



Alkali-metal peroxychromates: Cr(V)-based antiferromagnets with low-dimensional spin exchange and high specific heats

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Abstract

The Cr(V) based alkali-metal peroxychromates with the general formula M_3CrO_8 ($M = Li, Na, K, Rb, Cs$) are found to exhibit a variety of interesting thermodynamic and magnetic properties. These include: (a) simple molecular structures and single-ion ground states ($3d^1$) which depend sensitively on a specific cation as well as combinations of the cations in a solid solution (mixed crystals); (b) low dimensionality of the magnetic interactions that lead to a variety of phase transitions depending on the cation; (c) high specific heats throughout the liquid helium temperature range; and (d) possibility of tuning the thermodynamic properties via dilution with compatible lattices such as M_3NbO_8 . We envisage possible applications of these compounds as model systems for the theoretical studies of magnetic chains as well as heat sinks and refrigerants in the mK–4 K range. © 1999 Elsevier Science Ltd. All rights reserved.

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This communication reports on an improved crystal growth procedure and interesting new electronic and magnetic properties of alkali metal (M) peroxychromates, M_3CrO_8 . The motivation for this undertaking was manifold. First, these compounds contain Cr(V), $3d^1$ ions, and relatively little is known about the ferromagnetic or antiferromagnetic behavior of Cr(V)-based compounds [1,2]. Second, it was anticipated that the metal–dioxygen bonding could lead to structural and magnetic cooperative phenomena, significant entropy changes and magnetic phase transitions at low temperatures. Third, the $S = 1/2$, $I = 0$ electronic structure of the main $^{50,52,54}Cr$ isotopes (90.5% natural abundance) results in these compounds being amongst the simplest of magnetic entities, and in conjunction with diamagnetic dilution, they could serve as good model systems for theoretical investigations. As reported

below, indeed the peroxychromates appear to constitute a new class of materials with many interesting structural and thermodynamic properties.

The peroxychromates were synthesized by modification of the method of Riesenfeld [3]. In general, the synthesis procedure involves the reduction of Cr(VI) by H_2O_2 in the appropriate base or mixture of bases at temperatures of $5^\circ C$. A significant finding was that good quality crystals are obtainable only by crystallization around room temperature. Earlier reports [3,4] had mentioned lower temperatures around $-15^\circ C$, which we found suitable for the synthesis, but not for good quality crystals which were crucial for this study. Growth by slow evaporation at $\sim 5^\circ C$ produced dark red parallelepiped shaped crystals of typical $1 \times 1 \times 3 \text{ mm}^3$ size. Sample characterization was done by X-ray diffraction on K_3CrO_8 [5], K_2NaCrO_8 [6] and Rb_3CrO_8 [7], and by elemental analysis, EPR and magnetic susceptibility (χ) on all others. Specific heat was measured for K_3CrO_8 using a homemade adiabatic calorimeter over a range of

