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Magnetoelectric Compounds with Two Sets of Magnetic Sublattices: $UCrO_4$ and $NdCrTiO_5$*

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Using magnetic and magnetoelectric (ME) powder susceptibility measurements, the low temperature magnetic properties of antiferromagnetic $UCrO_4$ and $NdCrTiO_5$ have been studied. Their Néel temperatures T_N are 44.5 and 20.5°K, respectively, the Cr^{3+} spin systems of both materials ordering cooperatively at T_N. Below T_N, the U^{5+} and Nd^{3+} moments are polarized due to their exchange interaction with the ordered Cr^{3+} spins. It is argued that, for both compounds, each of the two spin systems contributes to the ME susceptibilities. They are thus the first known ME materials possessing two distinct magnetic sublattices. The effective magnetic moments calculated from the magnetic susceptibilities are in good agreement with those previously reported by neutron diffraction studies.

Introduction

The compound $UCrO_4$ was first synthesised by Borchardt (*1*). Its crystallographic space group, as determined by Smith et al. (*2*) and Bacmann et al. (*3*) by X-ray (*2* and *3*) and neutron diffraction (*3*) techniques, is *Pbcn* with both the Cr^{3+} and U^{5+} ions situated in 4(*c*) sites having site symmetry 2. Neutron diffraction patterns (*3*) recorded at 4.2°K were characteristic of antiferromagnetic order with both the Cr^{3+} and U^{5+} spin systems in A_y modes (*4*). The appropriate Shubnikov group is thus *Pbcn'*. A best fit to the measured, intensities of the magnetic peaks was obtained by assigning moments of $2.40 \pm 0.10\beta$ and $0.30 \pm 0.04\beta$ to the Cr^{3+} and U^{5+} ions, respectively, where β is the Bohr magneton. The reported Cr^{3+} moment is thus considerably lower than the theoretical isolated value ($\mu_T(Cr^{3+}) = 3\beta$ at 0°K). In addition, the U^{5+} moment is much smaller than the spin $\frac{1}{2}$ value of 1β reported (*5*) for U^{5+} in U_2O_5 but is comparable with the 0.4β found (*6*) for U^{5+} in $UFeO_4$. The reduction in the magnetic moment of $UCrO_4$ has been attributed to the covalent nature of the Cr–O and U–O bonds (*3*).

The compounds $MRTiO_5$ (M = Cr, Mn, Fe; R = Pr, Nd, Sm, Eu, Gd) have been studied by Buisson (*7*) using X-ray and neutron diffraction techniques. These compounds have the crystallographic space group *Pbam* with the M^{3+} and Ti^{4+} ions distributed over 4(*f*) and 4(*h*) sites and the R^{3+} ions in the 4(*g*) sites. The site symmetries are 2, *m*, and *m* for 4(*f*), 4(*g*) and 4(*h*) sites, respectively. For $CrNdTiO_5$, 95% Cr–5% Ti are in 4(*f*) sites and 5% Cr–95% Ti are in 4(*h*) sites. From neutron diffraction and magnetic measurements, Buisson (*5*) has reported that $CrNdTiO_5$ is antiferromagnetic below $T_N = 13$°K with

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both the Cr^{3+} and Nd^{3+} spin systems ordering cooperatively at this temperature. The spins of the Nd^{3+} and Cr^{3+} ions in the 4(*h*) sites order in a G_xA_y mode (*4*) and those of the Cr^{3+} ions in the 4(*f*) sites order in a A_z mode. The Shubnikov group is *Pbam'*. A best fit to the measured intensities at 4.2°K was obtained by assigning moments of $2.95 \pm 0.15\beta$ and $2.89 \pm 0.15\beta$ to the Cr^{3+} and Nd^{3+} ions, respectively. The reported Cr^{3+} moment is thus in agreement with the theoretical isolated ion value. Turning to the Nd^{3+} ions, the ground state term, $^4I_{9/2}$, can be split into five Kramer's doublets by the crystalline field. This complete lifting of the degeneracy is possible due to the relatively low symmetry of the Nd^{3+} sites. At sufficiently low temperatures only the lowest lying Kramer's doublet will be occupied. The maximum magnetic moment, at 0°K, is then $\mu_{max}(Nd^{3+}) = g_J J = 3.27\beta$ where $g_J = 8/11$ is the Lande *g* factor. The neutron diffraction results thus indicate that the lowest lying Kramer's doublet has a significant contribution from the $J_\zeta = \pm 9/2$ states.

