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To cite this version:

T. Mcguire, M. Shafer. MAGNETIC ANISOTROPY IN RbNiF3 WITH Co AND Ca SUBSTITUTIONS. Journal de Physique Colloques, 1971, 32 (C1), pp.C1-627-C1-628. <10.1051/jphyscol:19711213>. <jpa-00214039>

HAL Id: jpa-00214039
https://hal.archives-ouvertes.fr/jpa-00214039
Submitted on 1 Jan 1971

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MAGNETIC ANISOTROPY IN RbNiF₃ WITH Co AND Ca SUBSTITUTIONS

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Abstract. — The relationship of the magnetic anisotropy to the ion locations has been investigated in hexagonal 6L type crystals. The compositions studied were RbCoₓNi₁₋ₓCaₓF₃, where both Co and Ca have a preference for 2a sites. The data show there are differences of the Co²⁺ ion anisotropy on the two sites (2a and 4f) with a strong positive K₂ for ions on the less symmetric 4f site. For certain compositions cones of easy magnetization from about the hexagonal c-axis which are found to have equilibrum positions that are sensitive to the applied magnetic field.

The ABF₃ fluorides where A is monovalent Rb or Cs, and B is a divalent ion such as Ni, Co, Mn, or Fe form predominantly hexagonal compounds of the 6L type in which ferrimagnetism has been observed [1, 2]. Ferrimagnetism in the 6L structure occurs because two nonequivalent sites (4f and 2a) exist in the ratio two to one. Two antiparallel magnetic sublattices are formed and a net magnetic moment one third the total moment is observed. In this paper we report details of the magneto-crystalline anisotropy of Ca substituted RbNiₓ₋₁₋ₓCoₓCaₓF₃ together with a discussion of certain anomalous properties of the anisotropy of RbNiₓ₋₁₋ₓCoₓF₃.

Crystal Structure. — The hexagonal 6L Type ABF₃ structure is the hexagonal barium titanite type where the B²⁺ ion occupies octahedral coordinated fluoride sites. Two thirds the BF₆ octahedra in the structure occur in face sharing pairs to form B₂F₆ polyhedra (4f sites). The remaining one third BF₆ octahedra (2a sites) are connected to the B₂F₆ polyhedra by sharing corners. Recently Babel [3] and Weidenborner and Bednawitz [4] find that the 2a-sites have all Ni-F distances identical and the octahedron is almost regular (3m symmetry) while for the 4f sites the Ni-F distances and bond angles indicate a more distorted octahedron (3m symmetry). This difference in symmetry for the two sites accounts not only for the site preferences of different ions, but it is also the suggested mechanism for the magnetic anisotropy effects reported here.

Site Preferences and Magnetic Moment. — Site preferences of B²⁺ ions have been determined from magnetic moment measurements [5]. The general result is that the larger ion prefers the 2a sites. Thus Mg²⁺ (7.8 Å) has very little site preference while Ca²⁺ (1.06 Å) goes completely on the 2a sites as determined from the corresponding rise in magnetic moment. As will be seen the divalent cobalt ion also has a preference for the 2a sites. Based on both low temperature saturation moment and the effective paramagnetic moment we use Ni²⁺ = 2.31 μB and Co²⁺ = 3.68 μB [6].

Based on analyses of the magnetic moments in figure 1 are plotted the fraction of the Co and Ni on 2a sites for the Ca replacement of Ni. The preference of Co²⁺ for the 2a sites is shown here together with the fact that it almost completely replaces Ni²⁺. The Co site preference to some degree is due to the slightly larger Co²⁺ ion.

![Figure 1: Fraction of Co and Ni ions on 2a sites vs. Ca concentration for RbCo₂Niₓ₋₁₋ₓCaₓF₃.](http://dx.doi.org/10.1051/jphyscol:19711213)

Magneto-Crystalline Anisotropy. — Knowledge of the ion distribution lays the ground work toward an understanding of the anisotropy. The magneto-crystalline anisotropy is adequately represented by $E_K = K_1 \sin^2 \theta + K_2 \sin^4 \theta$. $K_1$ and $K_2$ can be obtained from the shape of magnetization curves. In addition when $0 < -K_1 < 2K_2$, the equilibrium position of the magnetic moment vector forms an angle $\theta_e$ with the $c$-axis of the crystal given by $\sin^2 \theta_e = -K_1/2K_2$.

