論 文 の 内 容 の 要 旨

First-principles and atomistic modeling analysis on mechanism of magnetism under large strain
（第一原理および原子モデリング解析による高ひずみ下の磁性変化メカニズムの解明）

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Nowadays, the industry is driving towards smaller devices and has entered the age of the micro- and nano-technologies (magnetoresistive random-access memory (MRAMs), nanoscale transistors for data storage, micro-electro-mechanical systems (MEMS), magnetic sensors, etc.) At such low dimensions, it is crucial to accurately describe the crystal structure of the material at the atomic scale. Simulations based on atom or electron models can be useful tools for understanding the structure-property relationships in magnetic materials. In particular, first-principles theoretical approaches based on the density functional theory have become a powerful tool for the design and understanding of complex material structures and properties.

The physical properties of the material can be significantly affected by the presence of residual stresses due to the manufacturing conditions or stresses occurring during the operation of the device. For instance, it is observed in the performance of hard disk devices. However, the device performance may deteriorate during operation, and it is suspected, empirically, that mechanical impact to the magnetic layer may be a culprit for the degradation. It is therefore of utmost importance to investigate the variations of magnetic properties under mechanical deformation, as well as the physical origins behind. In order to improve the mechanical properties, some elements are often added to the material (example: Mn in steel). Moreover, the addition of the elements can lead to substantial alterations of the magnetic properties of the

material. Thus, it draws our attention to the effect of substitutions.

The goal of this work is to examine the effect of strain and substitutions on various magnetic materials. This thesis is organized as follows: Chapter 1 introduces the motivations and background of this study. Chapter 2 provides the methodologies of first-principles density functional theory (DFT) and classical molecular dynamics (MD). While calculations in this study are mainly carried out by first-principles DFT calculations to identify the electronic and magnetic properties under the deformations and the effect of impurities, several classical MD simulations are performed on the polycrystalline solid with interface, surface, and grain boundaries to analyze the structure variation under deformations for neodymium magnets.

Chapters 3, 4, 5 and 6 are devoted to the main results, electronic and magnetic properties against deformation for various magnetic materials, i.e. thiogermanate, prussian blue analogue, hcp Co, and neodymium magnets. Chapter 3 describes the magnetic properties of the thiogermanate, which is an open-framework structure formed by interconnected FeS_4 and Ge_4S_{10} tetrahedrons. The complex crystal structure and 3*d* transition metal draw our attention on the influence of strain and impurities on the magnetism. Chapter 4 examines the prussian blue analogues, which exhibit an interesting magnetic and phase transition due to the Jahn-Teller effect. Influence of strain and impurities plays a key role on these materials because: 1) their magnetism is highly sensitive to the pressure; 2) prussian blue caged structure is easily substituted by other elements. Chapter 5 is devoted to hcp Co, which is widely used as microelectronic devices. It sustains highest magnetocrystalline anisotropy energy (MAE) among the transition metals, therefore the investigation on the variation of MAE under strain are performed. Chapter 6 focuses on the neodymium magnets used as permanent magnets. The role of MAE and microstructure is of vital importance for the coercivtiy of the neodymium magnets.

In Chapter 3, the influence on the magnetic properties of strain induced and substitutions of the thiogermanate $TMA_2FeGe_4S_{10}$ (TMA = $[(CH_3)_4N]^+$) are investigated. An analysis of the electronic structure is provided considering antiferromagnetic (AFM), ferromagnetic (FM) and nonmagnetic (NM) configurations for the thiogermanate at the equilibrium states. Small difference in total energy between the FM and AFM states suggests that the thiogermanate $TMA_2FeGe_4S_{10}$ may sustain a low Curie temperature. Variations in electronic structure and magnetic moment of the thiogermanate under strain are closely related to the distortion of FeS_4 tetrahedral units. With the help of a simplified molecule model H_4FeS_4, we show that, while the cause of the drastic change in magnetism under high compression mainly originates from the decrease in the Fe-S interatomic bond length, the changes in the electronic structure are mainly

due to the variations of the interatomic bond angles. Little effect of shear strain on the magnetic properties is found due to the fact that the FeS_4 tetrahedral units rotate under shear, hence keeping their shape. The results of substituting transition metals imply the possibilities that the magnetic properties can be tuned by doping with Cu and Ni.

Chapter 4 is devoted to analyzing various magnetic properties of prussian blue analogues (PBs). The electronic structures of cubic PBs ($Co_2Fe(CN)_6$, $Cs_2CoFe(CN)_6$, $K_2CoFe(CN)_6$) at equilibrium reveals that $Co_2Fe(CN)6$ exhibits metallic properties, however $K_2CoFe(CN)6$ and $Cs_2CoFe(CN)_6$ are half-metallic. The minimal total energy order $E_{cubic} > E_{tetra} > E_{monoc}$ indicates that the lower symmetric structure is more stable due to the Jahn-Teller effect. The crystal $K_2CoFe(CN)_6$ possesses a low Curie temperature, which is in agreement with the experiments. The cubic system is characterized by half-metallic properties. The magnetism in the majority spin (↑) mainly originates from the Co-*d* orbitals, and the hybridization of Co-*d* and N-*p* orbitals. However, the tetragonal structure is semiconducting. It is found that, as the reduction of the volume, the magnetic moments (MM) decreases and the band gap around the Fermi level increases. The total density of states (TDOS) under compression becomes symmetric, which is consistent with the fact that the MM is zero when $\varepsilon = -0.2$. Finally, for uniaxial strain, the band gap decreases with the expansion of the lattice parameters $a = b$ and the simultaneous reduction of c.

The magnetic anisotropy energy (MAE) of the bulk hcp Co under mechanical deformation is calculated in Chapter 5. We present a thorough investigation with respect to the choice of exchange-correlation functionals. The generalized gradient approximation (GGA) succeeds in predicting the easy axis of magnetization but underestimates the MAE in comparison to the experimental value, while the local density approximation (LDA) gives an incorrect magnetic easy axis. Furthermore, to achieve the experimental value the strong electronic corrections DFT+*U* approach was employed. Unfortunately, the associated strong distortions of the lattice parameters suggest that the DFT+*U* is not the most suitable choice for predicting the behavior of MAE under mechanical deformation. Our results with GGA suggest that the MAE can be tuned by normal strain. Meanwhile it is found that the MAE decreases against shear strain, which is consistent with experimental observation.

Chapter 6 describes the investigation of the tetragonal Nd-Fe-B based neodymium magnets. Neodymium magnet is the strongest type of permanent magnets and is therefore of considerable interests for industry. It sustains higher remanence (B_r) and energy product (BH_{max}), but lower coercivity (H_c) and Curie temperature (T_c). It is believed that the magnetocrystalline anisotropy

(MCA) energy could significantly affect the coercivity of the material, we thus perform first-principles calculations to examine the local magnetic moments (MM) and MCA energy for the bulk and impurities. Due to the fact that the complex microstructure of the neodymium magnets strongly affects the coercivity, the influence of magnetoelastic anisotropy for the systems including interface, surface and grain boundaries is analyzed, using classical MD methods. We found that coercivity is strongly affected by magnetocrystalline anisotropy and the microstructure.