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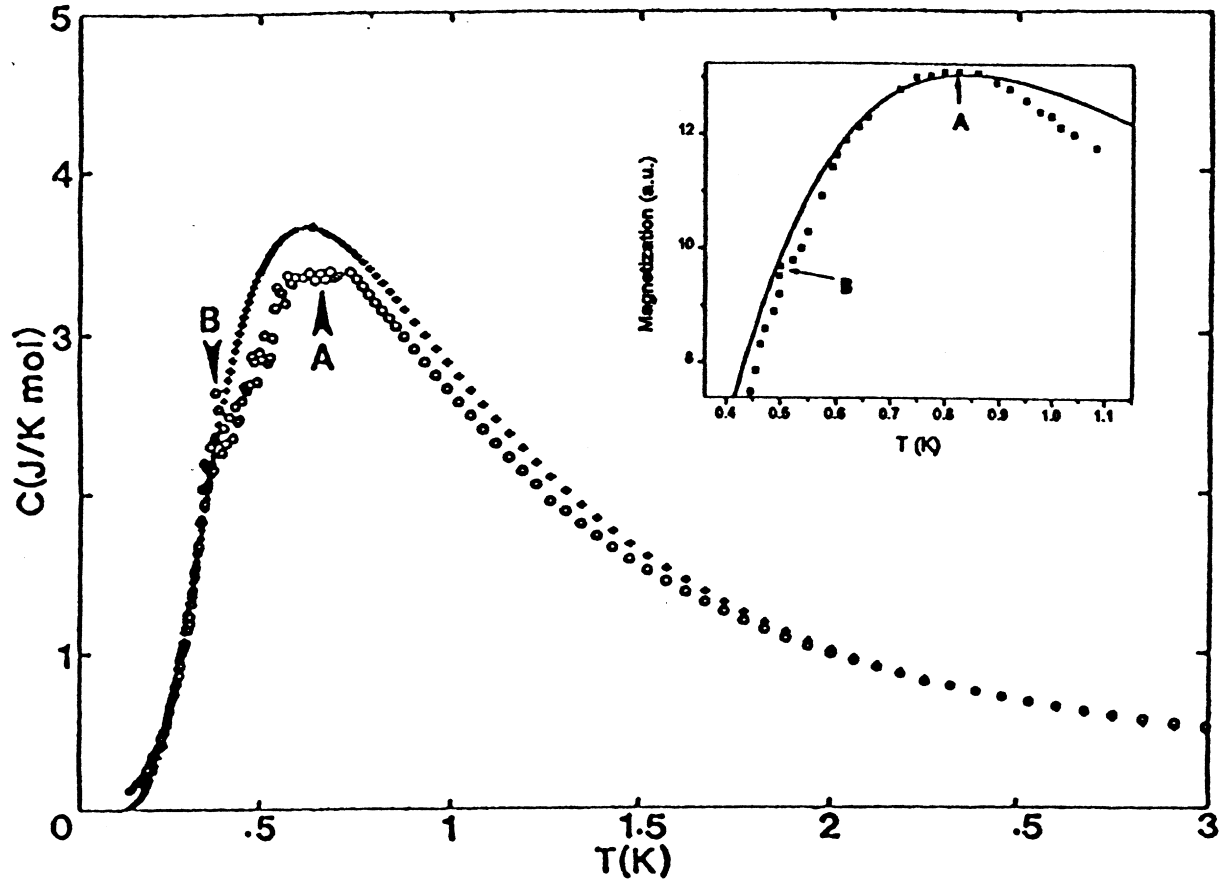


Fig. 1. Specific heat of K_3CrO_8 . Hollow circles are experimental data, (\blacklozenge) symbols are the fit using Eq. (1). Inset is the magnetization data. Squares are the experimental data; solid line is the fit using Eq. (2).

Table 1
Magnetic parameters of the peroxychromates

Compound	T_{\max} (K) ^a	θ (K)	C (emu K/g)·10 ^{−3}	J (K)	g_{\parallel}	g_{\perp}	b (J K)/mol
Li ₃ CrO ₈	—	−0.27	0.8765	−0.13	1.9532	1.9826	—
Na ₃ CrO ₈	3.7	−5.36	1.4337	−2.68	1.9491	1.9839	241
K ₃ CrO ₈	0.85	−2.7	1.2042	−1.35	1.9428	1.9851	4.2
Rb ₃ CrO ₈	0.52	−1.57	0.8036	−0.78	1.9418	1.9817	2.7 ^b
Cs ₃ CrO ₈	—	−0.17	0.4509	−0.08	1.9577	1.9723	0.049 ^b
K ₂ NaCrO ₈	2.5	−2.32	1.2066	−1.16	1.9853	1.9709	—

^a T_{\max} refers to the temperature of the maximum in the susceptibility curve.

^b Estimated from susceptibility data.

0.15–3 K at Carnegie Mellon University. χ was measured at Massachusetts Institute of Technology using a SHE corporation SQUID magnetometer over 1.60–100 K and a homemade a.c. susceptometer and a dilution refrigerator in the 300 mK–1.2 K range. EPR measurements were made at X-band (~9.5 GHz) using a Bruker ER-200D spectrometer (West Virginia University) and a homemade W-band (95 GHz) system (Florida State University).

