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Magnetic Behavior of Rare-Earth Iron-Rich Intermetallic Compounds

DOMINIQUE GIVORD, REMY LEMAIRE, WILLIAM J. JAMES, JEAN-MICHEL MOREAU, AND JAYANT S. SHAH

Abstract—The thermal variation of lattice parameters of rare earth-transition metal intermetallic compounds rich in Fe, Co, or Ni in the temperature range of 25–900°K is studied. For the Fe compounds, negative thermal expansion is observed below their magnetic ordering temperatures regardless of the nature of substitutional ordering. For Co and Ni compounds, the thermal expansion behavior is normal. It is then concluded that for the Fe compounds, the magnetic properties are mainly determined by the Fe-Fe interatomic distances and the number of Fe nearest neighbors, whereas for Co and Ni compounds the magnetic properties are determined by the conduction electron transfer from the rare earth to the 3 *d* band of Co or Ni. The anomalous thermal expansion of Fe compounds and the metamagnetic transition of the Lu compound is explained in terms of the distance dependence of the interaction energy as proposed by Néel.

INTRODUCTION

THE RCO_5 compounds with the $CaCu_5$ -type structure generally possess high permanent magnet properties, essentially due to the strong magnetocrystalline anisotropy of Co. This phase does not appear in the rare-earth-iron system. However, substitution of a certain amount of rare earth by Fe atom pairs creates enough deformation to stabilize crystallographic structures built on a $CaCu_5$ subcell. For rare earths with large atomic radii, the substitutions, one per three subcells, order with rhombohedral ($ABCABC\cdots$) symmetry and form the R_2Fe_{17} compound which is isostructural with Th_2Zn_{17} [1]. With the smaller rare earths like Lu, the substitutions partially order with the hexagonal ($ABAB\cdots$) Th_2Ni_{17} -type symmetry. However, some of these remain randomly disordered on the *C* positions so as to stabilize the $CaCu_5$ building block and the composition becomes $LuFe_{9.6}$ [2]. A completely disordered substitution has also been observed in the Gd compounds [3].

All these Fe-rich compounds generally exhibit high spontaneous magnetization below room temperature [4]. Their magnetic ordering temperatures are low in comparison to that of pure Fe, although their Fe magnetic moments are about the same as for pure Fe. This is not the case for the isostructural compounds with Co and Ni where the magnetic properties are mainly determined

by the changes in the electronic configuration of Co or Ni due to conduction electron transfer from the rare earth. For the Fe compounds, the Fe magnetic moments remain relatively insensitive to increasing rare-earth content. In this case it appears that the magnetic interactions are strongly dependent on the Fe-Fe interatomic distances. In order to confirm this, we have carried out detailed thermal expansion studies of these compounds.

EXPERIMENTS

All compounds in this investigation were prepared by melting the elements in a high-frequency levitation furnace. Compounds with the rhombohedral structure were obtained by annealing quenched samples at 1100°C for 3 days, whereas compounds with the hexagonal structure were obtained when homogenized at 950°C.

Thermal expansion studies were carried out by means of powder X-ray diffraction in the temperature range of 20–900°K. Below 300°K, a symmetrical back-reflection focusing camera cooled by means of a Joule-Thompson refrigerator was used [5]. For high-temperature X-ray diffraction, the powder samples were sealed in quartz capillaries under high vacuum. A $CrK\alpha_1$ ($\lambda = 2.28962\text{\AA}$) radiation was used. Neutron diffraction and Mössbauer studies on the Lu compound were performed at the Nuclear Center, Grenoble, France.

RESULTS

Compounds YNi_5 and YCo_5 with hexagonal $CaCu_5$ -type structures exhibit, without any anomalies, normal-linear thermal-expansion coefficients. For YNi_5 , $\alpha_a = 1.06 \times 10^{-5}/^\circ K$, $\alpha_c = 1.0 \times 10^{-5}/^\circ K$; and for YCo_5 , $\alpha_a = 1.2 \times 10^{-5}/^\circ K$, $\alpha_c = 0.35 \times 10^{-5}$.

