_2 (Goniakowski and Noguera 1994a, b). A full geometry optimization is associated with the electronic structure calculation. All atomic degrees of freedom are relaxed in order to find the energy minimum at 0 K. This is done by means of a steepest-descent technique, associated with a simplified Broyden scheme. The whole procedure is repeated until the energy minimum with respect to the atomic degrees of freedom is found (force values less than $10^{-2} \text{ eV } \text{Å}^{-1}$). The calculated lattice parameters, bulk moduli and cohesive energies are $a = 4.0 \text{ Å}$ (3.9 Å), $B = 151 \text{ GPa}$ (183 GPa) and $E_{\text{coh}} = 25.6 \text{ eV (formula unit)}^{-1}$ (31.7 eV) for SrTiO_3 and $a = 5.08 \text{ Å}$ (5.16 Å), $B = 95 \text{ GPa}$ (90 GPa) and $E_{\text{coh}} = 5.12 \text{ eV (formula unit)}^{-1}$ (6.14) for SrO. The experimental values (Abrahams and Bernstein 1991, Lide 1991) are given in parentheses. This method, although based on semiempirical grounds, has the advantage of being fast enough to allow the study of large systems such as the present system, while retaining the important character of self-consistency which is required when treating atoms in changing environments.

§ 3. ATOMIC STRUCTURE

The unit cells, containing two $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ formula units (i.e. 14, 24, 34 and 5 atoms for the compounds with $n = 2, 3, 4$ and ∞ , respectively) are shown in figure 1. In the Ruddlesden–Popper phases with $n = 2, 3$ and 4, the a and b lattice constants have been assumed to be equal to their values in SrTiO_3 . The lattice constant c has been optimized, together with all positions of the atoms in the unit cell, without any