Since the magnetic point group of $UCrO_4$ and $CrNdTiO_5$ is *mmm'*, magnetoelectricity (*8*) is allowed in both of these compounds. The magnetoelectric (ME) effect will be characterized by single crystal ME susceptibility tensors having two nonzero elements, α_{12} and α_{21} (*9*). $UCrO_4$ and $CrNdTiO_5$ are particularly interesting as no ME materials possessing two types of magnetic sublattices have previously been reported. The confirmation and study of the ME effect in these compounds was thus one of the objectives of this work. A further objective was to clarify the nature of the magnetic ordering in these materials.

Experimental Results

Samples of $UCrO_4$ and $CrNdTiO_5$ were prepared by intimately mixing stoichiometric quantities of UO_3 and Cr_2O_3; Nd_2O_3, Cr_2O_3, and TiO_2, respectively, and firing the pressed pellets for 24 hr in air at 1200°C. X-ray powder diffraction patterns obtained were in agreement with previously reported data (*7*, *10*). The magnetic susceptibility of each compound was measured over the range 4.2–300°K using a motor driven vibrating sample magnetometer (*11*). The sample was cooled by a stream of helium vapor. The desired flow rate was maintained by means of a temperature controller and a magnetic valve (*12*).

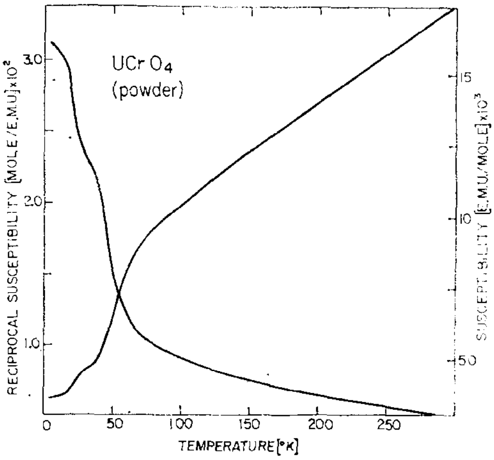

FIG. 1. Temperature dependence of the powder magnetic susceptibility of $UCrO_4$. The reciprocal susceptibility is also shown.

In Figs. 1 and 2 we show the powder susceptibility χ and reciprocal susceptibility $1/\chi$ of $UCrO_4$ and $CrNdTiO_5$, respectively, as a function of temperature *T*. For $UCrO_4$, the χ vs *T* curve of Fig. 1 exhibits an anomaly in the neighborhood of 40°K. The paramagnetic Curie temperature θ and effective moment p_{eff}, as determined from fitting the high temperature $1/\chi$ vs *T* curve to a Curie–Weiss law, are −126°K and 3.43β. Turning to $CrNdTiO_5$,

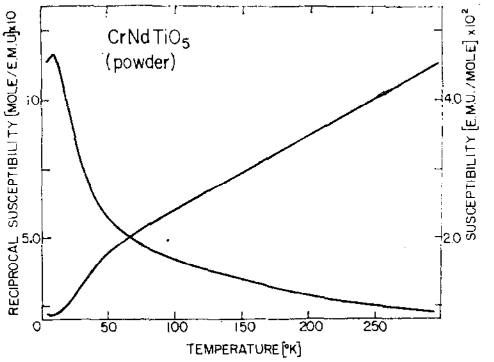

FIG. 2. Temperature dependence of the powder magnetic susceptibility of $NdCrTiO_5$. The reciprocal susceptibility is also shown.

the χ vs T curve has a peak at 9°K and a Curie–Weiss law fit to the $1/\chi$ vs T curve yielded $\theta = -47°K$ and $p_{eff} = 5.40\beta$.

