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Electrical and magnetic properties of 3d-transition metal vanadates

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Abstract. The electrical and magnetic properties of vanadates of the general formula $(MO)_n.V_2O_5$, where M=Mn, Co, Ni, Cu and Zn, and n=1, 2 and 3, are discussed. Conduction in these materials occurs due to small deviations from the stoichiometric composition in the form of anion-(n-type) or cation—(p-type) vacancies. The mechanism of electrical transport is of a thermally activated hopping of charge carriers on equivalent cation lattice sites. It has been found that the meta vanadates (n=1) are all n-type while the pyro—(n=2) and ortho—(n=3) compounds of Mn, Co and Ni are p-type; but Cu and Zn analogues remain n-type only.

The vanadates obey Curie-Weiss law at 80-340 K. The effective magnetic moments for MV_2O_6 are nearly the same as spin only values for the magnetic M^{2+} ions, and diminish with increasing MO contents. The predominant exchange interactions are the weak 90° MOM super-exchange and M—O—O—M super-super exchange. The Weiss constant is negative (antiferro-) for all the compounds except $Co_3V_2O_8$ which has a positive (ferro—) value. Cooperative phenomena, if any, have not been observed in this temperature range.

Keywords. Stoichiometric compositions; charge carriers; hopping conduction; exchange interactions.

1. Introduction

Phase equilibrium studies on the binary oxide system $MO\text{-}V_2O_5$ (Brisi 1957, 1958; Brown *et al* 1964; Dorm *et al* 1967; Makarov *et al* 1971; Amirova *et al* 1964; Joubert *et al* 1964; Fleury 1966, 1969; Raveau 1967), where M = Mn to Zn except Fe in the first transition metal series, have established the formation of vanadates of the general formula $(MO)_n.V_2O_5$, where n = 1 to 5. In the present paper, we shall confine our discussions to the electrical and magnetic properties of the meta—(n = 1, MV_2O_6), pyro—(n = 2,$M_2V_2O_7$) and ortho—(n = 3,$M_3V_2O_8$) vanadates only.

The crystal structures of most of these compounds have been determined. In general, the MV_2O_6 are Brannerite-type ($ThTi_2O_6$), $M_2V_2O_7$ are thortreitite-type ($Sc_2Si_2O_7$) and $M_3V_2O_8$ are orthorhombic (Space Group Cmca). The Cu-analogues have, however, structures of lower symmetry than the above because of strong, co-operative Jahn-Teller distortions of the anion polyhedra surrounding the $Cu^{2+}(3d^9)$ ions.

The room temperature effective magnetic moments for $M_2V_2O_7$ compounds of Mn, Co, Ni and Cu have been reported (Pedregosa *et al* 1973) to be 5·56, 4·85, 2·88 and 1·75 (BM) respectively. Also, it has been found by Fuess *et al* (1970) that $Co_3V_2O_8$ becomes ferromagnetic below 10 K(=T_c).

Except for the above few publications no other information is available regarding the electrical transport behaviour and magnetic interactions in these vanadates. We have undertaken a systematic study and a part of the results is described here.

tide unit is more likely to have a 4→1 type of hydrogen bond in it. In fact, as mentioned by Kopple (1972) this type of hydrogen bond forms a common feature in cyclic peptides with five or more residues. This hydrogen bond can subsequently be broken due to the packing effect when the molecules form a crystal. Further support for the occurrence of such hydrogen bonded peptide sections in a cyclic hexapeptide is available from crystal structures (Zalkin *et al* 1966; Karle *et al* 1970) and NMR studies (Torchia *et al* 1972; Kopple *et al* 1969).

Acknowledgements

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Except for the above few publications no other information is available regarding the electrical transport behaviour and magnetic interactions in these vanadates. We have undertaken a systematic study and a part of the results is described here.

2. Experimental

The compounds were prepared by the solid-solid reactions (Clark *et al* 1975) between appropriate molar ratios of V_2O_5 and $MnCO_3$, $CoCO_3$, NiO, CuO and ZnO at temperatures ranging between 900-1200 K for about 4 to 5 days. The products were characterised by x-ray powder diffraction using Cu-Kα radiation ($\lambda = 1{\cdot}5418$ Å; Ni filter).