Fig. 1 shows the thermal variation of the *a* and *c* parameters of the Y hexagonal compounds (Th_2Ni_{17} type) with Fe, Co, and Ni. A negative thermal expansion is observed only in the *c* parameter of the Fe compound. This anomalous behavior of the *c* parameter below the magnetic ordering temperature is typical of all the Fe compounds (see Fig. 2). In the same temperature range, the *a* parameters are almost constant. Furthermore, these anomalous properties are not dependent on the type of substitutional ordering, since they have been observed for all three different forms of the Gd compound [3]. No thermal hysteresis was observed within the limits of the experimental accuracy.

The Lu compound has a peculiar magnetic behavior; it is ferromagnetic up to 100°K and becomes metamagnetic at the Curie temperature. The magnetic ordering temperature being 270°K. A hysteresis is observed for the

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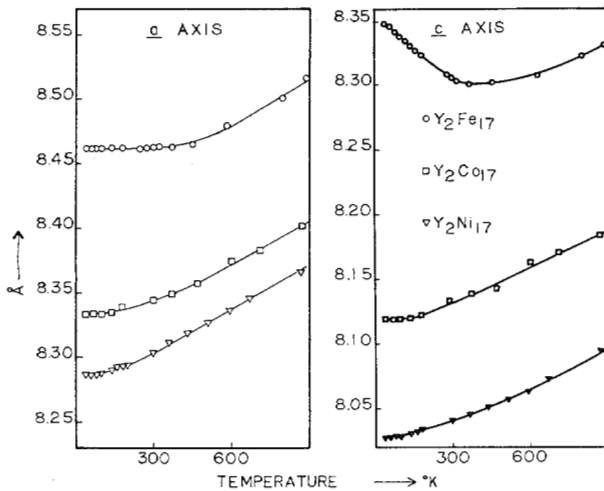


Fig. 1. Comparison of thermal variation of lattice parameters of Y_2Fe_{17} , Y_2Co_{17} , and Y_2Ni_{17} .

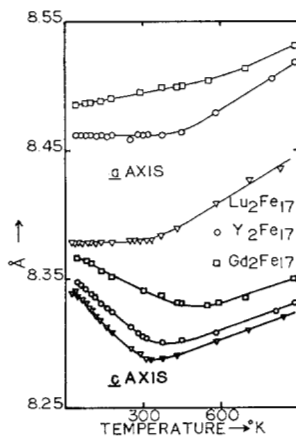


Fig. 2. Thermal variation of lattice parameters of Lu_2Fe_{17} , Y_2Fe_{17} , and Gd_2Fe_{17} .

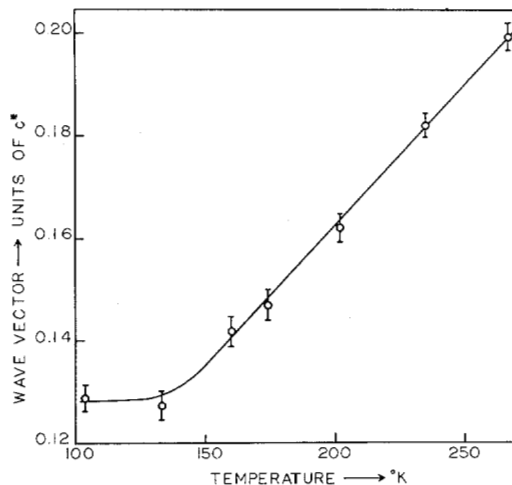


Fig. 3. Thermal variation of wave vector τ for helical magnetic configuration of Lu_2Fe_{17} . $\tau = 2C \sin \theta_{000} / \lambda$.

thermal-magnetization and neutron-diffraction studies [6]. Neutron-diffraction patterns at 77°K and also above the ordering temperature show the same diffraction peaks, confirming the ferromagnetic nature of this compound at low temperatures. Magnetic moments are perpendicular to the c axis. A diffraction peak appears between 100 and 270°K at a low angle when the temperature is decreased; at 160°K

$$\frac{\sin \theta}{\lambda} = 86 \times 10^{-4} \text{ \AA}^{-1}$$

(see Fig. 3). Its position varies linearly from 270–150°K. At lower temperatures this variation is less rapid and vanishes at approximately 125°K. In the same temperature range, two satellite peaks, (101^+) and (101^-) , were observed on both sides of the (101) peak. These results are typical of a helical-spin configuration where the screw axis is the c axis. The magnetic structure is therefore formed by ferromagnetic layers perpendicular to the c axis. The angle between two consecutive layers varies from 12° at 110°K to 19° at 270°K.

