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Lower Valence Fluorides of Vanadium. 1. Synthesis and Characterization of $NaVF_3$, KVF_3, and $RbVF_3$

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A method of preparation of $NaVF_3$, KVF_3, and $RbVF_3$ is described. The compounds KVF_3 and $RbVF_3$ have cubic perovskite structures with lattice constants $a = 4.131 \pm 0.004$ Å and $a = 4.182 \pm 0.004$ Å, respectively. The compound $NaVF_3$, however, has an orthorhombic structure probably of the $GdFeO_3$ type with lattice constants $a = 5.490 \pm 0.005$ Å, $b = 5.684 \pm 0.006$ Å, and $c = 7.887 \pm 0.008$ Å. The magnetic susceptibility of $NaVF_3$ measured from 4.2 to 300 K shows evidence of magnetic ordering near 35 K. A plot of χ_M^{-1} vs. T appears to be typical of a canted antiferromagnetic material with $C_M = 1.82$ cm^3 mol^{-1} deg and $\Theta = (-)59$ K. Magnetic susceptibility measurements on KVF_3 also indicate antiferromagnetic ordering but a plot of χ_M vs. T displays two maxima, one at 50 K and a second at 130 K. Only the lattice constants of $RbVF_3$ have been measured.

Introduction

The large volume of literature on divalent, trivalent, and mixed valence fluorides of the first transition series has been deficient of many vanadium analogues. Although VF_2[1] and VF_3[2] have proven to be novel antiferromagnetic materials, very little has been reported on the magnetic properties of related vanadium fluorides. Considerable interest has existed in these materials, but the problem has been primarily one of synthesis.

Three powerful techniques have been combined to prepare and delineate the lower valence vanadium fluorides. These are (1) preparation by first vacuum encapsulating solid state reacting materials inside refractory metal containers using electron beam welding techniques, (2) identification and classification of crystal structures by the combined capability of polarized microscopy and x-ray diffraction, and (3) characterization by measurement of magnetic susceptibilities from 4.2 to 300 K. This method has provided information on numerous vanadium fluorides, which will be reported in this series. It is appropriate to first report some of the divalent fluorides of vanadium, which have been among the most difficult materials to prepare.

Magnetic properties of divalent fluorides of the latter metals of the first transition series mixed with equimolar amounts of alkali fluorides have been studied. Antiferromagnetic ordering was found to occur in $NaMnF_3$ (60 K),[3] $NaFeF_3$ (97 K),[4] $NaCoF_3$ (74 K),[5] and $NaNiF_3$ (149 K).[6] These compounds were reported to have orthorhombic crystal structures[7-9] of the $GdFeO_3$[10] type. The cubic perovskites $KMnF_3$ (83.3 K),[11] $KFeF_3$ (115 K),[12] $KCoF_3$ (109.5 K),[13] and $KNiF_3$ (253.5 K)[13] also order antiferromagnetically. Shafer[14] reported that $NaVF_3$, KVF_3, and $RbVF_3$ have cubic perovskite structures at room temperature but do not show evidence of any long-range magnetic ordering above 4.2 K. The materials described were produced by solid state reactions in sealed Pt containers, but products were reported to be contaminated with various trivalent vanadium fluoride phases. Recently, Cros et al.[15] reported that magnetic susceptibilities of $NaVF_3$, KVF_3, and $RbVF_3$ show evidence of long-range magnetic ordering, but important details of these measurements appear to be obscured.

We have characterized $NaVF_3$, KVF_3, and $RbVF_3$. Because of difficulties encountered in the synthesis of these materials, their preparations are described in detail, including descriptions of disproportionation products which form under certain conditions.

Experimental Section

Vanadium difluoride was prepared from 99.9% V metal, as previously described by Stout and Boo.[1] Optical grade NaF, KF, and RbF were obtained commercially. Tared, pulverized, and thoroughly mixed samples were vacuum encapsulated in Pt, Mo, or V-lined Mo by electron beam welding techniques. These capsules were usually of dimensions 0.64 cm in diameter by 3.2 cm in length. The sealed samples were fired in the vacuum chamber of a 10 kW rf induction furnace or in an evacuated stainless steel tube of a Lindberg Hevi Duty furnace. Weight checks were made on the capsules following every operation throughout the procedure. All handling and transferring of materials was done inside an inert atmosphere glove box.

Various divalent, trivalent, and mixed valence vanadium fluoride phases were initially identified by polarized microscopy. Phases were separated when necessary under a stereoscopic microscope by Pasteur's method, and their structures were verified by Debye–Scherrer x-ray powder techniques using Cu Kα radiation. Mixed valence phases were further identified by synthesis from stoichiometric mixtures of AF, VF_2, and VF_3. Weissenberg x-ray methods were employed, when single crystals were available, to determine crystal symmetries and to check for superlattice structures. Densities were measured by a volume exclusion method modified for small samples.