We have investigated all the salts with the general formula $M_3\text{CrO}_8$, with $M = \text{Li, Na, K, Rb, Cs}$ and combinations thereof. Since early work [4] has concentrated on K_3CrO_8 , and also the data are representative of the other peroxychromates, we present the data for K_3CrO_8 . Fig. 1 shows the temperature dependence of the specific heat of K_3CrO_8 down to 0.15 K. Two transitions are discernable. The broad peak, whose maximum (0.60 K) is labeled 'A', is attributed to a Schottky-type anomaly [8]. This is a result of short range nearest neighbor spin–spin interactions. These interactions result in a splitting of energy levels,

with thermally accessible excited states. For a simple two-state system separated by an energy δ , the magnetic specific heat capacity C can be described by Ref. [8]:

$$C = R(\delta/kT)^2 \exp(\delta/kT)/(1 + \exp(\delta/kT))^2 \quad (1)$$

(where k is Boltzmann's constant, R the molar gas constant, and T the temperature). Eq. (1) describes a curve that is characterized by a maximum at $T_{\max} \cong 0.4\delta/k$. The curve indicated by the symbol (◆) in Fig. 1 is the fit using Eq. (1) with $\delta/k = -1.5$ K. The small sharp peak, labeled 'B' at 0.38 K, is postulated to result from long range antiferromagnetic three-dimensional (3D) ordering, as outlined below.

χ measurements (Fig. 1 inset) yielded a broad peak (A) at 0.85 K and a small but clear bump (B) at 0.52 K. The solid line is a normalized fit using a short range nearest-neighbor spin exchange model [8], Eq. (2), where $2J = -1.35$ K:

$$\chi = (1/T)[1 + 0.33(\exp(-2J/kT))]^{-1} \quad (2)$$

The magnetization plot agrees with the heat capacity data, therefore, the origin of the majority of entropy in the heat capacity (Fig. 1) is magnetic and predominately short range in nature. We can thus assign peak A to a short range (intra-chain) ordering and peak B to a 3D antiferromagnetic ordering, with a Neel temperature of 0.38 K (corresponding to peak B in the heat capacity). The magnetic susceptibilities of Li_3CrO_8 , K_2NaCrO_8 , Na_3CrO_8 , Rb_3CrO_8 , and Cs_3CrO_8 were also obtained. The Curie constants, Curie–Weiss temperatures (θ_s), and J_s were calculated as usual [4,8] and are presented in Table 1. The negative values of θ obtained for all systems imply the peroxychromates are antiferromagnets.

A particularly interesting result from Table 1 is the relationship of T_{\max} and J , to the cation¹ radius (r): both scale as r^{-1} . In contrast, the superexchange interaction [9] of the metal fluorides has been shown to have an r^{-12} (where r is the metal–metal radius) dependence. Since J can be manipulated by varying the counterions of the peroxychromates,

¹ Crystal structure data of K_3CrO_8 and Rb_3CrO_8 indicate the metal–metal bond lengths roughly scale with the cation size. The low value of J for Li_3CrO_8 is attributed to waters of hydration increasing the Cr–Cr distance.

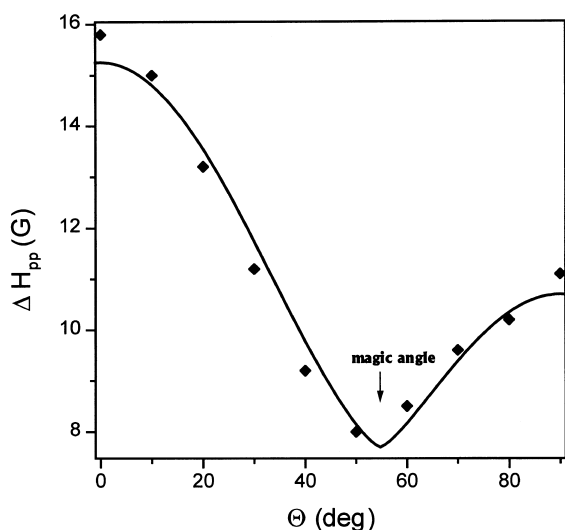


Fig. 2. The angular dependence of the peak to peak linewidth of the derivative of the EPR signal at 9.5 GHz for Li_3CrO_8 . The solid line represents the fit for a 1D spin system using Eq. (3).

as well as dilution with a diamagnetic host such as K_3NbO_8 , the peroxychromates should be valuable for theoretical modeling of the dependence of low-dimensional metal oxide exchange interaction on interion distance.

The low dimensionality of the spin exchange is suggested by single crystal EPR data. The EPR spectrum for all these compounds is a single exchange narrowed peak [4], but we now report that the linewidth is quite anisotropic. It has been shown that the angular dependence of the EPR peak to peak linewidth, ΔH_{pp} , for a 1D system is [10–12]:

$$\Delta H_{\text{pp}} = A + B|3\cos^2 \theta - 1|^{4/3} \quad (3)$$

where the constant A is representative of the residual linewidth as determined by spin–lattice relaxation and other lifetime processes, B is composed of the secular component of the dipolar field and the exchange energy, and θ is the angle between the chain axis and the Zeeman field. This relationship is characterized by a sharp minimum in the linewidth at the magic angle of $\theta \sim 54.7^\circ$. In contrast, 3D exchange [13] is proportional to $(1 + \cos^2 \theta)$, which exhibits a broad minimum at $\theta \sim 90^\circ$.