The D.C. electrical conductivity (σ) was measured by the two probe method and Seebeck coefficient (α) by integral method at 300-1000 K. The samples were in the form of sintered pellets, 18 mm dia. and 2 mm thick.

The magnetic susceptibility (χ) was determined by the Guoy method using $HgCo(CNS)_4$ as the calibrant.

3. Results and discussion

3.1. *Electrical properties*

The relevant experimental results are shown in table 1 and figures 1 to 6. The relationship between σ and T may be expressed as,

$$\sigma = (\sigma_0/T) \exp(-\triangle G^*/kT) \tag{1}$$

where σ_0 is a constant and $\triangle G^*$ is free energy of activation for electrical conduction.

$$\log_{10}(\sigma T) = \log_{10}\sigma_0 - \frac{\triangle G^*}{2{\cdot}3\,kT} \tag{2}$$

Table 1. Electrical data for vanadates

Compound M	Sign of Seebeck coefficient	Electrical resistivity range (ohm-cm) at 300°K-1000°K	Activation Energy $\triangle G^*$ eV
MV_2O_6			
Mn	*n* to *p*-type	10^6 to 10^2	0·40
Co	*n*-type	10^3 to 10	0·30
Ni	*n*-type	10^5 to 10^2	0·40
Cu	*n*-type	10^5 to 10^2	0·40
Zn	*n*-type	10^{10} to 10^4	0·97
V_2O_5	*n*-type	10^4 to 10^2	0·20
$M_2V_2O_7$			
Mn	*p*-type	10^{10} to 10^3	1·10
Co	*p*-type	10^6 to 10^3	0·60
Ni	*p*-type	10^{10} to 10^4	1·10
Cu	*n*-type	10^5 to 10^2	0·44
Zn	*n*-type	10^{10} to 10^4	1·05
$M_3V_2O_8$			
Mn	*p*-type	10^{10} to 10^2	1·00
Co	*p*-type	10^8 to 10^4	0·72
Ni	*p*-type	10^{10} to 10^5	1·40
Cu	*n*-type	10^6 to 10^2	0·45
Zn	*n*-type	10^{10} to 10^4	1·12

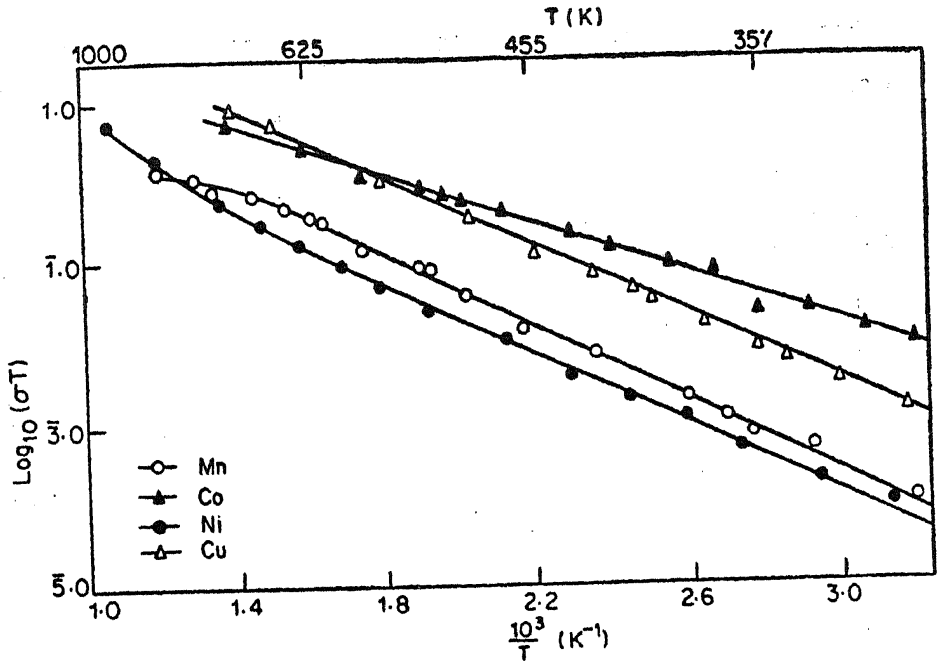

Figure 1. $\text{Log}_{10}(\sigma T)$ vs $1/T$ for meta-vanadates (MV_2O_6)