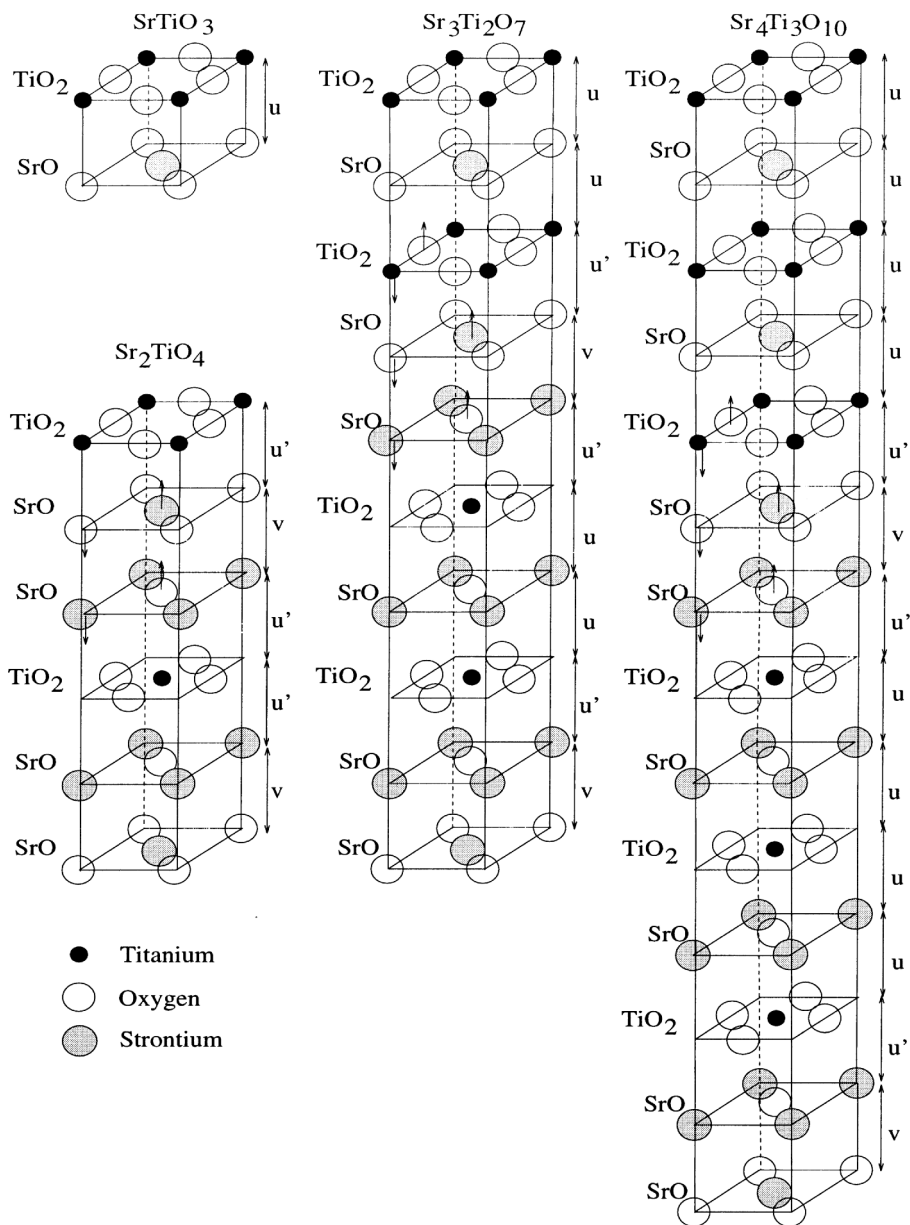


Figure 1. Structure of strontium titanate and Ruddlesden–Popper compounds with $n = 2, 3$ and 4. The arrows indicate the directions of the atomic displacements of inequivalent atoms, with respect to the average layer position, in half the unit cell.

Table 1. Structural parameters of the four compounds Sr_2TiO_4 , $\text{Sr}_3\text{Ti}_2\text{O}_7$, $\text{Sr}_4\text{Ti}_3\text{O}_{10}$ and SrTiO_3 : a , b and c are the lattice parameters, u , u' and v the interlayer spacings (figure 1) and δ_{SrO} and δ_{TiO_2} the rumplings of the SrO bilayers and their adjacent TiO_2 layers. Experimental values of c (Ruddlesden and Popper, 1957, 1958, Tilley 1977) are given in parentheses.

| Compound | a (Å) | b (Å) | c (Å) | u (Å) | u' (Å) | v (Å) | δ_{SrO} (Å) | δ_{TiO_2} (Å) |
|---------------------------------------|------------|------------|---------------|------------|-------------|------------|------------------------------|--------------------------------|
| Sr_2TiO_4 | 4.0 | 4.0 | 12.68 (12.60) | | 1.94 | 2.47 | 0.12 | 0.0 |
| $\text{Sr}_3\text{Ti}_2\text{O}_7$ | 4.0 | 4.0 | 20.62 (20.38) | 1.98 | 1.93 | 2.48 | 0.19 | 0.07 |
| $\text{Sr}_4\text{Ti}_3\text{O}_{10}$ | 4.0 | 4.0 | 28.88 (28.1) | 2.00 | 1.97 | 2.50 | 0.20 | 0.13 |
| SrTiO_3 | 4.0 | 4.0 | 4.0 (3.9) | | | | | |

symmetry constraint. Table 1 gives the lattice parameters at equilibrium that we have determined. The discrepancy between the calculated and experimental (Ruddlesden and Popper 1957, 1958, Tilley 1977) c values is less than 3% and is mainly associated with the 2.5% overestimation of the SrO– TiO_2 interplanar distance in SrTiO_3 .

The stacking may be characterized by three parameters u , u' and v , which represent the SrO– TiO_2 spacing inside and outside the SrTiO_3 units, and the SrO–SrO interplanar distance respectively, as indicated in figure 1. Indeed, we have found that the SrO and TiO_2 layers are equidistant inside the perovskite units, which allows one to write $c = 4(n - 2)u + 4u' + 2v$. In addition some layers are rumpled; this is true for the SrO bilayers and, in the higher-order members of the family, for the adjacent TiO_2 layers. We note the rumpling amplitudes δ_{SrO} and δ_{TiO_2} . In $\text{Sr}_4\text{Ti}_3\text{O}_{10}$, layers inside the SrTiO_3 units are also slightly rumpled. Similar distortions of the perovskite units have been reported for $\text{CsCa}_2\text{Nb}_3\text{O}_{10}$ (Dion *et al.* 1984). It should be noted that the structure refinement performed by Ruddlesden and Popper (1957, 1958) assumed no rumpling and $u = u'$. We have found that both hypotheses are incorrect, as shown in table 1.

The calculated values for u , u' and v are very similar in all compounds. We find that the SrO– TiO_2 interlayer distance u inside the perovskite units is very close to that in bulk SrTiO_3 , while u' , between a TiO_2 layer and a SrO bilayer, is noticeably shorter. However, in the latter case, owing to the rumpling δ_{SrO} , which pushes the oxygen and strontium atoms away from and towards the TiO_2 planes respectively, the interplanar Ti–O bond lengths are increased to $u + \delta/2$ and the Sr–O distances are slightly decreased to $[(a/2)^2 + (u - \delta/2)^2]^{1/2}$ (e.g. from 1.94 to 2.00 Å and from 2.78 to 2.74 Å respectively in Sr_2TiO_4). As a comparison, the Ti–O interatomic distance in SrTiO_3 is equal to 2 Å and the Sr–O distance in SrO is 2.54 Å. The rumpling thus allows accommodation of the Sr–O and Ti–O first-neighbour distances to values closer to those typical of these atomic pairs in the parent oxides.

