compared both to experimental structures and to those obtained at the STO-3G level. In all but two cases (SeH_2 and HBr) calculated STO-2G bond lengths are shorter than the corresponding STO-3G values; in every example considered, except SeH_2, are the STO-3G bond distances closer to experimental values. The most significant shortenings are for the GeF and GeH linkages in fluorogermane, reduced by 0.033 and 0.028 Å from their respective STO-3G values. Equally disturbing in the tabulated data are the calculated bond angles for SeH_2 and AsH_3, both of which are considerably larger than both the STO-3G and experimental values.

Conclusion

STO-3G minimal basis sets for the main group elements of the third row have been developed in a manner analogous to that employed for first- and second-row representations. Application of these basis sets to the calculation of the equilibrium structures of one and two heavy-atom molecules has been explored. Overall, the agreement between calculated (STO-3G) and experimental equilibrium structures is remarkable in view of the simplicity of the theoretical model. It suggests the utility of the method as a generally applicable means of structure determination for compounds involving main-group third-row elements.

Registry No. K, 7440-09-7; Ca, 7440-70-2; Ga, 7440-55-3; Ge, 7440-56-4; As, 7440-38-2; Se, 7782-49-2; Br, 10097-32-2; Kr, 7439-90-9; KH, 7693-26-7; KOH, 1310-58-3; KF, 7789-23-3; CaH_2, 7789-78-8; CaF_2, 7789-75-5; GaH_3, 13572-93-5; GaF_3, 7783-51-9; GeH_4, 7782-65-2; CH_3GeH_3, 1449-65-6; GeH_3F, 13537-30-9; CH_3AsH_2, 593-52-2; AsH_3, 7784-42-1; AsF_3, 7784-35-2; COSe, 1603-84-5; CH_3SeH, 6486-05-1; H_2Se, 7783-07-5; CH_3Br, 74-83-9; Br_2, 7726-95-6; KCN, 151-50-8; H_3GeCN, 1863-70-3; H_3GeCl, 13637-65-5; H_3GeGeH_3, 13818-89-8; H_3GeBr, 13569-43-2; LiBr, 7550-35-8; BrF, 13863-59-7; H_3SiBr, 13465-73-1; HBr, 10035-10-6.

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Lower Valence Fluorides of Vanadium. 5. Dependence of Structure and Magnetic Properties of Tetragonal K_xVF_3 on Composition

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Received December 28, 1979

Ten samples of tetragonal tungsten bronze like K_xVF_3 of evenly spaced compositions between $x = 0.45$ and 0.56 were prepared and studied. Guinier–Hägg X-ray data showed an approximately linear dependence of sublattice dimensions on composition with $a = 12.190 + 0.815x$ and $c = 3.735 + 0.411x$. An orthorhombic superlattice was found to be independent of composition with dimensions $a(\text{super}) = 2^{3/2}a(\text{sub})$, $b(\text{super}) = 2^{1/2}a(\text{sub})$, and $c(\text{super}) = 2c(\text{sub})$. Magnetic measurements revealed K_xVF_3 to be ferrimagnetic (low x) and to change abruptly at $x = 0.49$ to antiferromagnetic (high x). The spontaneous moment of the ferrimagnetic phase depends on the field in which the sample is cooled. At large fields (10–12 kG) these moments approach the theoretical value $\sigma = x[g(V^{2+})S(V^{2+}) - g(V^{3+})S(V^{3+})]$. The vanadium ions occupy two lattice sites, 8j and 2c, in the tungsten bronze structure ($P4/mbm$), and the ferrimagnetic–antiferromagnetic behavior is explained by two mechanisms. In the ferrimagnetic phase, the mechanism for long-range order between vanadium ions on 8j sites does not include vanadium ions on 2c sites. In the antiferromagnetic phase, the vanadium ions on 2c sites are included in the ordering mechanism.