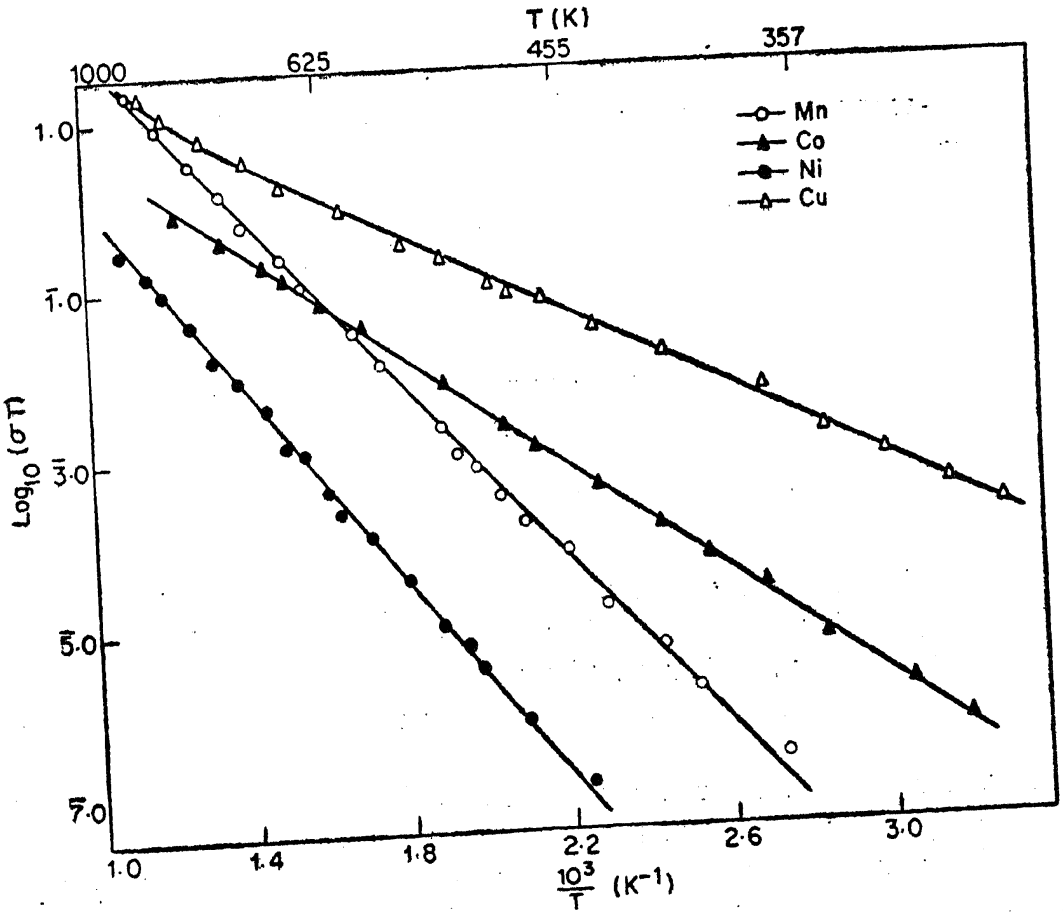

Figure 2. $\text{Log}_{10}(\sigma T)$ vs $1/T$ for pyro-vanadates ($M_2V_2O_7$)