For the ME measurements, samples of $UCrO_4$ and $CrNdTiO_5$ were pressed into cylindrical pellets approximately 2.5 mm high and 6 mm in diameter. Silver electrodes were painted on the faces and the samples were cooled down to 4.2°K in the presence of either parallel ($E \| H$) or perpendicular ($E \perp H$)) electric and magnetic fields. This prior ME annealing is necessary in order to induce a ME remnant state in an antiferromagnetic material (*13*). The magnetic moment induced in the material by the application of an alternating voltage to the electrodes was then measured as a function of temperature.

As is well known (*14*), the magnitude of the measured ME susceptibilities will depend upon the magnitude EH of the annealing fields. We found that 10^8 V-G/cm (22 kV/cm × 9 kG) was sufficient to achieve better than 90% of saturation for either annealing treatment. All measurements were performed using a technique described previously (*15*).

The results obtained are shown in Fig. 3 and 4 for $UCrO_4$ and $CrNdTiO_5$, respectively. For each compound, we show $\alpha_{zz} = M_z/E_z$, measured in the z direction following an annealing treatment $H_z \| E_z$ and $\alpha_{xy} = M_x/E_y$, the ME susceptibility measured in the x direction following an annealing treatment $H_x \perp E_y$. For $UCrO_4$ the ME susceptibilities extrapolate to zero at 44.5 ± 0.5°K, which we therefore identify as the Néel temperature T_N of this material. For $CrNdTiO_5$, T_N, as determined from the ME measurements, is 20.5 ± 0.5°K.

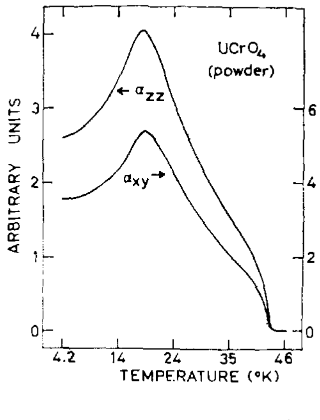

FIG. 3. Temperature dependence of the powder magnetoelectric susceptibilities of $UCrO_4$ following annealing in parallel electric and magnetic fields and annealing in perpendicular fields.

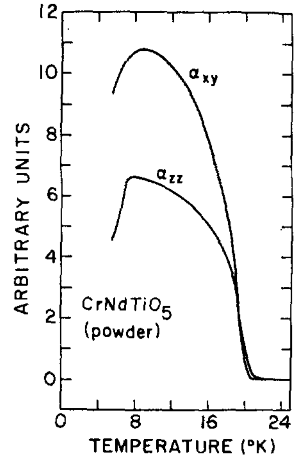

FIG. 4. Temperature dependence of the powder magnetoelectric susceptibilities of $NdCrTiO_5$ following annealing in parallel electric and magnetic fields and annealing in perpendicular fields.

Discussion

By ME measurements, we have established that $UCrO_4$ orders at $T_N = 44.5°K$. The nature of the ordering process is however not immediately obvious. Most probably it is the Cr^{3+} spins that order cooperatively at this temperature in an A_y mode. For $T < T_{N'}$ the ordered Cr^{3+} spin system then induces, by means of exchange coupling, the observed A_y structure of the paramagnetic U^{5+} moment array. The following two observations support this picture.

1. The isomorphous compound $UFeO_4$ orders at 55°K and ^{57}Fe Mössbauer measurements (*6*) show clearly that the Fe spin system orders cooperatively below this temperature.

2. The anomaly (of magnitude $\Delta\chi \simeq 2.5 \times 10^{-3}$ emu/mole), in the powder susceptibility curve at $T \simeq 40°K$ (see Fig. 1) can be identified

with the onset of the Cr^{3+} ordering. The continued rise in χ with decreasing temperature can then be attributed to the polarization of the electrons occupying the low lying crystal field doublets of the U^{5+} ions. To illustrate this, let us ignore any U^{5+}–U^{5+} interaction and assume that only the lowest lying doublet is occupied. Then the polarization in the single ion or molecular field approximation, will result in contributions to the U^{5+} susceptibilities of the form