INTERPRETATION AND CONCLUSIONS

From the results of the thermal-expansion studies, it is evident that, for Fe compounds, the magnetic properties are determined primarily by the Fe–Fe interatomic distances and the number of Fe nearest neighbors; while for Co and Ni compounds, these factors play a secondary role.

Except in the substitution zone, the Fe–Fe interatomic distances are of the same order of magnitude as in pure iron. This leads to an overall ferromagnetic behavior for these Fe compounds. However, in the substitution zone, the Fe–Fe interatomic distances are shorter than those in pure iron. The $3d$ shell of iron is larger than those of Co and Ni; therefore, for these very short Fe–Fe interatomic distances, there is a direct exchange giving rise to an antiferromagnetic coupling [8] which is highly strain dependent. Due to the positive interactions in the rest of the crystal, all the magnetic moments are parallel. Because of this, a large amount of magnetic energy is stored in the substitution zone along the shortest Fe–Fe interatomic distance, where the local magnetic interaction is negative. As a consequence, a compromise is attained between the stored magnetic energy and the elastic energy. This leads to an increase of shortest Fe–Fe interatomic distances in order to minimize the negative interaction. Since these shortest Fe–Fe interatomic distances are dependent only on the c axis, a large negative thermal expansion is observed in the c direction.

In agreement with the previous work [7] our experiments on the Lu compound show almost no change in Mössbauer spectra at the ferromagnetic–helimagnetic transition. From this it is concluded that the transition is not due to a change in the electronic configuration of iron. Instead, the dependence of the interaction energy on the transition metal interatomic distances, as proposed by Néel [8], is applicable. For the helimagnetic state, the negative interactions dominate over the positive interactions leading to a helical spin configuration. But as the

temperature decreases more, there is a tendency for minimization of these negative interactions such that the Fe-Fe distances in the substitution zone actually increase. Accordingly, below 100°K positive interactions dominate over the negative and the compound becomes ferromagnetic. In the Y_2Fe_{17} , due to the larger atomic radius of Y, the Fe-Fe distances are large enough to stabilize only the ferromagnetic configuration.

This anomalous thermal expansion of the Fe compounds is quite similar to the Invar anomaly and the model of compromise between the stored magnetic energy and elastic energy is quite in accordance with Zener's theory of ferromagnetism [9].

In conclusion, the number of Fe nearest neighbors and their interatomic distances play a major role in determining the magnetic properties of the R-Fe compounds. In the analogous R-Co compounds, the magnetic properties are determined by conduction electron transfer from the rare earth to Co whose 3d electrons are less strongly bound. These two different types of behavior should lead to an Fe-Co ordering in the R-Fe-Co ternary compounds reinforcing the magnetocrystalline anisotropy since the crystal structure is uniaxial. Further studies in these directions will be of interest in developing permanent magnets.

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Theoretical and Experimental Aspects of Coercivity Versus Particle Size for Barium Ferrite

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Abstract—The Stoner-Wohlfarth coherent rotation model has been extended to particle sizes approaching the superparamagnetic critical size S_c for the case of barium ferrite. It is shown that at particle volumes up to 100 S_c , the coercivity factor will be lower than the Stoner-Wohlfarth factor of 0.48. Experimentally, micro-powders of barium ferrite with variable particle size have been formed using the glass-ceramic process. The particle size was determined with X-ray and electron microscope techniques. Although coercivities in excess of 5000 Oe were measured, the comparison between experiment and theory is not good. This has been attributed to the fact that the particles are poorly crystallized even though formation proceeded by a precipitation and crystal growth process.

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I. INTRODUCTION

STONER and Wohlfarth [1] calculated magnetization curves for single domain magnetic particle assemblies which fall under the coherent rotation model. Subsequent research has disclosed that other incoherent mechanisms will also lead to demagnetization [2]. However, some classes of materials, notably the hard ferrites, appear to be governed by a Stoner-Wohlfarth type of mechanism. Indeed, H_{ci} values on experimental powders of barium or strontium ferrite closely approaching the Stoner-Wohlfarth predictions have been achieved by Mee and Jeschke [3]. Recently Joffe [4] has shown how the coercivity of a particle assembly which is governed by the coherent rotation model will vary as a function of particle size. We have obtained independent verification of Joffe's arguments, and in this paper the theory is extended to the case of barium ferrite microcrystals.