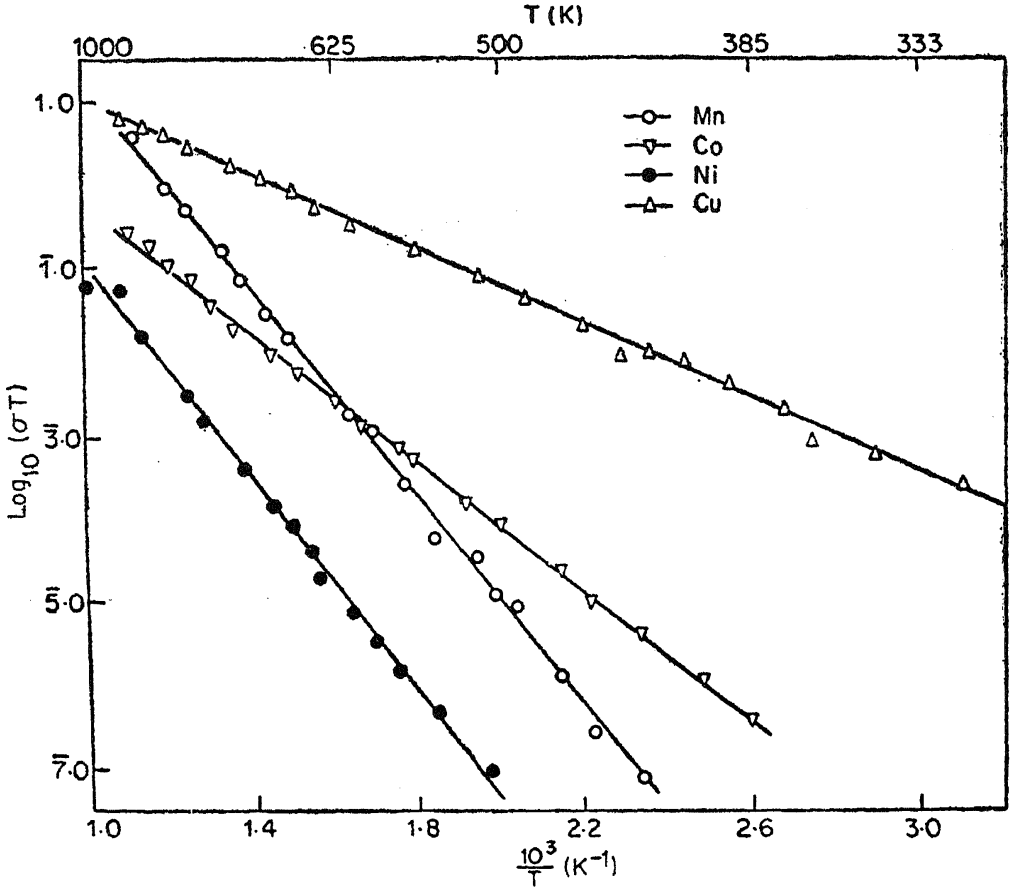

Figure 3. $\text{Log}_{10}(\sigma T)$ vs $1/T$ for ortho-vanadates ($M_3V_2O_8$)

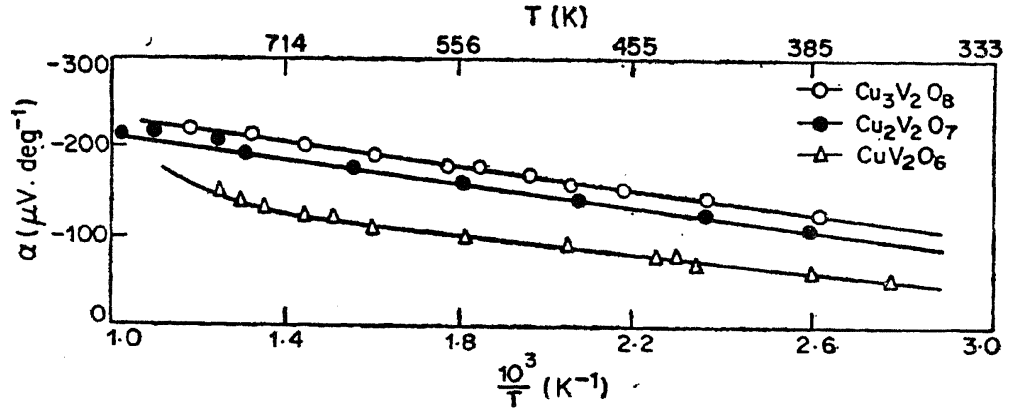

Figure 4. α vs $1/T$ for coper vanadates

From eq. (2) it may be seen that a plot of log (σT) versus $1/T$ should be linear with a slope of $\triangle G^*/2{\cdot}3\,k$, provided eq. (1) is obeyed. Figures 1-3 confirm the validity of the expression in the case of the vanadates.