One can thus conclude that the c parameter, well approximated by the relationship $c = 4(n - 2)u + 4u' + 2v$, is a linear function of the strontium-to-titanium ratio. The local structure of the perovskite units remains nearly identical with that of bulk SrTiO_3 , and the insertion of SrO layers mainly affects the TiO_2 layers in contact with them. This conclusion is expected to hold in non-stoichiometric thin films in which random insertion of SrO layers takes place.

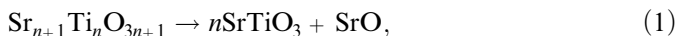
§ 4. ELECTRONIC STRUCTURE

The total densities of states (DOSs) in Sr_2TiO_4 , $\text{Sr}_3\text{Ti}_2\text{O}_7$, $\text{Sr}_4\text{Ti}_3\text{O}_{10}$ and SrTiO_3 are shown in figure 2. The general shapes of the DOS are very similar in all cases, with only small variations in peak intensities from one compound to the other. The valence band (VB) is divided into two parts. The lower VB and the upper VB, in the energy ranges -30 eV and $[-10, -6]$ eV, are assigned to O 2s and O 2p states respectively hybridized with titanium orbitals. The conduction band (CB) also displays two structures mainly related to Ti 3d_{4s} orbitals and Sr sp orbitals. A bandgap G of about 3 eV exists between the VB and the CB, which slightly decreases as n increases ($G = 3.05, 2.9$ and 2.85 for $n = 1, 2$ and 3 respectively).

The projection of the DOS on specific atoms allows one to specify the contributions of inequivalent atoms. From their local environment, one may distinguish two kinds of inequivalent oxygen and strontium atoms, those belonging to the SrO double layers and those from the SrTiO_3 units, as exemplified in figure 3 in the case of $\text{Sr}_3\text{Ti}_2\text{O}_7$. Indeed, we find that the oxygen atom and the strontium atom in the SrO bilayers have charges which are 0.2 and 0.03 electrons respectively higher (in absolute value) than in the perovskite layers. This increase in ionicity is due to the presence of stronger Madelung potentials acting on these atoms. In the case of the oxygen atoms, for example, this comes from a delicate balance between the number of titanium and strontium atoms in the first coordination shell (1 and 5 respectively for oxygen in the SrO bilayers, compared with 2 and 4 in the SrTiO_3 units). The oxygen charge is actually intermediate between its value in SrTiO_3 and in SrO. The inequivalence between oxygen atoms and between strontium atoms also yields a slight asymmetry in the shape of the lower VB peak and of the higher CB peak.

§ 5. STABILITY

The stability of the $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ compounds is characterized by two energies $E_1(n)$ and $E_2(n)$, which are associated, for the former, with phase segregation into SrTiO_3 and SrO, according to



and, for the latter, with segregation into SrTiO_3 and another phase of lower n value, for example

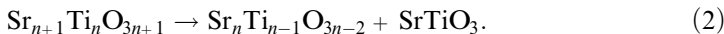


Table 2 summarizes the values that we obtain for $E_1(n)$ and $E_2(n)$. When positive, they indicate an instability of the $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ compound. All segregation energies are very small and, because of the absence of optimization of the lateral lattice parameters of the unit cell and the limitations of the method, only trends can be discussed. Table 2 tentatively suggests that the two first compounds are stable with respect to phase separation, while the latter may dissociate into SrTiO_3 and $\text{Sr}_3\text{Ti}_2\text{O}_7$. In agreement with experimental studies (Ruddlesden and Popper 1957, 1958), we thus predict a limit of stability of the $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ compounds close to $n \approx 3$.

§ 6. CONCLUSION

In conclusion, using semiempirical total energy Hartree–Fock method, we have modelled the Ruddlesden–Popper phases $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ with $n = 1, 2$ and 3 and compared their structure and electronic structure with those of the parent oxides

