Current Opinion in Solid State and Materials Science 20 (2016) 85–106

Contents lists available at ScienceDirect

Current Opinion in Solid State and Materials Science

journal homepage: www.elsevier.com/locate/cossms

Recent progress in simulations of the paramagnetic state of magnetic materials

I.A. Abrikosov [a,b,*], A.V. Ponomareva [b], P. Steneteg [c], S.A. Barannikova [b,d,e], B. Alling [a]

[a] Department of Physics, Chemistry and Biology (IFM), Linköping University, 58381 Linköping, Sweden
[b] Materials Modeling and Development Laboratory, National University of Science and Technology 'MISIS', 119049 Moscow, Russia
[c] Department of Science and Technology (ITN), Linköping University, 601 74 Norrköping, Sweden
[d] National Research Tomsk State University, 634050 Tomsk, Russia
[e] Institute of Strength Physics and Materials Science, SB RAS, 634055 Tomsk, Russia

ARTICLE INFO

Article history:
Received 21 July 2014
Revised 17 July 2015
Accepted 19 July 2015
Available online 13 August 2015

Keywords:
Paramagnetic state
Magnetic materials
First-principles simulations

ABSTRACT

We review recent developments in the field of first-principles simulations of magnetic materials above the magnetic order–disorder transition temperature, focusing mainly on *3d*-transition metals, their alloys and compounds. We review theoretical tools, which allow for a description of a system with local moments, which survive, but become disordered in the paramagnetic state, focusing on their advantages and limitations. We discuss applications of these theories for calculations of thermodynamic and mechanical properties of paramagnetic materials. The presented examples include, among others, simulations of phase stability of Fe, Fe–Cr and Fe–Mn alloys, formation energies of vacancies, substitutional and interstitial impurities, as well as their interactions in Fe, calculations of equations of state and elastic moduli for *3d*-transition metal alloys and compounds, like CrN and steels. The examples underline the need for a proper treatment of magnetic disorder in these systems.

1. Introduction: A description of the paramagnetic state of magnetic materials

Materials play very important role in the history of humankind. In the 1900-s the advent of electricity, aviation, nuclear power, and information technology was governed by the explosion of materials discoveries. Plastic and silicon, superconductors and biomaterials, photonic materials and ceramic composites became available. Moreover, accelerating technological development greatly increased demands for the materials design. So far, the prevailing search methods were based on trial-and-error development. However, the time it takes to discover advanced materials and to prove their usefulness to a commercial market is far too long. Thus, there is a need to reduce it significantly, from 10 to 20 years at present to 5–10 years or less [1]. Theoretical understanding of fundamental properties of materials and a possibility to carry out advanced computer simulations of materials properties should be considered as a key in achieving this goal.

A challenging problem for the condensed matter theory in this respect is to bring simulations as close as possible to conditions at which materials operate when used as tools and devices. Indeed, the physical and mechanical properties of materials depend on the chemical content, on the internal structure, which is formed during their manufacturing and service, as well as on temperature, stresses, and other external parameters. In the case of a magnetic material the situation becomes even more complex, turning fundamental study of magnetism into a subject of great scientific and practical interest, and leading to enormous amount of experimental and theoretical investigations in this field [2].

Great progress has been achieved in understanding of magnetically ordered materials. Consideration of relatively trivial types of collinear magnetic order, ferromagnetic, with all magnetic moment pointing in the same direction, or simple antiferromagnetic, say with magnetic moments in neighboring planes of the crystal pointing antiparallel to each other, is nowadays extended to significantly more rich spin textures, e.g. helical and skyrmion structures [3]. First principles calculations in the framework of Density Functional Theory (DFT) [4] have been recognized in the field as an extremely useful research tool. With a development of efficient computational methods [5] and increasing power of modern computers calculations of key magnetic characteristics,

* Corresponding author at: Department of Physics, Chemistry and Biology (IFM), Linköping University, 58381 Linköping, Sweden.
E-mail address: igor.abrikosov@ifm.liu.se (I.A. Abrikosov).

http://dx.doi.org/10.1016/j.cossms.2015.07.003
1359-0286/

like the local magnetic moments or magnetic exchange interactions, have transformed into a routine task, and theoretical treatments of noncollinear spin configurations [6,7], magnetic phase transitions [8], and spin dynamics [9–13] have become possible.

An interplay between magnetic and chemical effects in magnetic materials was recognized several decades ago [14,15]. Unfortunately, the effects of finite temperature magnetic excitations on their structural and elastic properties attracted much less attention. Often these effects were assumed small, the second-order effects, which should not be taken into account in simulations of phase stability and mechanical behavior. Moreover, paramagnetic phases of magnetic materials were modeled as non-magnetic in many works, and researchers did not distinguish between the two terms. Such misinterpretation could lead to erroneous conclusions [16]. Indeed, in most cases local magnetic moments survive above the magnetic transition temperature, seriously modifying the picture obtained in theoretical simulations [17]. The proper treatment of magnetic disorder is essential for the predictive description of materials properties [18,19], especially just below or above the Curie temperature [20].