Introduction

The tetragonal system K_xVF_3 ($x = 0.45$–0.56) was reported to be a fluoride analogue of tetragonal tungsten bronze K_xWO_3, space group $P4/mbm$.[1-3] A superstructure was reported for K_xVF_3 in which the a dimension was increased by $2^{3/2}$ and the c dimension by 2.[1] Below the magnetic ordering temperature (~50 K) K_xVF_3 displays a strong ferrimagnetic moment at $x = 0.45$[1,4] and almost ideal antiferromagnetic behavior at $x = 0.56$.[1]

A ferrimagnet is defined as a substance in which two kinds of ions with magnetic moments of different magnitude are located on two distinct sublattices such that below the long-range magnetic ordering temperature the two moments are opposed, giving rise to a resultant spontaneous moment. This moment per magnetic ion can be expressed in Bohr magnetons as

$$\sigma = \tfrac{1}{2}[g(A)S(A) - g(B)S(B)]$$

where $g(A)$, $g(B)$, $S(A)$, and $S(B)$ are the Lande splitting factors and spin quantum numbers of ions A and B, respectively. A prerequisite for the two-sublattice model is that the two kinds of magnetic ions exist in an ordered arrangement. Consequently, a more detailed study of the spontaneous moments of K_xVF_3 should reveal important structural information. Toward this end, ten samples, designated as the "B" series, spanning the composition range $x = 0.450$–0.5625, were characterized and studied.

Experimental Section

The K_xVF_3 compounds were prepared by solid-state reactions as described previously for preparation of the "A" series.[1] In this work, the compounds are designated "B" series and were prepared in 1.91-cm diameter by 3.18-cm length molybdenum containers. Vacuum encapsulation was done by electron-beam welding at the University of Mississippi. Products were analyzed optically by stereoscopic and polarized microscopy. Chemical analyses were performed by Galbraith Laboratories. Vanadium was determined volumetrically, fluorine by specific ion electrode, and potassium by atomic absorption. Samples were characterized by Guinier–Hägg X-ray techniques using Cu Kα_1 and Cr Kα_1 radiations. Magnetic measurements were made from 4.2 to 300 K between 0.14 and 12 kG by using a Foner type PAR vibrating-sample magnetometer equipped with a Janis liquid helium Dewar, gallium arsenide temperature controller, and copper–constantan thermocouples. Magnetic fields were measured with a F. W. Bell hall-probe gaussmeter, Model 8860. Magnetic data were corrected for core diamagnetism, and an additional temperature-independent orbital paramagnetic correction of 6×10^{-4} cm^3 mol^{-1} was made for the V^{3+} ion.

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Table I. Chemical Analysis of K_xVF_3 Compounds

sample designatn	element	% calcd	% found	exptl formula	theoret formula
B-K450VF3	K	14.02	14.43	$K_{0.467}VF_{3.01}$	$K_{0.45}VF_3$
	V	40.58	40.25		
	F	45.40	45.11		
B-K4625VF3	K	14.35	14.56	$K_{0.469}VF_{2.98}$	$K_{0.4625}VF_3$
	V	40.42	40.47		
	F	45.23	44.83		
B-K475VF3	K	14.68	14.53	$K_{0.471}VF_{3.03}$	$K_{0.475}VF_3$
	V	40.27	40.19		
	F	45.05	45.37		
B-K4875VF3	K	15.01	15.24	$K_{0.493}VF_{2.97}$	$K_{0.4875}VF_3$
	V	40.11	40.29		
	F	44.88	44.55		
B-K500VF3	K	15.34	15.59	$K_{0.511}VF_{3.00}$	$K_{0.50}VF_3$
	V	39.96	39.72		
	F	44.71	44.47		
B-K5125VF3	K	15.66	15.85	$K_{0.518}VF_{2.98}$	$K_{0.5125}VF_3$
	V	39.81	39.83		
	F	44.54	44.24		
B-K525VF3	K	15.98	16.08	$K_{0.527}VF_{3.01}$	$K_{0.525}VF_3$
	V	39.65	39.74		
	F	44.37	44.56		
B-K5375VF3	K	16.30	16.34	$K_{0.537}VF_{2.97}$	$K_{0.5375}VF_3$
	V	39.50	39.65		
	F	44.20	43.93		
B-K550VF3	K	16.61	16.85	$K_{0.537}VF_{2.98}$	$K_{0.55}VF_3$
	V	39.35	39.40		
	F	44.03	43.84		
B-K5625VF3	K	16.93	17.05	$K_{0.565}VF_{2.98}$	$K_{0.5625}VF_3$
	V	39.21	39.33		
	F	43.87	43 74		