While preliminary data have shown an anisotropic linewidth of the EPR signals from all these compounds, we here report data for Li_3CrO_8 (Fig. 2). The linewidth shows marked angular dependence, with a minimum at the magic angle. The solid line is a fit using Eq. (3) with $A = 7.7$ G and $B = 3$ G, in agreement with the experimental data, indicating a linear chain spin exchange mechanism, which was unexpected and needs further investigation.

Further analysis of magnetic susceptibility and heat capacity data suggests that the peroxychromates are good candidates as magnetic refrigerants. This claim is supported by the heat capacity coefficient (b) which is derived from the high temperature behavior of the magnetic specific heat (C) such that, $C = b/T^2$. The lower the magnitude of b , the greater the adiabatic demagnetization refrigeration potential [8]. Our analysis shows that a general trend is followed where introducing larger cations significantly lowers b (see Table 1), while basically maintaining the spin concentration. The conclusion drawn is that Cs_3CrO_8 ($b = 0.049$ J K/mol) would be a superior magnetic refrigerant to the commonly used material chrome alum [8] ($b = 1.49$ J K/mol) in the 30 mK–4 K range. Additionally, since the saturation moment of many of the peroxychromates is ~ 9 T or greater, they may be used as coolants at high magnetic fields.

The ground state wavefunction of the lone $3d^1$ electron of the CrO_8^{3-} ion can be determined using EPR spectroscopy [4,14]. The hybridization of the peroxychromates has been shown to be d^4sp^3 with the unpaired electron residing in either the d_{z^2} orbital or the $d_{x^2-y^2}$ orbital [4]. A tetragonal distortion of the crystal field removes the degeneracy. For a compression [15] along z , the high symmetry axis, the d_{z^2} orbital lies lowest in energy, and for this case $g_\perp < g_\parallel$, where g_\perp and g_\parallel are the g -factors with the Zeeman field

perpendicular and parallel to the magnetic symmetry axis. However, an elongation along z results in the $d_{x^2-y^2}$ orbital being lowered in energy and then $g_\perp > g_\parallel$. We have measured the g_\perp and g_\parallel values for all of these compounds and find that the ground state electronic wavefunction depends sensitively on the cation. This is clearly evident from the EPR data presented in Table 1. For example, for K_3CrO_8 , $g_\perp > g_\parallel$, therefore, the electronic ground state is $d_{x^2-y^2}$. However, substitution of one K cation by Na results in $g_\perp < g_\parallel$, and, therefore, the ground state switches to d_{z^2} . Further, at high fields the EPR spectrum of K_2NaCrO_8 exhibits three nonequivalent extremes of the g -tensor [16], which indicates that the magnetic symmetry of the system has been altered from tetragonal (K_3CrO_8) to orthorhombic. Similar results were noted for Rb_2Na and Cs_2Na salts. This points to the fact that one could possibly obtain an isotropic system with a proper combination of the alkali cations. Such a system with just one unpaired electron and isotropic Zeeman interactions in the absence of a hyperfine field would be a useful system for comparison with theoretical models of exchange interaction.

In summary, while the M_3CrO_8 salts were first reported [1] in 1905, not much is known about their electronic structure and bulk thermodynamic properties, perhaps because they are thought to be unstable and hard to grow as large crystals. This study shows that they can be grown as large single crystals, as both pure, solid solutions (mixed crystals), and as guest molecules diluted into the isostructural diamagnetic host K_3NbO_8 . They exhibit low-dimensional magnetic and unusual specific heat properties, and have potential for use as magnetic coolants in the mK to 4 K range. Also, their electronic ground state and crystal symmetry are tunable via cation mixing. They can be grown either as mainly a $S = 1/2$, $I = 0$ system, or as $S = 1/2$, $I = 3/2$ systems using the ^{53}Cr isotope. Preliminary data suggest that this study can be extended to at least some of the MoO_8^{3-} analogs, and as KMgCrO_8 , thus rendering this report to be of further wide theoretical and experimental interest.

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