Magnetic susceptibilities of selected samples were measured from 4.2 to 300 K using a Princeton Applied Research, Foner type, vibrating sample magnetometer equipped with a liquid helium cryostat and gallium arsenide thermometer and temperature controller. Randomly oriented powder samples ranging from 20 to 100 mg were measured at a constant field of 11 000 G.

Results

Numerous methods of preparing the equimolar alkali fluoride–vanadium difluoride (AVF_3) compounds were pursued before a successful procedure was found. Some of these provided valuable information in solving the problem and also produced other materials worthy of investigation. It was necessary to first optimize the container material in which the solid state reactions were carried out. Results are described in which containers of Pt, Mo, and V-lined Mo were used.

Reactions in Pt. Initial experiments were carried out in Pt containers at 1200 C for 12 h. Products formed by the reaction of NaF with VF_2 were approximately 20% reddish phase of moderate optical density and birefringence when viewed between crossed nikols, 60% green phase of low optical density and moderate birefringence, and 20% unreacted VF_2. The KF–VF_2 sample produced approximately 20% blue cubic KVF_3, 40% red phase of moderate optical density and birefringence, and 40% isotropic green phase of low optical density. A mixture of RbF–VF_2 produced a small quantity of blue, cubic $RbVF_3$ and approximately equal amounts of red and green phases which were weakly birefringent and had moderate and low optical densities, respectively. The red mixed valence phases were identified by synthesis and x-ray diffraction to be $Na_2V_2F_7$, similar in structure to weberite;[16] KV_2F_6, related in structure to the tetragonal potassium tungsten bronze (K_xWO_3, where x varies from 0.4 to 0.6);[17] and RbV_2F_6, an orthorhombic, modified pyrochlore structure.[18] The trivalent green phases were identified from the x-ray data of Cretenet[19] to be Na_3VF_6, K_3VF_6, and Rb_3VF_6.

Table I. X-Ray Powder Data of $NaVF_3$ ($a = 5.490 \pm 0.005$ Å, $b = 5.684 \pm 0.006$ Å, $c = 7.887 \pm 0.008$ Å)

hkl	d_{obsd}	d_{calcd}	I_{obsd}	*hkl*	d_{obsd}	d_{calcd}	I_{obsd}
110	3.937	3.949	100	320	1.539	1.539	2
002		3.943		321	1.513	1.510	2
111	3.532	3.531	4	133	1.480	1.480	6
020	2.837	2.842	25	232	1.450	1.450	6
112	2.790	2.790	100	040	1.420	1.420	10
200	2.744	2.745	20	224	1.394	1.395	25
120	2.519	2.524	6	400	1.373	1.372	6
210	2.468	2.472	15	042	1.339	1.337	6
121	2.402	2.402	10	134	1.326	1.326	10
103	2.367	2.371	20	314	1.303	1.305	2
113	2.186	2.188	15	402	1.296	1.296	4
122	2.124	2.126	15	240	1.261	1.262	6
212	2.094	2.094	4	332	1.248	1.249	20
220	1.972	1.974	100	116		1.247	
004		1.972		420	1.236	1.236	4
023	1.928	1.930	4	242	1.202	1.202	6
221	1.914	1.915	4	206	1.185	1.186	2
123	1.817	1.821	2	422	1.179	1.179	4
130	1.789	1.791	20	044	1.153	1.153	4
222	1.764	1.765	30	243	1.138	1.138	4
114		1.764		404	1.126	1.126	4
310	1.745	1.742	15	150	1.113	1.113	2
311	1.701	1.701	2	325	1.102	1.101	2
132	1.629	1.631	30	226	1.094	1.094	4
024	1.619	1.620	30	152	1.070	1.071	2
204	1.600	1.601	15	244	1.062	1.063	6
312	1.593	1.593	40	316	1.049	1.049	6

Reactions in Mo. In the same manner, equimolar amounts of AF and VF_2 were vacuum encapsulated inside Mo and heated according to the same schedule. Products included unreacted AF and VF_2, some AVF_3, and the same phases as were formed in Pt. However, the amount of formation of V(III) was significantly less in Mo than in Pt. Although the products formed in both Pt and Mo suggest disproportionation of V(II) to V(III) and V(0), no reduced vanadium was found in either set of experiments.