Results

Every K_xVF_3 sample appeared homogeneous and single-phased except for B-K450VF3 which contained a small amount of the pseudohexagonal phase $K_{0.27}VF_3$. This pseudohexagonal phase was removed by Pasteur's method before chemical analysis, X-ray diffraction, and magnetic susceptibility measurements were made. Chemical analyses of the ten K_xVF_3 samples are shown in Table I. In every case, the analyzed values correspond to the nominal values within experimental error. The samples will be referred to by their nominal values to avoid confusion in the text.

X-ray Diffraction. Guinier–Hägg X-ray data were fitted to a tetragonal unit cell of approximately the same dimensions as those of K_xWO_3.[5] Weak superlattice reflections which did not fit this unit cell were all fitted to an orthorhombic superlattice unit cell with dimensions $a(\text{super}) = 2^{3/2}a(\text{sub})$, $b(\text{super}) = 2^{1/2}a(\text{sub})$, and $c(\text{super}) = 2c(\text{sub})$. These superlattice reflections were indexed as (261), (143), (4,13,1), (253), (563), (5,10,3), and (2,14,3) and were observed at every composition with no apparent changes in intensity. A summary of the sublattice unit cell dimensions is given in Table II.

Magnetic Susceptibilities. The magnetic susceptibilities of $K_{0.450}VF_3$, $K_{0.4625}VF_3$, $K_{0.475}VF_3$, and $K_{0.4875}VF_3$ vs. temperature at 10 kG are shown in Figure 1. Spontaneous magnetic moments of the first three are large and were found to depend upon the field under which the sample was cooled. $K_{0.450}VF_3$ was cooled from room temperature to 4.2 K in a field of 0.14 kG to demonstrate this effect. The field was then increased to 10 kG and the moment measured at successively lower field strengths. The sample was then warmed to room temperature and cooled to 4.2 K in a field of 5 kG. Again, the field was increased to 10 kG and the moment measured at successively lower field strengths. The experiment was repeated by cooling in fields of 10, 12, and again 0.14 kG. These results are shown in Figure 2. The higher the field in which the sample was cooled, the greater the remanent moment. A hysteresis effect was observed in the final cooling in a 0.14 kG field (dashed line). This effect can be explained as an orientation of the crystallite moments with the field as a consequence of successive warming and cooling. The moments of $K_{0.450}VF_3$, $K_{0.4625}VF_3$, $K_{0.475}VF_3$, and $K_{0.4875}VF_3$ extrapolated to zero field vs. temperature, obtained by cooling in a 10-kG field only, are shown in Figure 3.

Table II. Summary of Lattice Constants for Tetragonal K_xVF_3 (Å; ±0.05%)

K_xVF_3	Cu data	Cr data
B-K4500VF3	12.611	12.611
	3.921	3.920
B-K4625VF3	12.623	12.617
	3.924	3.925
B-K4750VF3	12.636	12.633
	3.930	3.930
B-K4875VF3	12.643	12.640
	3.937	3.937
B-K5000VF3	12.657	12.654
	3.942	3.943
B-K5125VF3	12.668	12.663
	3.947	3.947
B-K5250VF3	12.677	12.673
	3.951	3.952
B-K5375VF3	12.680	12.674
	3.954	3.954
B-K5500VF3	12.698	12.693
	3.961	3.964
B-K5625VF3	12.707	12.701
	3.965	3.968

