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MAGNETIC ANISOTROPY IN RbNiF_3 WITH CO AND Ca SUBSTITUTIONS

T. R. McGUIRE and M. W. SHAFER

Thomas J. Watson Research Center, Yorktown Heights, New York

Résumé. — La relation entre l'anisotropie magnétique et la position des ions a été examinée dans des cristaux hexagonaux du genre 6 L. Les compositions étudiées étaient $\text{RbCo}_2\text{Ni}_{1-y}\text{Ca}_y\text{F}_3$ dans lesquelles le Co et le Ca ont une préférence pour les sites 2a. Les données montrent qu'il y a une différence entre les anisotropies ioniques du Co^{2+} dans les sites 2a et dans les sites de moindre symétrie 4f pour lesquels K_2 a une valeur élevée positive. Pour certaines compositions des cônes de facile aimantation existent autour de l'axe c hexagonal. Ceux-ci ont des positions d'équilibre qui dépendent du champ magnétique appliqué.

Abstract. — The relationship of the magnetic anisotropy to the ion locations has been investigated in hexagonal 6 L type crystals. The compositions studied were $\text{RbCo}_2\text{Ni}_{1-y}\text{Ca}_y\text{F}_3$ where both Co and Ca have a preference for 2a sites. The data show there are differences of the Co^{2+} ion anisotropy on the two sites (2a and 4f) with a strong positive K_2 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 equilibrium positions that are sensitive to the applied magnetic field.

The ABF_3 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 6 L type in which ferrimagnetism has been observed [1, 2]. Ferrimagnetism in the 6 L 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 $\text{RbNi}_{1-y}\text{Co}_y\text{F}_3$ together with a discussion of certain anomalous properties of the anisotropy of $\text{RbNi}_{1-x}\text{Co}_x\text{F}_3$.

Crystal Structure. — The hexagonal 6 L Type ABF_3 structure is the hexagonal barium titanite type where the B^{2+} ion occupies octahedral coordinated fluoride sites. Two thirds the BF_6 octahedra in the structure occur in face sharing pairs to form B_2F_9 polyhedra (4f sites). The remaining one third BF_6 octahedra (2a sites) are connected to the B_2F_9 polyhedra by sharing corners.

Recently Babel [3] and Weidenborner and Bednowitz [4] find that the 2a-sites have all Ni-F distances identical and the octahedron is almost regular ($\bar{3}m$ 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 B^{2+} ions have been determined from magnetic moment measurements [5]. The general result is that the larger ion prefers the 2a sites. Thus Mg^{2+} (.78 Å) has very little site preference while Ca^{2+} (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 $\text{Ni}^{2+} = 2.31 \mu_B$ and $\text{Co}^{2+} = 3.68 \mu_B$ [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 Co^{2+} for the 2a sites is shown here together with the fact that it almost completely replaces Ni^{2+} . The Co site preference to some degree is due to the slightly larger Co^{2+} ion.

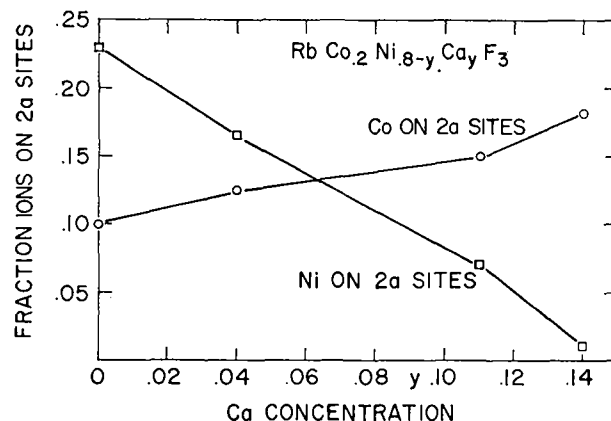
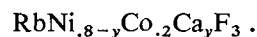


FIG. 1. — Fraction of Co and Ni ions on 2a sites vs. Ca concentration for $\text{RbCo}_2\text{Ni}_{1-y}\text{Ca}_y\text{F}_3$.

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 θ_c with the c-axis of the crystal given by $\sin^2 \theta_c = -K_1/2K_2$.

In figure 2 we give K_1 and K_2 as determined from magnetization curves on single crystals of



Referring to the ion distribution indicated in figure 1 we note that with the removal of Co^{2+} 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

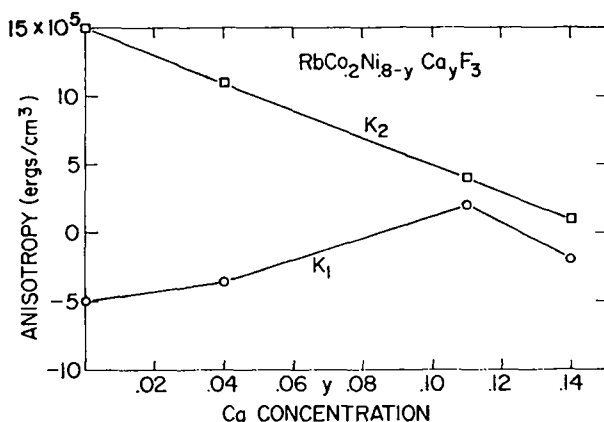
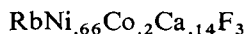


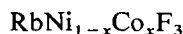
FIG. 2. — Anisotropy constants K_1 and K_2 vs. Ca concentration for $\text{RbCo}_2\text{Ni}_{8-y}\text{Ca}_y\text{F}_3$.

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 $\text{RbNi}_{.85}\text{Ca}_{.15}\text{F}_3$ we find $K_1 = -2.0 \times 10^6$ and $K_2 = .8 \times 10^6$ ergs/cm³, 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 strong positive K_2 while on 2a sites K_2 becomes small. The fact that the measured K_1 is slightly negative for the



sample simply means there is a balance between the $-K_1$ for Ni^{2+} and $+K_1$ for Co^{2+} . In the



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 °K, for compositions $x = .08$ to $.25$. Further, a cone ($\theta_c \approx 25^\circ$) is associated with the composition $\text{RbNi}_{.76}\text{Co}_{.2}\text{Ca}_{.04}\text{F}_3$.

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

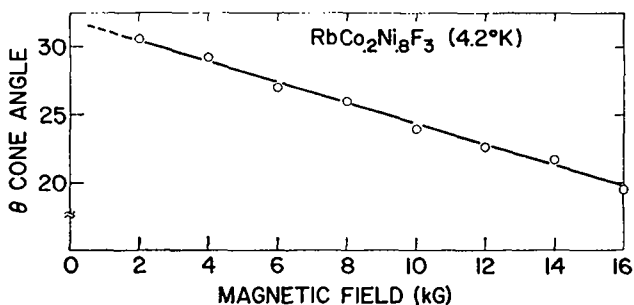


FIG. 3. — Cone angle vs. applied magnetic field for $\text{RbCo}_2\text{Ni}_8\text{F}_3$ at 4.2 °K.

the cone angle changes from 31° to about 19° when the field is increased 2 to 16 kG. First consider that the anisotropy field along the cone direction, θ_c , can be expressed by $H_K(\theta) = -2(K_1/K_2)(K_1 + 2K_2)/Ms$, which for the $x = .2$ sample is $H_K(31^\circ) = 16\,700$ 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° (2 kG) to 19° (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 θ for increasing H) than the $\text{RbNi}_{.8}\text{Co}_{.2}\text{F}_3$ samples. In a subsequent paper we will discuss these effects more fully.

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