The Seebeck coefficient (α) is essentially temperature independent (c.f. figures 4 and 5).

The aforementioned observations illustrate sufficiently clearly that $(MO)_n.V_2O_5$ are ' hopping ' type semiconductors. This is quite expected because these compounds are predominently ionic so that the charge carriers are localised. Therefore, the only mode of charge transport is via thermally activated ' jumps ' on equivalent lattice sites.

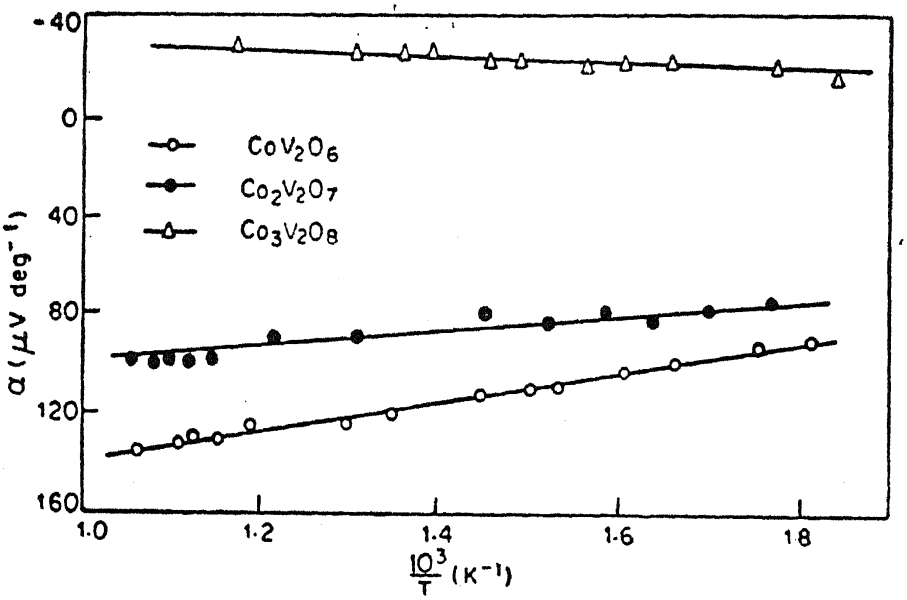

Figure 5. α vs $1/T$ for cobalt vandates

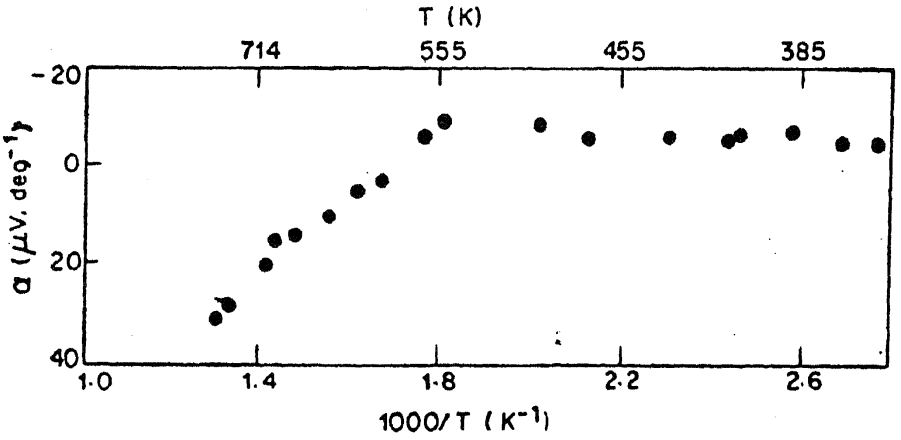

Figure 6. α vs $1/T$ for MnV_2O_6

The sign of α gives the nature of majority charge carriers. It is found that all MV_2O_6 are *n*-type conductors; $M_2V_2O_7$ and $M_3V_2O_8$ (M = Mn, Co and Ni) are *p*-type and, those of Cu and Zn are *n*-type in the temperature range studied (300-1000 K). However, only MnV_2O_6 exhibits a transition from *n*- to *p*-type at $\sim$ 570 K. This is not observed by any corresponding anomaly in σ -T behaviour of the compound. At present, we are unable to trace any specific reason for this change in the nature of charge carriers.

