摘要

在塊材狀態下反磁性的CoSi合成CoSi-SiO_2奈米線後出現了異常的鐵磁性質。我們將藉由第一原理計算來探討異常鐵磁性背後的緣由。奈米線鐵磁性的其中一個來源是在CoSi與SiO_2界面處由於Co原子未完全配位鍵結及鍵結的扭曲，使得Co原子3d軌域的自旋向上和自旋向下的電子數不同，而產生鐵磁性，但是鐵磁性還有其他來源。由電子顯微鏡(TEM)的選區繞射(SAD)分析奈米線區域中的CoSi發現了超晶格的存在，這些超晶格是由CoSi內的缺陷所致，經過選區繞射分析，這些缺陷以有序Si空孔的方式出現在CoSi立方晶體中，使的繞射圖中出現比較微弱的訊號。第一原理計算發現Co 原子受到奈米線表面效應以及內部有序空孔的影響，使得其態密度在自旋向上以及自旋向下的圖形產生不對稱，因此產生了磁化量。模擬結果顯示沒有有序空孔結構的CoSi-SiO_2奈米線即使將內部磁化量加到表面上，平均磁化量也只有$0.1638\mu_B$，比奈米線的實驗值$0.8400\mu_B$還小了80%。計算有序空孔結構時則平均磁化量可提升至$0.8074\mu_B$，只比實驗值小3.881%，表示奈米線內部的有序空孔是造成磁化量的主要因素。進一步研究有序空孔附近的Co原子的磁性質後發現擁有較低配位數的Co原子會有較高的磁化量，因為Co與Si空孔之間的未成對電子使的自旋向上與自旋向下的態密度分布不對稱。但是某些有序空孔結構的Co平均磁化量反而略低於沒有空孔結構Co的平均磁化量，因為這些沒有空孔結構的Co鍵長坐落在鐵磁性質中比較強的自旋交換作用範圍，使得這些原子的磁軌域重疊比較多，產生比較高的磁化量。

Abstract

The diamagnetic semimetal CoSi presents unanticipated ferromagnetism as CoSi/SiO_2 nanowires.[1] Using first-principles calculations, we offer physical insights into the origins of this unusual magnetism. Due to the distorted and dangling bonds near the nanowire surface with different bond lengths, the transition metal (Co) d-orbital electron spin up and spin down populations become asymmetric from the exchange interactions, providing the mechanism for some of the measured magnetization. However, the distorted and dangling bonds are clearly not the only factor contributing to the magnetization of the nanowires. The transmission electron microscopy selected area diffraction (SAD) analysis of the CoSi region suggested a superlattice structure existed in the cubic CoSi, and defects existing as ordered vacancies in the CoSi resulted in the observed SAD lower contrast image components. The simulation's results for the Co moment in the CoSi nanowires without these ordered vacancies, but incorporating the surface and internal spin moments, is only 0.1638μB/atom, which is a ~80% shortfall compared to the experimental value of 0.8400μB/atom. When the effects of ordered vacancies are incorporated into the simulation, 0.8074μB per Co atom, a much better match with the experimental value (within ~3.881%) results, indicating that the internal ordered vacancies in the CoSi nanowires is a dominant mechanism of the ferromagnetism. Investigation on the density of states (DOS) of Co atoms around the ordered vacancies shows that the Co atoms with lower coordination number induce more magnetization due to the unpaired electrons created by the break of Co-Si bonds, which cause the unbalance between spin up and spin down states. But in some cases, the magnetization of Co in the structure without ordered vacancies is higher than the Co in the structure with ordered vacancies. In such case, the bond length of Co in the structure without ordered vacancies falls in a range that leads to stronger interacting spin-exchange through the overlap between magnetic orbitals.

[1] K. Seo, K. S. K. Varadwaj, P. Mohanty, S. Lee, Y. Jo, M. H. Jung, J. Kim, B. Kim, Nano Lett. 7, 1240 (2007)