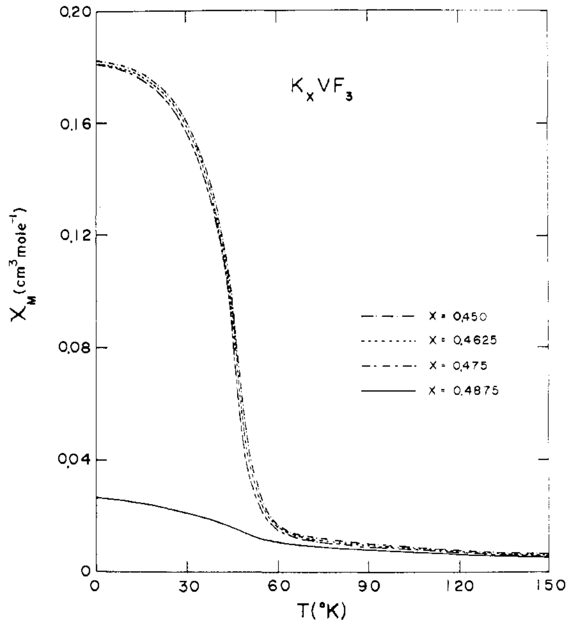

Figure 1. Magnetic susceptibilities of $K_{0.450}VF_3$, $K_{0.4625}VF_3$, $K_{0.475}VF_3$, and $K_{0.4875}VF_3$ vs. T at 10 kG.

Magnetic susceptibilities of $K_{0.500}VF_3$, $K_{0.5125}VF_3$, $K_{0.525}VF_3$, $K_{0.5375}VF_3$, $K_{0.550}VF_3$, and $K_{0.5625}VF_3$ vs. temperature are shown in Figure 4. The Néel temperature for each of these samples is seen as a sharp maximum near 45 K. Each of these samples displayed a very small spontaneous moment (<0.01 μ_B). A summary of the magnetic constants is shown in Table III.

Discussion

There must first be an ordered arrangement of the two ions having different magnetic moments in order for a crystal to be ferrimagnetic. In the tetragonal bronze structure, the heavy-metal ions occupy 8j and 2c sites. First, consider the possibility of ordered V^{2+} and V^{3+} ions on the 8j sites such

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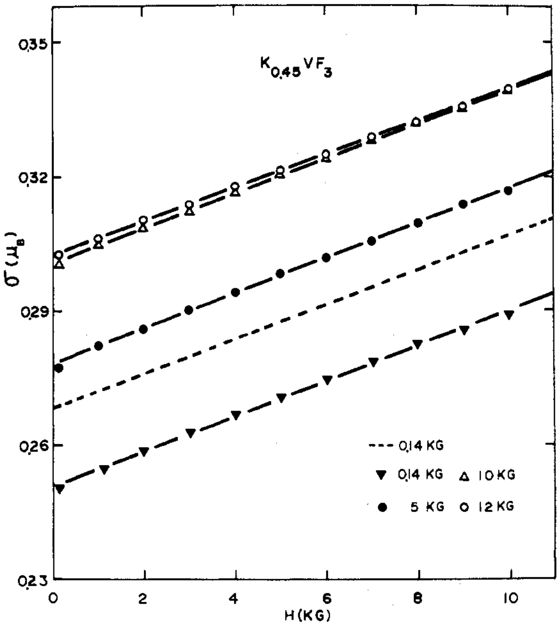

Figure 2. Magnetic moments of $K_{0.450}VF_3$ vs. magnetic field for samples cooled to 4.2 K in different magnetic fields.

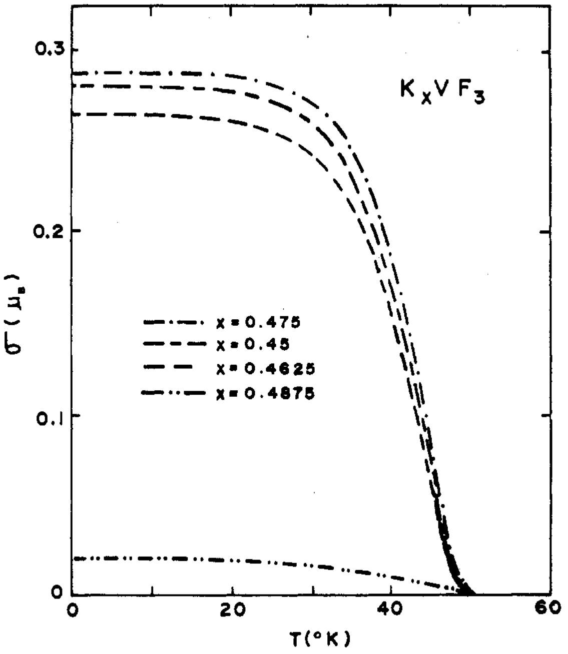

Figure 3. Spontaneous magnetic moments of $K_{0.450}VF_3$, $K_{0.4625}VF_3$, $K_{0.475}VF_3$, and $K_{0.4875}VF_3$ vs. temperature for samples cooled in 10-kG field.

