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Magnetic and Optical Properties of the High- and Low-Pressure Forms of $CsCoF_3$*

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$CsCoF_3$ has hcp (h) and ccp (c) CsF_3 layers alternating *hhchhchhc* at atmospheric pressure ($9L$ structure of $BaRuO_3$) but a *cchcch* sequence ($6L$ structure of $RbNiF_3$) if quenched from 700°C at pressures greater than 20 kbar. The octahedral-site Co^{2+} ions are between the layers and give the $9L$ structure a pink color, the $6L$ structure a lavender hue. The $9L$ phase obeys a Curie–Weiss law above 70°K with $C_m=3.7$ emu°K/mole and $\Theta_p=-62$°K. It has $T_N=8$°K with evidence for a spin-flop transition at $H_c\approx11$ kOe and an anisotropy constant $K\approx5\times10^4$ ergs/cm³ at 4.2°K. The $6L$ phase has $C_m=3.3$ emu°K/mole, $\Theta_p=-65$°K and is ferrimagnetic below $T_C=50$°K. The magnetization is not saturated at 17.2 kOe and 4.2°K, where $\bar{\mu}=0.8\ \mu_B/Co^{2+}$ is smaller than the 1.23 μ_B/Co^{2+} anticipated at saturation for $RbNiF_3$-type ordering. Optical data show a larger trigonal-field splitting for the $6L$ structure. For both phases, $Dq\approx760$ cm^{-1}, spin–orbit interaction parameter $\zeta\approx500$ cm^{-1}, and long wavelength cutoff ≈13 μm.

The structures of $CsCoF_3$ are characterized by different ratios of ccp and hcp CsF_3 layers with Co^{2+} occupying the fluorine octahedra between layers. At atmospheric pressure[1] $CsCoF_3$ has the nine-layer ($9L$) $BaRuO_3$ structure with $a=6.20$ Å, $c=22.36$ Å. At 700°C and pressures greater than 20 kbar, a six-layer ($6L$) $RbNiF_3$ structure is formed (as anticipated for this class of compounds)[2] with $a=6.09$ Å, $c=14.67$ Å.[3] As indicated in Fig. 1, Co^{2+}-occupied octahedra share common faces across an hcp layer, common corners across a ccp layer. Samples were prepared by the reaction of stoichiometric mixtures of CsF and CoF_2. All handling of the reagents was done in a glove bag filled with dry nitrogen. The samples, contained in gold capsules (4-mm diameter×10 mm) were first subjected to the desired pressure in a belt apparatus and then brought rapidly to temperature with an internal graphite heater. After a half-hour at temperature, they were rapidly quenched before the pressure was released. The lavender $6L$ form is retained at atmospheric pressure to several hundred degrees.

Magnetic susceptibility measurements have been made with a vibrating-sample magnetometer calibrated with nickel. Samples of 100–200 mg were studied from 4.2°K to room temperature and in fields up to 17 kOe. The atmospheric pressure ($9L$) form is characterized at low temperatures by a maximum in its susceptibility, which we interpret as a Néel point $T_N=8$°K. Above 70°K, the susceptibility obeys the Curie–Weiss law $\chi_m=C_m/(T-\Theta)$ with $C_m=3.70$ emu°K/mole $[\mu_{\rm eff}^{Co^{2+}}\equiv(8C_m)^{1/2}=5.4\ \mu_B]$ and $\Theta_p=-62$°K. These results, which are shown in Fig. 2, are in good agreement with Rudorff *et al.*,[4] who examined the susceptibility over the temperature range 77°–475°K and found $C_m=3.65$ emu°K/mole and $\Theta_p=-60$°K. The value of C_m is within the range expected for a high-spin Co^{2+} ion in an octahedral interstice.[5] Below 70°K, the susceptibility deviates from Curie–Weiss behavior (Fig. 2) and is consistent with ferromagnetic correlation within the Co^{2+}-ion triples sharing common octahedral-site faces [Fig. 1(a)]. However, long-range antiferromagnetic order occurs only below $T_N=8$°K, indicating that the antiferromagnetic 180° Co^{2+}–F–Co^{2+} interactions are relatively weak. Such antiferromagnetic order would double the unit cell along the c axis.

At 77°K and at room temperature the field dependence of the magnetization is linear. At 4.2°K, which is below T_N, the magnetization and its field dependence, Fig. 3, show an anomalous increase between 7 and 11 kOe. This indicates a Co^{2+}-ion spin flop at a critical field $H_c\approx11$ kOe. For applied fields $H\ll H_c$, the average susceptibility for a powder sample is $\bar{\chi}(H\ll H_c)=$

FIG. 1. Octahedral linkages for the two structural forms of $CsCoF_3$.

$\frac{1}{3}\chi_{\parallel}+\frac{2}{3}\chi_{\perp}$. Above H_c, the average susceptibility is $\bar{\chi}(H>H_c)=\chi_{\perp}$ which gives the ratio $\bar{\chi}(H>H_c)/\bar{\chi}(H\ll H_c)=3/[2+(\chi_{\parallel}/\chi_{\perp})]$. The measured ratio is 1.5, indicating that $\chi_{\parallel}\approx0$ at 4.2°K. For a uniaxial anisotropy energy density $E_a=K\sin^2\alpha$, the spin-flop critical field is given by[6] $H_c=[2K/(\chi_{\perp}-\chi_{\parallel})]^{1/2}$, so that for $\chi_{\parallel}\approx0$ we can calculate the anisotropy constant as $K=\frac{1}{2}\chi_{\perp}H_c^2=\frac{1}{2}\bar{\chi}(H>H_c)H_c^2\approx5\times10^4$ erg/cm³. Since the fluorine atoms common to neighboring triplets are centers of inversion, there can be no Dzialoshinskii vector associated with the 180° cation–anion–cation interactions. Nevertheless Fig. 3 indicates a weak ferromagnetism in low fields, $[\sigma_m(H\ll H_c)=\sigma_0+\bar{\chi}_mH$,

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where $\sigma_0 \approx 0.002\ \mu_B/Co^{2+}$ ion] that seems to disappear for $H > H_c$. Without identification of the origin of this weak moment, it is not possible to say anything about the plane in which the spins rotate.