Early attempts to understand the behavior of magnetic materials were dominated by two seemingly orthogonal pictures, the local magnetic moments model and the itinerant (band electrons) model. The former could be traced to the work of Heisenberg [21], and assumed that electrons were localized on atoms producing a local spin moment. The inter-atomic exchange interactions determined the magnetic order, and transverse spin fluctuations were excited at finite temperature, eventually leading to a disorder of the localized moments above the magnetic transition temperature. The itinerant model was based on the band theory of electrons, and was best represented by the Stoner description [22]. The competition between the kinetic energy of the itinerant electrons and the exchange interaction between them could give rise an imbalance in the numbers of spin up and spin down electrons, stabilizing a magnetic order, e.g. ferromagnetism. The longitudinal components of the local spin fluctuation lead to the variation of the magnetic moment with temperature and dominated the thermodynamic properties of magnetic materials.

Experimental data for the Curie–Weiss constant and the saturation magnetization of a wide variety of ferromagnetic substances were used by Rhodes and Wohlfarth to calculate values for the numbers of magnetic carriers from the former and from the latter, q_C and q_S, respectively [23]. Plotting their ratio as a function of the Curie temperatures of corresponding materials, Rhodes and Wohlfarth revealed two branches, one with $q_C/q_S \sim 1$, and the other with $q_C/q_S > 1$. The former corresponded to substances, such as Gd and MnSb, which could be described with a purely localized model of ferromagnetism. The second branch corresponded to substances, such as nickel and its alloys, dilute alloys of palladium and the compounds Sc_3In and $ZrZn_2$, which Rhodes and Wohlfarth classified according to collective electron model of ferromagnetism.

Probably, purely localized or the purely itinerant moment models could describe some materials. However, in general any of them alone should not be sufficient. Nowadays we understand that itinerant electrons determine the magnetic properties of transition metals and their alloys. Electronic structure calculations within DFT, which can be viewed as a modern extension of the Stoner-type description of magnetism, are capable to reproduce ground state magnetic properties of *3d* transition metals and their alloys with very high accuracy, and to explain them [24]. However, applications of the Stoner picture fail for the description of magnetism at finite temperature. It greatly overestimates the Curie temperatures for ferromagnetic metals T_c, by factor of five, and there are no moments and no Curie–Weiss law above T_c [25].

Very important step in the development of modern understanding of transition metal magnetism can be traced back to works of Moriya, who resolved the controversy between the itinerant and localized models into a more general problem of spin density fluctuations [26]. His interpolation theory was based on the functional integral formalism and the average amplitude of the local spin fluctuation was taken as one of the most important physical variables. Moriya has developed a method of taking into account the nonlocal nature of spin fluctuations so that the local moment limit and the weakly ferro- and antiferromagnetic limit were properly interpolated.

Moriya's works inspired the development of several first-principles approaches for the description of paramagnetic materials that we review in this paper. We restrict ourselves with a discussion of *3d*-series transition metals, their alloys and compounds, to limit nearly endless field to a manageable amount of information. However, the approaches and concepts that we discuss have sufficient generality, and should be applicable to a broad set of substances. Our starting point can be described as follows. Itinerant electrons determine the magnetism of *3d*-transition metals. However, they are relatively strongly bounded to their sites. Fig. 1 illustrates that the magnetization density in these systems is well localized. Consequently, each atom could be associated with a local moment parallel to the net magnetization density at the site. These local moments behave in a Heisenberg-like manner, that is like localized moments, and become disordered above the magnetic order–disorder transition temperature, the Cure T_C or Neel T_N temperature for ferromagnets and antiferromagnets,

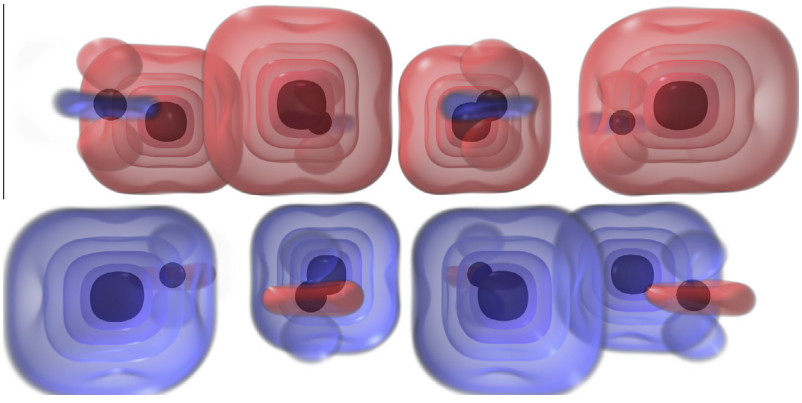

Fig. 1. Magnetization density calculated for orthorhombic antiferromagnetic phase of CrN simulated by $2 \times 1 \times 1$ unit cells. The density is shown by iso-surfaces at 0.06, 0.57, 1.14, and 1.71 electrons/Å^3. Red (blue) colors correspond to a surplus of majority (minority) spin electrons. It is seen that the magnetization density is well localized at Cr atoms (large bulbs) though some induced spin polarization at N atoms is also seen. Details of calculations are the same as in Ref. [27].