Table III. Summary of Magnetic Constants for Tetragonal K_xVF_3 System

K_xVF_3	C_M, cm^3 mol^{-1} deg	Θ, K	T_N, K	σ, μ_B
B-K4500VF3	1.26	−55	50	0.28
B-K4625VF3	1.34	−63	50	0.26
B-K4750VF3	1.42	−72	50	0.29
B-K4875VF3	1.47	−95	50	0.020
B-K5000VF3	1.47	−96	45	0.003
B-K5125VF3	1.45	−88	45	0.002
B-K5250VF3	1.47	−66	45	0.008
B-K5375VF3	1.49	−79	45	0.002
B-K5500VF3	1.47	−79	45	0.002
B-K5625VF3	1.49	−79	45	0.002

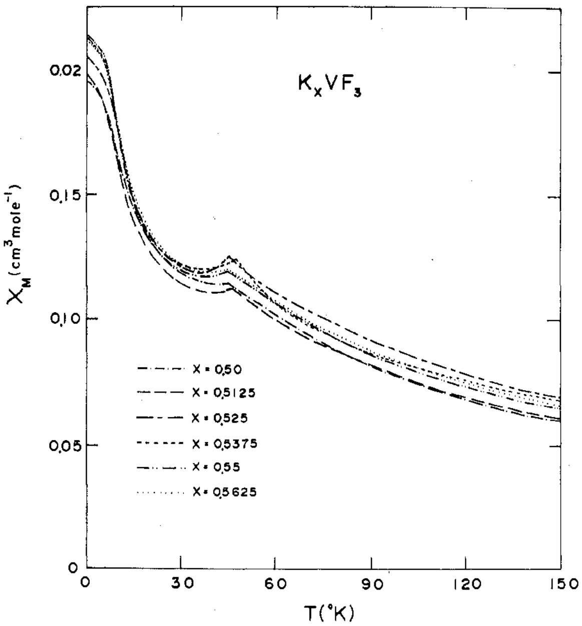

Figure 4. Magnetic susceptibilities of $K_{0.500}VF_3$, $K_{0.5125}VF_3$, $K_{0.525}VF_3$, $K_{0.5375}VF_3$, $K_{0.550}VF_3$, and $K_{0.5625}VF_3$ vs. T at 10 kG.

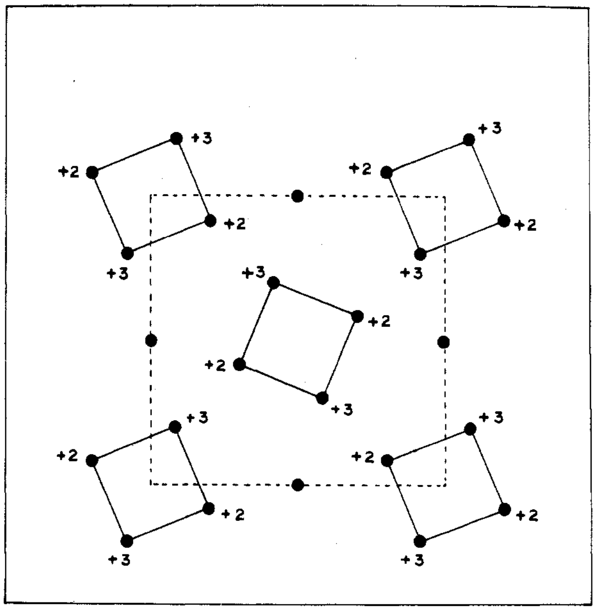

Figure 5. Ordering of V^{2+} and V^{3+} ions on 8j sites of K_xVF_3.