$$\chi_y(U) = \frac{N\mu^2}{k_B T}\operatorname{sech}^2\left(\frac{\Delta}{2T}\right), \qquad (1a)$$

$$\chi_{x,z}(U) = \frac{N(g_{x,z})^2\beta^2}{2\Delta}\tanh\left(\frac{\Delta}{2T}\right), \qquad (1b)$$

where $\Delta(T)$, the splitting of the U^{5+} ground state doublet, is given by

$$\Delta(T) = 2\mu H_{\text{eff}}(T/T_N)/k_B. \qquad (2)$$

Here μ is the 0°K magnetic moment of a U^{5+} ion, g_x and g_z are effective g factors in the x and z directions, $H_{\text{eff}}(T/T_N)$ is the effective field at temperature T on a U^{5+} moment due to the ordered Cr^{3+} spins, and N and k_B are Avagadro's and Boltzman's constants.

Since the contribution of the U^{5+} moments to the total powder susceptibility χ is given by the mean of the principal susceptibilities, it follows from Eq. (1) that $\chi = \chi(\text{Cr}) + \chi(\text{U})$ can continue to increase strongly with decreasing temperature in the region $T < T_N$ as long as $T > \Delta$. Finally, we stress that there can be other contributions to $\chi(\text{U})$ in addition to those given in Eq. (1). These can be due to significant electron occupation of higher lying crystal field levels and/or terms of the Van Vleck type. The latter, in particular, will also increase with decreasing temperature.

The ME susceptibilities of $UCrO_4$ (see Fig. 3) exhibit peaks at $T = 17.5$°K, essentially the same temperature at which the magnetic susceptibility undergoes a pronounced change in slope. This would indicate a crystal field splitting of this order of magnitude between the two lowest lying Kramer's doublets of the U^{5+} ground term. (It is possible, but highly unlikely that this is instead the doublet splitting Δ of Eqs. (1) and (2) as this would require an H_{eff} of 5×10^5 Oe).

The effective magnetic moment per molecule unit may be calculated from

$$\mu_{\text{eff}} = [g_1{}^2 J_1(J_1+1) + g_2{}^2 J_2(J_2+1)]^{1/2}\beta \qquad (3)$$

where g_i, J_i $(i = 1, 2)$ refer to the g factors and angular momentum quantum numbers of the two magnetic sublattices. Using an isolated ion picture for the Cr^{3+} and U^{5+} moments, Eq. (3) yields $[2^2(1.5)(2.5) + (6/7)^2(2.5)(3.5)^{1/2}\beta = 4.62\beta$, considerably higher than the 3.34β obtained from Fig. 1. If, from the 4.2°K neutron diffraction results (*3*), we take an effective g factor of 1.6 for the Cr^{3+} moments and further assume that the U^{5+} moments can be described by $J = 5/2$, $g_{\text{eff}} = 0.3$, we obtain from Eq. (3) the value $[(1.6)^2(1.5)(2.5) + (0.3)^2(2.5)(3.5)]^{1/2}\beta = 3.22\beta$, in reasonable agreement with the 3.34β found from the magnetic measurements. This supports the conclusion of Bacmann et al. (*3*) that the magnetic moments of the Cr^{3+} and U^{5+} ions are significantly lower than those expected from simple crystal field considerations. The ratio $(-\theta/T_N) = 126/44.5 = 2.8$ indicates that a given Cr^{3+} ion has strong exchange interactions with more than its nearest Cr^{3+} neighbors, these interactions may be with more distant Cr^{3+} ions and/or U^{5+} ions.

Turning to $CrNdTiO_5$, the ME measurements (see Fig. 4) show that this compound orders at $T_N = 20.5$°K. This is considerably higher than the 13°K ordering temperature reported by Buisson (*7*). Again, as in the case of $UCrO_4$, there arises the question of which spin system(s) is (are) in fact ordering cooperatively at this temperature.