Reactions in V-Lined Mo. Ultimately, V-lined Mo capsules were employed to prepare the $AF-VF_2$ compounds. Trial and error, along with results published by Shafer,[14] led to a heating schedule of 800 C for 30 days. Equimolar ratios of $NaF-VF_2$ and $KF-VF_2$ produced bright-blue, single-phase materials. The $NaVF_3$ was weakly birefringent, and KVF_3 was isotropic. A sample of $RbF-VF_2$ attacked the V liner and resulted mostly in opaque material with approximately 10% light-blue, isotropic $RbVF_3$. Thus far, attempts to grow large single crystals of KVF_3 have been unsuccessful, but crystals up to 1 mm on an edge were obtained from a melt at 1200 C in V-lined Mo. These bright-blue crystals appeared to be free of impurities.

The compounds KVF_3 and $RbVF_3$ were verified to have cubic perovskite structures with $a = 4.131 \pm 0.004$ Å and $a = 4.182 \pm 0.004$ Å, respectively. The x-ray powder data of $NaVF_3$, however, were fit to an orthorhombic unit cell of dimensions $a = 5.490 \pm 0.006$ Å, $b = 5.684 \pm 0.006$ Å, and $c = 7.887 \pm 0.008$ Å. Values of d(obsd) compared with d(calcd) of $NaVF_3$ are shown in Table I. No variation in lattice constants of AVF_3 compounds prepared under different conditions was found. X-ray studies of single crystals of KVF_3 showed no evidence of a superlattice structure. Elemental analyses and experimental densities of $NaVF_3$ and KVF_3 vs. calculated values are shown in Table II.

Magnetic Measurements. The molar magnetic susceptibility (χ_M) vs. T and χ_M^{-1} vs. T of $NaVF_3$ from 4.2 to 300 K are shown in Figure 1. From this plot, T_N is estimated to be approximately 35 K. The constants C_M and Θ for $NaVF_3$ were found to be 1.82 ± 0.02 cm^3 mol^{-1} deg and (−)59 ± 3 K, respectively. The magnetic susceptibilities of KVF_3 (1) prepared by solid state reaction in Mo, (2) prepared by solid state reaction in V-lined Mo, and (3) melted in V-lined Mo [after corrections made for impurities in (1)] were found to be identical. Figure 2 shows χ_M vs. T from 4.2 to 300 K of KVF_3 melted in V-lined Mo.

Table II. Chemical Composition and Densities of $NaVF_3$ and KVF_3

	Chemical composition		Density	
	Found	Calcd	Found	Calcd
		$NaVF_3$		
Na	17.60	17.56	3.58	3.53
V	39.10	38.91		
F	43.38	43.53		
		KVF_3		
K	26.45	26.59	3.40	3.46
V	34.54	34.64		
F	38.89	38.76		

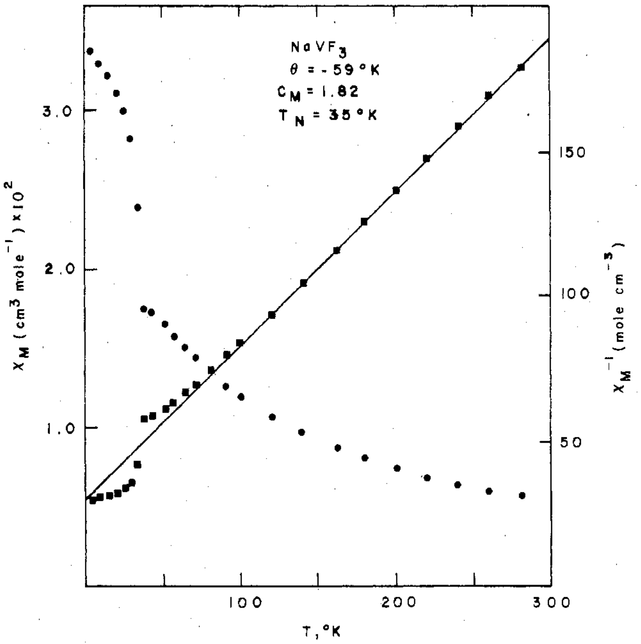

Figure 1. Molar magnetic susceptibility and inverse susceptibility vs. temperature of $NaVF_3$.