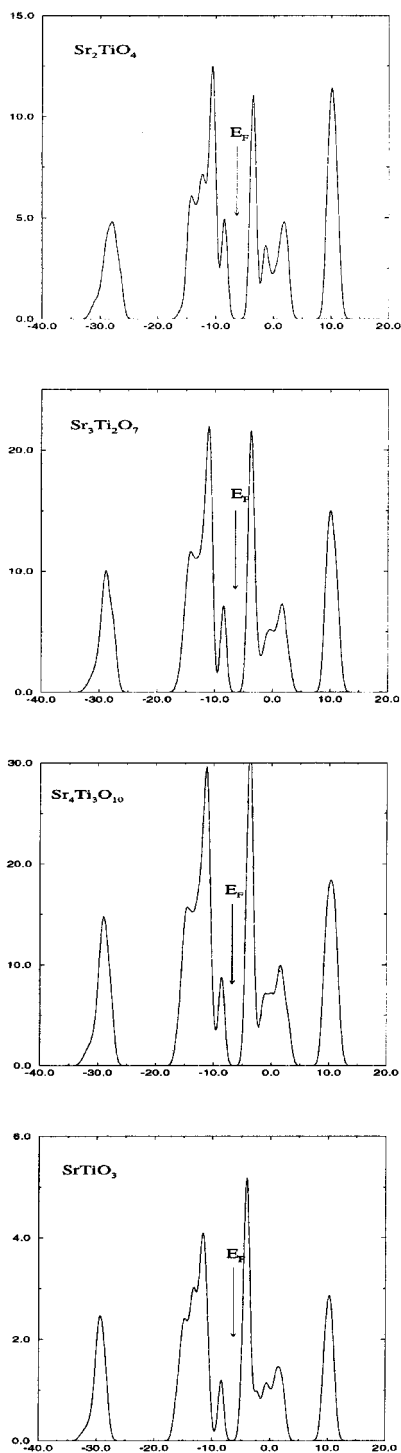


Figure 2. DOSs (in arbitrary units) of Sr_2TiO_4 , $\text{Sr}_3\text{Ti}_2\text{O}_7$, $\text{Sr}_4\text{Ti}_3\text{O}_{10}$ and SrTiO_3 as a function of energy (in electron volts). The DOSs have been convoluted by a 0.7 eV Gaussian function. The Fermi level is close to -8 eV.

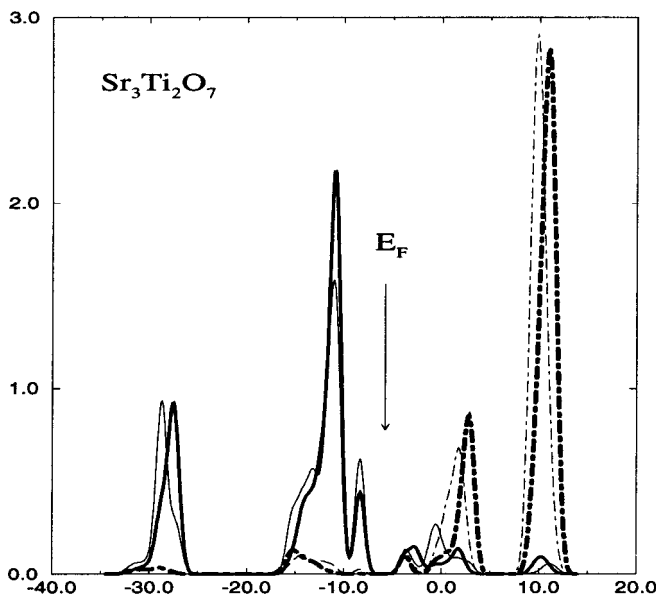


Figure 3. Local DOSs (in arbitrary units) of $\text{Sr}_3\text{Ti}_2\text{O}_7$, as a function of energy (in electron volts): solid curves, oxygen contributions; dashed curves, strontium contributions; bold curves, atoms in the SrO bilayers; fine curves, strontium and oxygen atoms in the SrTiO_3 units.

Table 2. Energies of dissociation of the $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ compound into bulk SrTiO_3 and bulk SrO (first row) or bulk SrTiO_3 and $\text{Sr}_n\text{Ti}_{n-1}\text{O}_{3n-2}$ (second row). The experimental value is given in parentheses (Lide 1991).

| Energy (eV (formula unit) ⁻¹) | $n = 1$ | $n = 2$ | $n = 3$ |
|--|--------------|---------|---------|
| $E_1(n)$ | -0.04(-0.24) | -0.10 | +0.02 |
| $E_2(n)$ | | -0.06 | +0.12 |

SrTiO_3 and SrO. We have shown that the perovskite units are hardly distorted and that the atomic and electronic modifications induced by the non-stoichiometry are localized in the close vicinity of the inserted SrO layers. In particular, both the oxygen and strontium charges and the Sr–O interatomic distances are intermediate between those found in SrTiO_3 and SrO. We have obtained lattice parameters in excellent agreement with experimental results and we have predicted the existence of a rumpling of the perturbed layers. This allows the structure to be as compact as possible, while maintaining interplanar Ti–O and Sr–O bond lengths close to the values expected from their local environment. The first two members of the family are found to be just stable with respect to phase separation, while the third member is likely to be on the other side of the border line. This work exemplifies the potentialities of modern electronic structure calculations, not at their highest level of sophistication, to yield information on ordered compounds with large unit cells, of relevance for potential applications.

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