The most likely process, as before, is that it is the Cr^{3+} spin system (or possibly only the 95% of the Cr spins located in (*4f*) sites) that orders cooperatively. The ordered Cr^{3+} spin system then induces, by means of exchange coupling, the $G_x A_y$ mode of the paramagnetic Nd^{3+} array. In support of this process, we note that:

1. In the orthorhombic compounds $NdFeO_3$ and $NdCrO_3$, the magnetic moments of the Nd^{3+} ions are known to be polarization-induced by the ordered transition metal spins down to 1°K (*16*) and 4.2°K (*17*), respectively. The Nd–Nd interaction in these two systems

has been estimated to be 3°K ($NdFeO_3$ (*18*)) and 2°K ($NdCrO_3$ (*17*)). It is most unlikely that the Nd–Nd interaction in $CrNdTiO_5$ will be an order of magnitude greater.

2. The powder susceptibility curve of $CrNdTiO_5$ (see Fig. 2) shows no observable anomaly in the neighborhood of 20.5°K and continues to increase smoothly with decreasing temperature, reaching a peak at 9°K. This supports a picture wherein a part of the spins remains paramagnetic below T_N. (Note that, since χ at $T = T_N$ is 3–4 greater in $CrNdTiO_5$ than in $UCrO_4$, the relative anomaly $(\Delta\chi/\chi)_{T_N}$ associated with the ordering will be correspondingly smaller.)

If the peak in χ is associated with the contribution of the lowest lying doublet to the xy plane susceptibility tensor elements, it follows that $\Delta(0)$ is approximately equal to 14°K and $H_{eff}(0) \simeq 18$ kg. (In order to obtain better estimates of $\Delta(0)$ and $H_{eff}(0)$, single crystal magnetization studies are necessary (18). Effective fields of this magnitude are found in most of the rare earth orthoferrites (*19*) and orthochromites (*20*) (not however in $NdCrO_3$ (*17*)) and this is a further indication that the observed Nd^{3+} moments in $CrNdTiO_5$ are induced by the ordered Cr^{3+} spins rather than being the result of a cooperative ordering of the Nd^{3+} spin system.

The measured effective magnetic moment per molecular unit as obtained from Fig. 2, is 5.40β. This is in excellent agreement with the theoretical value $[2^2(1.5)(2.5) + (8/11)^2 \times (4.5)(5.5)]^{1/2}\beta = 5.40\beta$ obtained using Eq. (3) and an isolated ion picture for the Cr^{3+} and Nd^{3+} moments. The ratio $(-\theta/T_N) = 47/20.5 = 2.3$, indicating that here also a given Cr^{3+} ion has strong exchange interactions with more than its Cr^{3+} nearest neighbors.

The maximum measured values of the powder ME susceptibilities are (in gaussian units) 5.4×10^{-5} and 1.1×10^{-5} for $UCrO_4$ and $CrNdTiO_5$, respectively. For both compounds (*21*)

$$\alpha_{zz} = (1/3\pi)(\alpha_{12} + \alpha_{21}), \qquad (4)$$

and, since $\alpha_{zz} \neq 0$, it follows that the single crystal ME susceptibility tensor is not antisymmetric. At the maximum value of α_{zz}, we have

$$(|\alpha_{12}|, |\alpha_{21}|) \geqslant (3\pi/2)(\alpha_{zz})_{max}, \qquad (5)$$

where (a, b) denotes the greater of the quantities a,b at the temperature at which $\alpha_{zz} = (\alpha_{zz})_{max}$. From Figs. 2 and 4 we then have

$$\begin{aligned} (|\alpha_{12}|, |\alpha_{21}|) &\geqslant 1.9 \times 10^{-4}, \\ (|\alpha_{12}|, |\alpha_{21}) &\geqslant 3.0 \times 10^{-5}, \end{aligned} \qquad (6)$$

for $UCrO_4$ and $CrNdTiO_5$, respectively. These values may be compared with $(\alpha_{33})_{max} = 6.4 \times 10^{-5}$ in Cr_2O_3 (*22*), the only other known ME material containing Cr^{3+} ions.