that all nearest neighbors of a V^{2+} ion are V^{3+} ions, and vice versa, as shown in Figure 5. In this figure, the 8j sites are illustrated as belonging to squares on the corners and in the center of the unit cell, and the 2c sites are located in the centers of the unit cell edges. This ordering would extend to vanadium ions located on 8j sites in the layers directly above and below the layer shown in Figure 5. We then speculate what would happen at the theoretical extremes of compositions $x = 0.40$ and $x = 0.60$. In the former, all 2c sites would be completely occupied by V^{3+} ions, but in the latter by V^{2+} ions. From all previous magnetic information, the magnetic interactions between vanadium ions through intermediate fluoride ions should be antiferromagnetic. One could surmise that below the magnetic ordering temperature this would give rise to magnetically ordered square columns in which all V^{2+} ions would be parallel to each other but antiparallel to V^{3+} ions. These square columns, therefore, would have a resultant magnetic moment per vanadium ion

$$\sigma = \tfrac{1}{2}[g(V^{2+})S(V^{2+}) - g(V^{3+})S(V^{3+})]$$

Since it is reasonable to assume the orbital contribution is

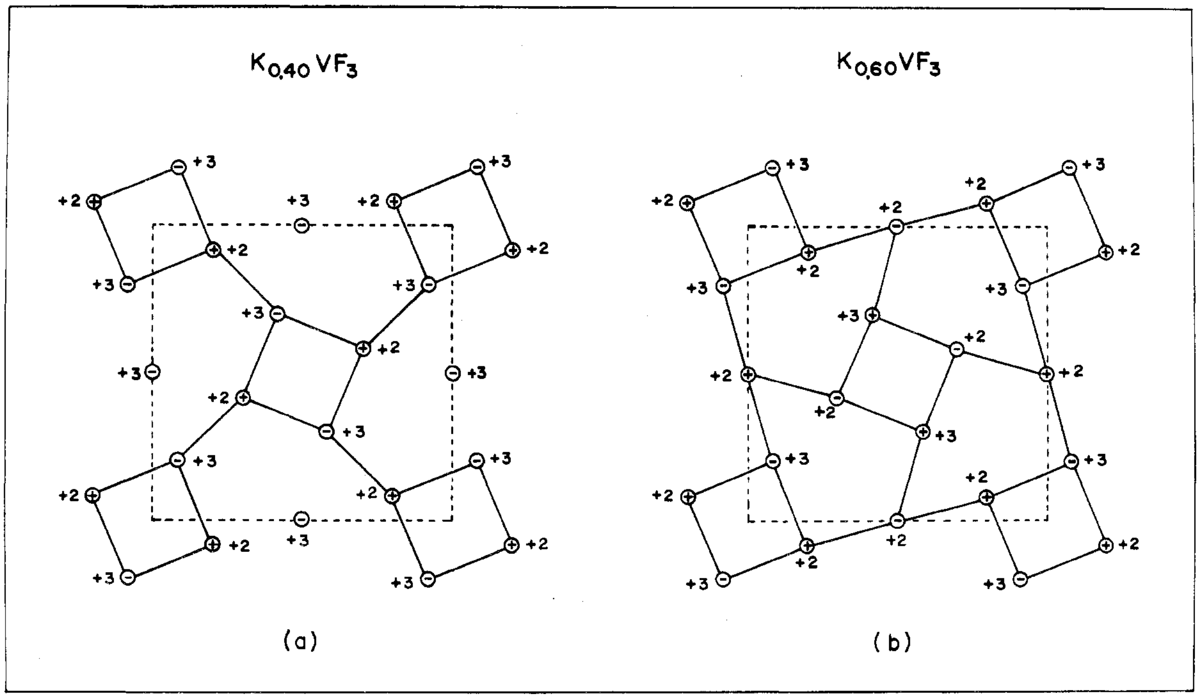

Figure 6. Magnetic ordering mechanisms for (a) $K_{0.40}VF_3$ and (b) $K_{0.60}VF_3$.

quenched in the magnetically ordered state, the best estimates of $g(V^{2+})$ and $g(V^{3+})$ would be 2.00. The values $gS(V^{2+})$ and $S(V^{3+})$ are $^3/_2$ and 1, respectively. In the case of $K_{0.40}VF_3$, one could speculate that the V^{3+} ions on the 2c sites would have weak magnetic interactions and, hence, would not take part in the ordering mechanism. In this case, as shown in Figure 6a, ordering between corner and center columns would be direct, and the overall ordered structure of 8j ions would be ferrimagnetic. For $K_{0.60}VF_3$, the V^{2+} ions on the 2c sites, providing relatively strong magnetic interactions, would be involved in the ordering mechanism, and the magnetic moments of the corner columns would be antiparallel to those of the center columns as shown in Figure 6b. This would give a magnetic structure which is antiferromagnetic overall, including vanadium ions on both 8j and 2c sites.