One can expect these vanadates to be good electrical insulators in their pure and stoichiometric state as in the case of, say, MnO, CoO and NiO. But as we have already seen $(MO)_n.V_2O_5$ exhibit appreciable conduction which can be due to deviations from stoichiometry or the presence of impurities. The latter may be considered as insignificant since the compounds have been prepared from high purity raw materials. Therefore, charge carriers may be said to be produced by oxygen or metal deficiency resulting in *n*- or *p*-type conductivity respectively. Now, in the light of these arguments we can explain the observed electrical behaviour as follows:

In the MV_2O_6, anion vacancies occur leaving behind two electrons per $\frac{1}{2}$ molecule of O_2 leaving the lattice; in other words, the metavanadates can be represented as

(a) $M^{1+}M^{2+}_{1-2x}V_2O_{6-x}$ and (b) $M^{2+}V^{4+}_{2x}\ V^{5+}_{2-2x}O_{6-x}$. It is to be determined as to whether the defects (electrons) arise as in (a) or (b). ESR spectra of these compounds consist of a signal at $g=1{\cdot}96$ which is typical of localized V^{4+} centre. Thus it becomes established that MV_2O_6 exhibit *n*-type conduction due to electron hopping on equivalent $V^{4+} - V^{5+}$ sites in the lattice.

The *p*-type conduction in $M_2V_2O_7$ and $M_3V_2O_8$ of Mn, Co and Ni is ascribed to metal vacancies in the lattice. Charge neutrality may be achieved by the formation of M^{3+} or V^{6+} or O^-. The formation of the last two is not energetically favourable. Hence we conclude that the holes execute 'jumps' on M^{2+}—M^{3+} sites in the crystal.

The *n*-type conductivity of Zn compounds is quite understandable in the sense that individually both ZnO and V_2O_5 have a tendency to lose oxygen and form lower valent M-ions or V^{4+} ions. From the present σ, α and ESR data we are unable to offer any specific comment on the mechanism of hopping.

In the Cu-vanadates, electron conduction arises because the oxides CuO and Cu_2O lose oxygen even when heated in air (0·2 atom O_2). The electron exchange taking place may be of the type $M^{2+} + V^{4+} \rightleftharpoons M^{1+} + V^{5+}$.

We can summarise the above electrical data as: The 3d-metal vanadates $(MO)_n.V_2O_5$ are hopping semiconductors in which conduction is rendered possible due to non-stoichiometry—i.e. cation (*p*-type) and anion (*n*-type) vacancies in the lattice. The exact nature of conductivity, its composition dependence and, the defect structures of these materials have to be confirmed by measuring σ and α of single crystals as a function of temperature, and partial pressure of oxygen.

3.2. *Magnetic properties*

The magnetic data are presented in figures 7 to 9 and table 2. It may be observed that,

(a) the compounds are paramagnetic down to 80 K and obey the Curie-Weiss law;

(b) the Weiss constant (θ) is negative for all except $Co_3V_2O_8$ for which it is positive; and

Table 2. Magnetic data for vanadates

Compound	χ_M cgs/mol at 300°K	μ_{eff} observed (B.M.)	μ_{spin} only value	Weiss constant θ (K)
MV_2O_6				
Mn	$1{\cdot}60\times10^{-3}$	6·00	5·92	−20
Co	$1{\cdot}0\times10^{-3}$	4·19	3·87	−90
Ni	$5{\cdot}1\times10^{-3}$	3·52	2·83	−20
Cu	$1{\cdot}57\times10^{-3}$	1·95	1·73	−150
$M_2V_2O_7$				
Mn	$2{\cdot}6\times10^{-3}$	3·96	5·92	−15
Co	$2{\cdot}75\times10^{-3}$	4·10	3·87	−20
Ni	$9{\cdot}20\times10^{-3}$	2·36	2·83	−25
Cu	$2{\cdot}36\times10^{-3}$	1·20	1·73	−85
$M_3V_2O_8$				
Mn	$3{\cdot}4\times10^{-3}$	3·00	5·92	−10
Co	$3{\cdot}6\times10^{-3}$	3·11	3·87	+12
Ni	$1{\cdot}35\times10^{-3}$	1·91	2·83	− 7
Cu	$3{\cdot}5\times10^{-3}$	1·00	1·73	−75