The magnetic properties of the high-pressure ($6L$) form of $CsCoF_3$ are quite different from those of the atmospheric form. This phase exhibits a ferrimagnetic transition at $T_c = 50°K$ (Fig. 2) and a saturation magnetization (Fig. 3) at 17.2 kOe and 4.2°K of $0.8\ \mu_B$/Co. The magnetic ordering of the Co^{2+} ions is probably the same as for the Ni^{2+} ions in the $6L$ forms of $RbNiF_3$ and $CsNiF_3$. The pairs of face-shared octahedra (90° Co^{2+}–F–Co^{2+}) are ferromagnetically ordered while the corner shared octahedra (180° Co^{2+}–F–Co^{2+}) are antiferromagnetically ordered [Fig. 1(b)]. In the $6L$ structure of $CsCoF_3$ this would align four Co spins in one direction and two in the opposite direction. Since each octahedral-site Co^{2+} ion has a net atomic moment of about $3.7\ \mu_B$, as can be determined from the magnetization of $CoFe_2O_4$ and $CoMnO_3$, this ordering predicts an average of $1.2\ \mu_B$ per Co^{2+} ion. The lower value of the saturation magnetization found for the $6L$ form of $CsCoF_3$ ($0.8\ \mu_B$/Co) is attributed to a large anisotropy in this hexagonal structure, the magnetization still remaining unsaturated at 17.2 kOe (Fig. 3). The magnetic susceptibility of this form obeys the Curie–Weiss law for $T > 100°K$ with $C_m = 3.3$ emu°K/mole ($\mu_{eff}^{Co^{2+}} = 5.1\ \mu_B$) and $\Theta_p = -65°K$ (Fig. 2),

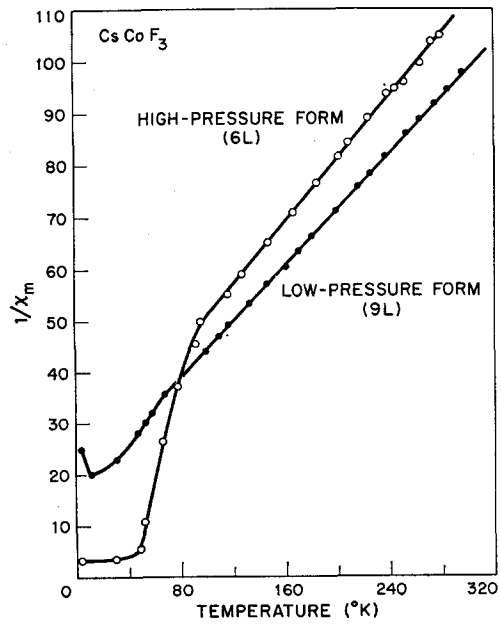

FIG. 2. Inverse molar susceptibility ($1/\chi_m$) vs temperature for the high- and low-pressure forms of $CsCoF_3$.

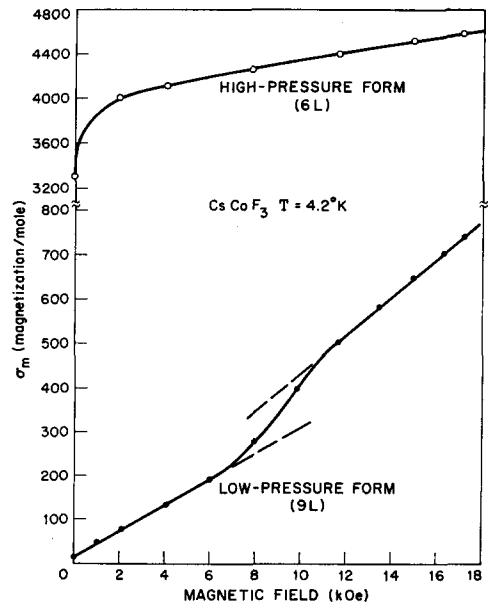

FIG. 3. Magnetization vs magnetic field at 4.2°K for the high- and low-pressure forms of $CsCoF_3$.

showing that both forms of this material are similar in their paramagnetic region.

Optical transmission and diffuse reflectance measurements (0.2–16 μm) were made on $6L$ and $9L$ $CsCoF_3$ powders. For both crystal forms, the spectra are similar and can be described by $Dq \approx 760\ cm^{-1}$, a spin–orbit interaction parameter $\zeta \approx 500\ cm^{-1}$, and a long-wavelength cutoff at $\approx 13\ \mu$m. Stark splittings show that for both compounds the Co^{2+} ions are in distorted octahedral sites. However, the ground-state absorptions of the $Co^{2+}(3d^7)$ ion at $\approx 1600\ cm^{-1}$ in the $6L$ modification are substantially (6×) greater. This indicates that the trigonal crystal field present in the $6L$ material is much larger than that in the $9L$ form. These data are consistent with the magnetic properties as well as the bluish color of $6L$ $CsCoF_3$. The $9L$ form has the pink color commonly associated with Co^{2+} ions in octahedral sites.

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