In the actual case, the limits of x do not extend from 0.40 to 0.60, but from 0.45 to 0.56. One would expect the compositions between 0.40 and 0.60 to show ferrimagnetic behavior for lower values of x and antiferromagnetic behavior above some critical composition. In the ferrimagnetic case, some of the 2c sites would be occupied by V^{2+} ions which would not be part of the long-range ordering mechanism of the 8j vanadium ions. In the absence of an external field, one would expect these V^{2+} ions to lie antiparallel or randomly parallel and antiparallel to the V^{2+} ions on 8j sites. Above some critical field they could be forced to lie parallel to the V^{2+} ions on 8j sites, adding an additional contribution to the total spontaneous moment of the crystal. In this case (providing x is less than 0.50), the predicted moment would be

$$\sigma = x[g(V^{2+})S(V^{2+}) - g(V^{3+})S(V^{3+})] \qquad \sigma = x$$

or for a randomly ordered powder sample

$$\bar{\sigma} = x/\sqrt{3}$$

The experimental spontaneous moments generated by the K_xVF_3 series cooled to 4.2 K in a 10-kG field are shown in Figure 7. The samples $K_{0.450}VF_3$, $K_{0.4625}VF_3$, and $K_{0.475}VF_3$ are ferrimagnetic with values reasonably close to the theoretical ones (dashed line). The higher values of x display antiferromagnetic behavior, which is also consistent with the model.

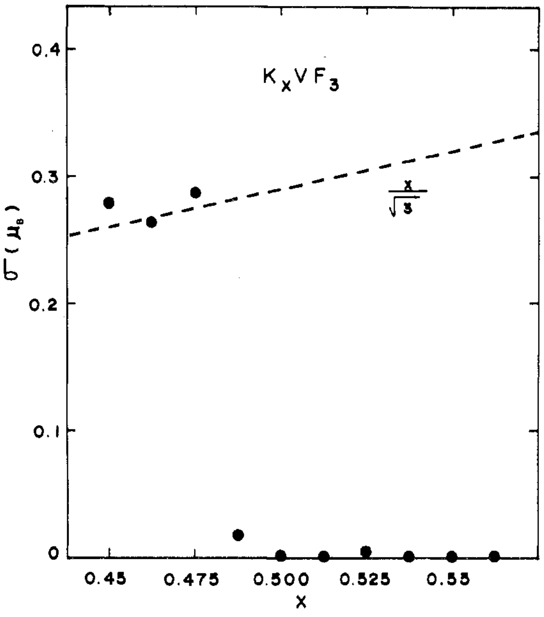

Figure 7. Spontaneous moments of K_xVF_3 extrapolated to zero field and 0 K vs. composition.

Guinier–Hägg X-ray data of this system revealed the lattice dimensions vary approximately linearly with composition (nominal values). The Cr $K\alpha_1$ and Cu $K\alpha_1$ data gave the equations

$$a = 12.244 + 0.819x \qquad c = 3.735 + 0.411x$$

The orthorhombic superlattice structure, with dimensions

$$a(\text{super}) = 2^{3/2}a(\text{sub}) \qquad b(\text{super}) = 2^{1/2}a(\text{sub})$$
$$c(\text{super}) = 2c(\text{sub})$$

was observed in every sample. It is significant that this structure is not composition dependent. In view of the magnetic results, one could conclude the superstructure is associated with ordering of V^{2+}–V^{3+} ions on 8j sites. The modulations, however, may involve a cooperative Jahn–Teller effect of the V^{3+} ions. Such effects have been reported for $PbCu(NO_2)_6$ and other Cu^{2+} compounds.[6]

Acknowledgment. The authors gratefully acknowledge the National Science Foundation (Grants DMR 79-00313, DMR 76-83360, and DMR 74-711970) for financial support, including the purchase of major equipment, and the University of Mississippi for the purchase of equipment and other support. They also thank NASA Langley Research Center for the loan of an electromagnet and power supply. Appreciation is expressed to the University of Mississippi Computer Center for providing data reduction time.