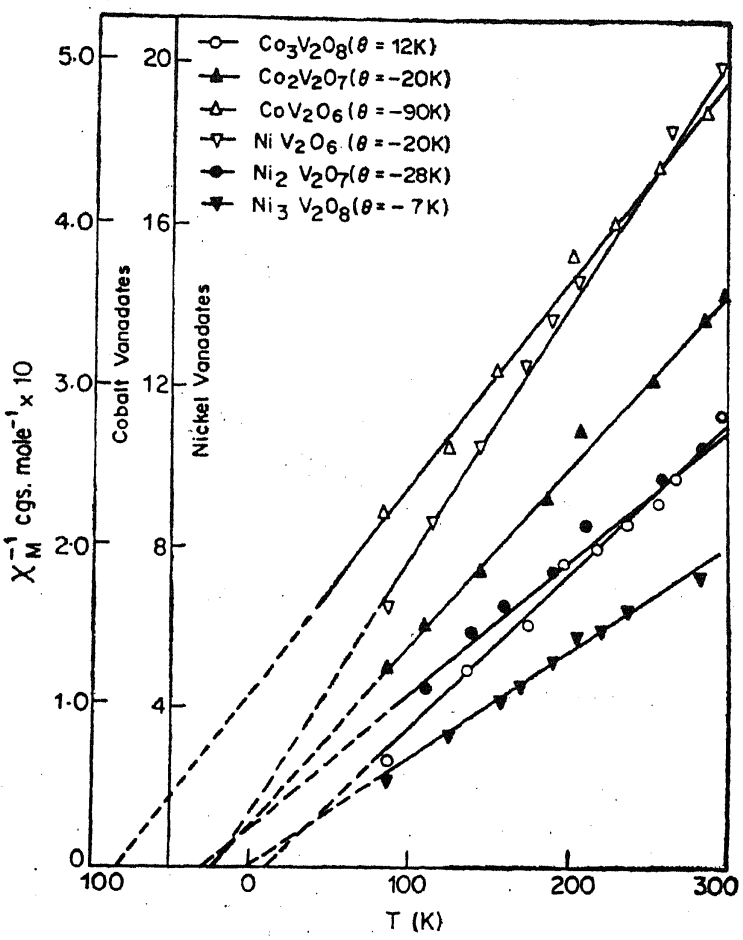

Figure 7. χ_M^{-1} vs T for cobalt and nickel vanadates

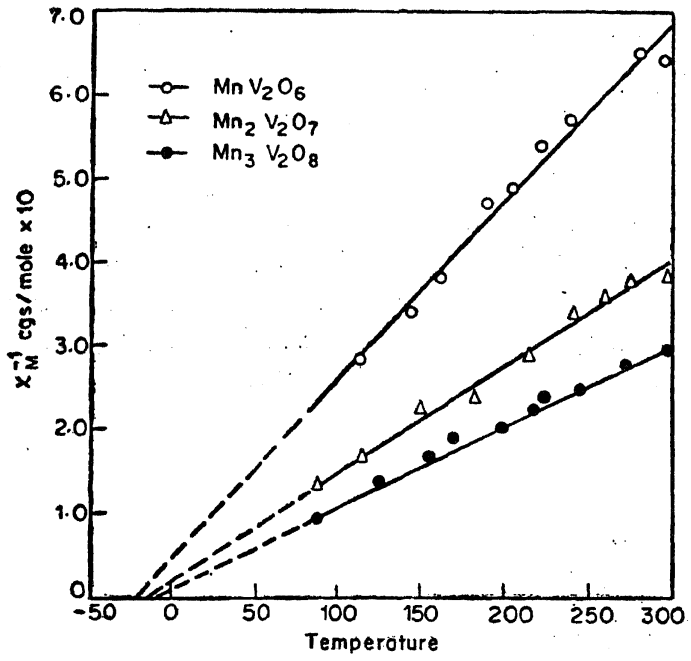

Figure 8. χ_M^{-1} vs T for manganese vanadates