In figure 2 we give $K_1$ and $K_2$ as determined from magnetization curves on single crystals of RbNiₓ₋₁₋ₓCoₓCaₓF₃.

Referring to the ion distribution indicated in figure 1 we note that with the removal of Co²⁺ ions from 4f sites, $K_1$ goes from negative to positive and then slightly negative again; also $K_2$ decreases to almost zero. This suggests substantial differences in the
anisotropy of the Co\(^{2+}\) on the two sites. It is important to note that the removal of Ni\(^{2+}\) ions from 2a sites is not responsible for the changes in anisotropy because in the composition RbNi\(_{1.85}\)Ca\(_{1.15}\)F\(_3\) we find \(K_1 = -2.0 \times 10^6\) and \(K_2 = 8 \times 10^6\) erg/cm\(^3\), values more representative of pure RbNiF\(_3\) [2].

Based on the one ion model, the total anisotropy we measure is the sum of the individual anisotropies of the magnetic ions in the crystal. We assign a negative \(K_1\) to a Ni\(^{2+}\) on 4f sites and a strong positive \(K_1\) to Co\(^{2+}\) on both 4f and 2a sites. In addition, the Co\(^{2+}\) on 4f sites must have a small positive \(K_2\) while on 2a sites \(K_2\) becomes small. The fact that the measured \(K_1\) is slightly negative for the RbNi\(_{1.85}\)Co\(_{2}\)Ca\(_{1.15}\)F\(_3\)

sample simply means there is a balance between the 

- \(K_1\) for Ni\(^{2+}\) and \(+K_1\) for Co\(^{2+}\). In the

RbNi\(_{1-x}\)Co\(_{2}\)F\(_3\)

system [2] the irregular values of \(K_1\) and \(K_2\) with \(x\) are also due to the distribution of cobalt ions, reflecting the above assignments.

As mentioned previously when values for \(K_1\) and \(K_2\) fulfill the relations \(0 < -K_1 < 2K_2\), cones of easy magnetization appear. It is known from earlier work [2] that cones are found, at 4.2 °OK, for compositions \(x = .08\) to .25. Further, a cone (\(\theta_0 \approx 25^\circ\)) is associated with the composition RbNi\(_{1.78}\)Co\(_{2}\)Ca\(_{0.04}\)F\(_3\).

There is an interesting phenomenon associated with the cone angle for certain compositions. It involves the equilibrium or stable value for \(\theta\) when an applied field is present. As shown in figure 3 for RbNi\(_{8}\)Co\(_{2}\)F\(_3\)

the cone angle changes from \(31^\circ\) to about \(19^\circ\) when the field is increased 2 to 16 kG. First consider that the anisotropy field along the cone direction, \(\theta_0\), can be expressed by \(H_K(\theta) = \frac{2(K_1/K_2)(K_1 + 2K_2)/M_s}{\text{ergs/cm}^3}\), which for the \(x = .2\) sample is \(H_K(31) = 16,700\) gauss. Thus the applied field is comparable to the anisotropy field. However, this is not the complete answer since the effect is not as simple as a rotation of the magnetic vector. Instead a new equilibrium position is defined by maxima in the magnetic moment vs. angle curve as the field is rotated 360°. In a fixed field of 16 kG this maximum is clearly shifted from \(31^\circ\) (2 kG) to \(19^\circ\) (16 kG). It is believed that the explanation of this effect is a result of strong anisotropy fields in different directions, associated with the two sublattices. We have previously [7] invoked such a model to explain the increase in moment in CsFeF\(_3\) with magnetic field. CsFeF\(_3\) also shows shifts in the cone angle but in the opposite direction (i.e. larger \(\theta\) for increasing \(H\)) than the RbNi\(_{8}\)Co\(_{2}\)F\(_3\) samples. In a subsequent paper we will discuss these effects more fully.

References