We have seen that the powder ME susceptibilities of $CrUO_4$ exhibit peaks at the same temperature at which the slope of the magnetic susceptibility changes abruptly. Since, as argued earlier, such a change in slope can only be due to the magnetic behavior of the U^{5+} spin system, it appears that the contribution of the U^{5+} moments to the ME susceptibilities is a significant one. The same conclusion can be reached regarding the contribution of the Nd^{3+} spin system to the ME susceptibilities of $NdCrTiO_5$, where both sets of data (α and χ) exhibit sharp peaks at 8–9°K. A more exact determination of the relative contributions of the different spin systems to the ME susceptibility tensors of $CrUO_4$ and $NdCrTiO_5$ will require single crystal measurements.

In conclusion, we have studied the magnetic and ME powder susceptibilities of $UCrO_4$ and $CrNdTiO_5$. Their Néel temperatures were found to be 44.5 and 20.5°K, respectively, the Cr^{3+} spin systems of both materials ordering cooperatively at T_N. Below T_N, the U^{5+} and Nd^{3+} moments are polarized by exchange interactions with the ordered Cr^{3+} spins. It is argued that both of the spin systems in each of the two compounds contribute to the ME susceptibilities, making them the first known ME materials possessing two distinct magnetic sublattices. The effective magnetic moments calculated from the magnetic susceptibilities are in good agreement with those previously reported (*3*, *7*) by neutron diffraction studies. Magnetization studies on single crystals and neutron diffraction measurements of the temperature dependence of the magnetic moments of the individual sublattices would be useful to further clarify the ordering process in these compounds.

References

1. H. C. Borchardt, *J. Inorg. Nucl. Chem.* **12**, 113 (1959).
2. D. K. Smith, C. F. Cline, and D. E. Sands, *Nature (London)* **192**, 861 (1961).
3. M. Bacmann, E. F. Bertaut, and G. Basse, *Bull. Soc. Franc. Mineral. Crist.* **88**, 214 (1965).
4. E. F. Bertaut, *in* "Magnetism" (G. T. Rado and H. Suhl, Ed.) Vol. III, p. 149. Academic Press, New York (1963).
5. N. I. Blinova, G. A. Romanov, V. M. Solntsev, and Yu. M. Tolmachev, *Dokl. Akad. Nank. SSSR* **147**, 1112 (1962).
6. M. Bacmann, E. F. Bertaut, A. Blaise, R. Chevalier, and G. Roult, *J. Appl. Phys.* **40**, 1131 (1969).
7. G. Buisson, *J. Phys. Chem. Solids* **31**, 1171 (1970).
8. For recent reviews, see E. F. Bertaut and M. Mercier, *Mater. Res. Bull.* **6**, 907 (1971), and R. M. Hornreich, *IEEE Trans. Mag.* **8**, 584 (1972).
9. R. R. Birss, *Rept. Progr. Phys.* **26**, 307 (1963).
10. E. J. Felton, E. F. Juenke, and S. F. Bartram, *J. Inorg. Nucl. Chem.* **24**, 839 (1962).
11. P. J. Flanders and W. D. Doyle, *Rev. Sci. Instr.* **33**, 691 (1962).
12. Manufactured by "Ricor", Ein Harod-Ichud, Israel.
13. S. Shtrikman and D. Treves, *Phys. Rev.* **130**, 986 (1963).
14. T. H. O'Dell, *Phil. Mag.* **13**, 921 (1966).
15. S. Bukshpan, E. Fischer, and R. M. Hornreich, *Solid State Commun.* **10**, 657 (1972).
16. R. M. Bozorth, H. J. Williams, and D. E. Walsh, *Phys. Rev.* **103**, 572 (1956).
17. R. M. Hornreich, Y. Komet, and B. M. Wanklyn, *Solid State Commun.* **11**, 969 (1972).
18. R. M. Hornreich and I. Yaeger, *Int. J. Magnetism* **4**, 71 (1973).
19. D. Treves, *J. Appl. Phys.* **36**, 1033 (1965).
20. e.g. $TmCrO_3$; See R. M. Hornreich, B. A. Wanklyn, and I. Yaeger, *Int. J. Magnetism*, in press.
21. R. M. Hornerich, *J. Appl. Phys.* **41**, 950 (1970).
22. T. J. Martin and J. C. Anderson, *Phys. Lett.* **11**, 109 (1964).