Discussion

The mechanism by which V(II) was converted to V(III) apparently included reactions of vapor phases with the solid container material. The extent to which disproportionation occurred was demonstrated to be less in Mo than in Pt. Since V metal was not found as a product, it was concluded that V(0) alloyed with the container material. This conclusion is supported by the V–Pt phase system,[20] which contains several intermetallic compounds including VPt_3, and the V–Mo phase diagram,[20] which shows a continous region of solid solutions all of which are stable at the temperatures in question. The relative amounts of these disproportionation products then can be explained quite satisfactorily by the following equations:

$$11NaF + 11VF_2 \rightarrow Na_2V_2F_7 + 3Na_3VF_6 + 4VF_2 + 2V(0)$$

$$4KF + 4VF_2 \rightarrow KV_2F_6 + K_3VF_6 + V(0)$$

$$4RbF + 4VF_2 \rightarrow RbV_2F_6 + Rb_3VF_6 + V(0)$$

Whereas the AVF_3 compounds are formed very slowly by solid state reaction, the mixed valence compounds form more easily from the solid state or the melt. A useful property in identifying the different valence states of vanadium fluorides is their transmitted colors. It was observed that the divalent vanadium fluorides are blue, mixed valence phases are red, and trivalent compounds are green without exceptions.

The magnetic properties of $NaVF_3$ are qualitatively close

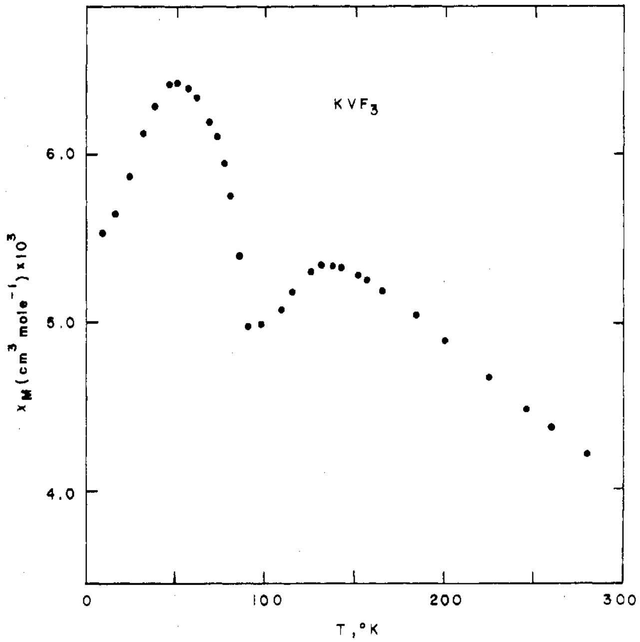

Figure 2. Molar magnetic susceptibility vs. temperature of KVF_3.

to those of VF_2 as reported by Stout and Lau.[21] Above 120 K, the powder susceptibilities of both compounds display paramagnetic behavior typical of spin only systems. Curie constants are in agreement with the theoretical value 1.82 cm^3 mol^{-1} deg calculated from $g = 1.97$ and $S = {}^3/_2$. Furthermore, the Θ values of $NaVF_3$ and VF_2 of (–)59 K and (–)85 K, respectively, are of the same magnitude. In both compounds, there is evidence that short-range magnetic ordering commences above 100 K. The shape of χ_M^{-1} vs. T of $NaVF_3$, as seen in Figure 1, is typical of a canted antiferromagnetic material. Other materials which display this phenomena include $NaNiF_3$[22] and VF_3.[2]

The χ_M vs. T plot of KVF_3 shown in Figure 2 has two maxima, one near 50 K and a second near 130 K. These maxima, conbined with an apparent large negative Θ value, suggest some type of antiferromagnetic ordering. Above 220 K, KVF_3 appears to display paramagnetic behavior. However, values of C_M and Θ obtained from χ_M^{-1} in the temperature region 220 to 300 K are disturbingly different from those of $NaVF_3$ and VF_2, which raises some doubt that it is truly a paramagnetic region. Further investigation of KVF_3 is in progress, as the evidence available at this time is insufficient to explain these phenomena.

Magnetic susceptibility measurements on $NaVF_3$ and KVF_3 as reported by Shafer[14] and Cros et. al.[15] are significantly different from those obtained in this laboratory. Shafer detected no long-range magnetic ordering in $NaVF_3$ or KVF_3 above 4.2 K. The materials reported allegedly contained trivalent vanadium fluoride impurities. Cros et al. observed a minimum near 45 K in χ_M^{-1} vs. T of $NaVF_3$, whereas the measurements in this laboratory indicated no minimum but instead a sharp decrease near 35 K in this plot. Data from both laboratories are in agreement that χ_M of KVF_3 goes through a maximum near 130 K. The second maximum near 50 K was not reported by Cros et al.; however, close examination of their plot of χ_M^{-1} vs. T suggests that this anomaly is also present in their material even though it is not clearly resolved. The reason for these differences is not certain as the conditions of their synthesis were not duplicated in this laboratory. It was observed, however, that divalent vanadium fluorides prepared in Pt or Mo were always contaminated with trivalent and mixed valence phases.

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Registry No. $NaVF_3$, 27498-33-5; KVF_3, 27498-34-6; $RbVF_3$, 12449-46-6.

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