Registry No. Potassium vanadium fluoride, 55957-20-5.

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Solvent Dependence of the Circularly Polarized Luminescence of the Terbium(III) Chelate of 3-Acetyl-*d*-camphor

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Received February 29, 1980

The circularly polarized luminescence (CPL) spectra of $Tb(atc)_3$ have been obtained in 18 different amine solvents. Different CPL line shapes were obtained, which was interpreted to imply that certain diastereomers were preferred at the expense of others. It is proposed that the formation of a chelate adduct forces the chiral β-diketone ligands to interact and that they do so in a stereoselective fashion. The steric nature of the alkyl side chains of the amines was found to influence the degree of CPL observed and also determined the sign of the observed optical activity.

Introduction

The direct determination of enantiomeric compositions using optically active lanthanide shift reagents has been well documented,[1,2] with the Eu(III) and Pr(III) β-diketone complexes derived from *d*-camphor having received the widest actual use. These ligands are prepared from 3-bromo-*d*-camphor, and the absolute configuration of this material is well-known.[3] The most common ligands used have R = CF_3 (3-trifluoroacetyl-*d*-camphor or facam) or R = C_3F_7 (3-heptafluoropropylhydroxymethylene-*d*-camphor or hfpc). The most successful use of these shift reagents in NMR spectroscopy requires a complete knowledge of their solution bonding and steric requirements, and in addition one also needs to know about solution stereochemistries in order to perform meaningful theoretical calculations. In this laboratory, we have been quite interested in this problem and have determined binding ratios and formation constants for the complexes formed when $Eu(facam)_3$ and $Eu(hfpc)_3$ are titrated with simple alkylamines.[4]

While crystal-structure determinations of chiral shift reagent–substrate complexes yield maximum information,[5] important information can be gathered by employing chiroptical methods such as circular dichroism (CD). Unfortunately, CD of lanthanide complexes is difficult to obtain except at very high concentrations of complex due to the very low molar absorptivities of the lanthanide f–f transitions and hence has not been widely used. However, several of the lanthanide ions are known to emit in fluid solution at room temperature, and it is thus possible to record the circularly polarized luminescence (CPL) spectrum of these complexes. The theory of the CPL effect has been described by Riehl and Richardson.[6]

The CPL of $Eu(facam)_3$ and $Eu(hfpc)_3$ has been reported in a variety of chiral and achiral solvents,[7] where it was found that the strongest CPL was obtained when $Eu(facam)_3$ was dissolved in dimethyl sulfoxide. It was also found that CPL was only obtained for this chelate in 7 out of 28 neat solvents.[7a] That CPL should be observed at all is rather striking, since it is known that tris chelates of chiral β-diketonates are capable of existing in a total of four diastereomers and that when one starts with an equal mixture of all four isomers, no net CD is obtained.[8] Our previous work with $Eu(facam)_3$ and $Eu(hfpc)_3$ indicated that two molecules of alkylamine could be bound by each chelate but that they did so in a cooperative manner.[4] This observation was interpreted to imply that some sort of reorganization of the β-diketone ligands took place upon binding, and we used this conclusion to infer that when CPL was obtained in the Eu(III) chelates the geometry change was of a stereoselective type.[4]

In the present work, the CPL spectra are reported for a new chiral lanthanide β-diketone complex in a variety of solvents. The chelate, $Tb(atc)_3$ (atc = 3-acetyl-*d*-camphor, where R = CH_3), differs in its behavior from that of $Eu(facam)_3$ in that CPL was observed in every solvent used. A definite stereoselective behavior was found, however, and CPL of different line shape could be obtained by varying the steric nature of the solvent. The previous work involving luminescence titrations[4] indicated that "pockets" exist on the lanthanide ion coordination sphere and that the steric nature of the complexed substrates governs the extent of interaction. The present work demonstrates that in these labile complexes, the steric nature

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