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Oxides and Other Compounds I

Some Magnetic Properties of Spinels with Compositions $NiFe_{2-x}V_xO_4$

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Measurements of saturation magnetization σ and susceptibility χ against temperature T have been carried out for the solid solution series $NiFe_{2-x}V_xO_4$ ($x<1.75$), which has the spinel structure. Arguments for the presence of V^{3+} ions are given. For $x\leqq 1$ the V^{3+} ion is completely in octahedral sites. The result of this is that the saturation magnetization passes through zero with increasing x. All Néel's anomalous σ-T curves have been found in a wide range of compositions. This phenomenon is discussed in terms of the molecular field hypothesis. From this it can be shown that there is a certain negative BB interaction between V^{3+} ions.

1. Experimental

A series of materials with composition $NiFe_{2-x}V_xO_4$ was prepared by sintering a mixture of NiO, Fe_2O_3 and V_2O_3 in the required proportion in vacuo in sealed quartz tubes. X-ray diffraction patterns show that the samples have the spinel structure up to $x=1.75$. With higher V-content the lines of V_2O_3 and NiO are observed. Analysis of the vanadium content and the total reducing power were carried out for many samples. Those with deviations from the stoichiometric formula of more than 0.2% V or O respectively were discarded.

Saturation magnetization values were measured versus temperature for all preparations with spinel structure at 21000 Oe. Figs. 1 and 2 give the results. It is seen that for several samples anomalous $\sigma-T$ curves occur (Néel's types N and P[5],).

Fig. 3 gives the experimental values of the saturation moments (Bohr magnetons/formula unit), obtained from the $\sigma-T$ curves by extrapolation to 0°K. The Curie temperatures and cell edges are given in Fig. 4.

For a number of preparations the susceptibility was measured as a function of temperature (Fig. 5).

2. Discussion of the results

a. Susceptibilities

The aim of the susceptibility measurements was to decide whether Fe^{3+} and V^{3+} ions or Fe^{2+} and V^{4+} ions are present in these spinels. However the Curie constants determined from the experimental susceptibility versus temperature curves have too high a value compared with the spin-only values of the

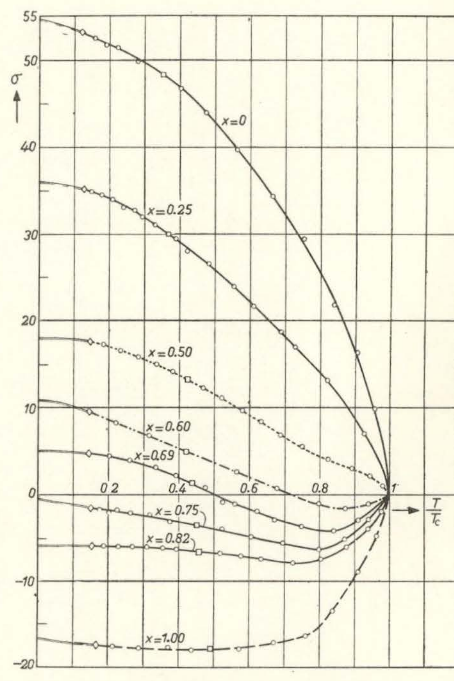

Fig. 1. Saturation magnetization per gram vs reduced temperature for the system $NiFe_{2-x}V_xO_4$. ($0\leqq x\leqq 1$).
○ experimental points.
◇ idem at liquid oxygen temperature.
□ idem at room temperature.

Curie constants of the magnetic ions present, the deviation being the largest for $NiFe_2O_4$. Néel[1] ascribes this phenomenon to the temperature dependence of the molecular field and assumes that the magnetic interaction coefficient varies with temperature as $n=n_0 \times(1+\gamma T)$. According to this author γ has a value of about -2×10^{-4}.

From our experimental data (Curie constant and asymptotic Curie temperature) we have determined γ graphically assuming Fe^{2+} and V^{4+} ions and Fe^{3+} and V^{3+} ions to be present respectively. In the first case a value $\gamma\sim -10^{-3}$ is found for $x>1$ and $\gamma\sim-4\times10^{-5}$ for $x<1$. Such a variation in γ is quite improbable. The assumption of trivalent ions results in $\gamma\sim-4\times10^{-4}$. This value is nearly independent of composition and agrees with

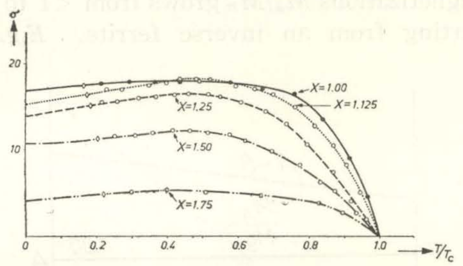

Fig. 2. Saturation magnetization per gram vs reduced temperature for the system $NiFe_{2-x}V_x0_4$ $(1<x<1.75)$. For meaning of symbols see Fig. 1.

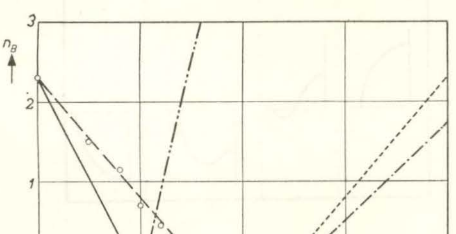

Fig. 3. Saturation moments for the system $NiFe_{2-x}V_xO_4$.

- o experimental points.
- — — — calculated for V^{3+} and Ni^{2+} ions both in octahedral sites $(x\leqq1)$.
- -·-·-·- calculated for all V^{3+} ions in octahedral sites $(x>1)$.
- - - - - - calculated for all Ni^{2+} ions in octahedral sites $(x>1)$.
- ——— calculated for Fe^{2+} and V^{4+} ions, both in octahedral sites $(0<x<0.5)$,
- ······· calculated for all V^{4+} in octahedral sites $(0.5<x<1)$.
- -··-··- calculated for all Fe^{2+} in octahedral sites $(0.5<x<1)$.

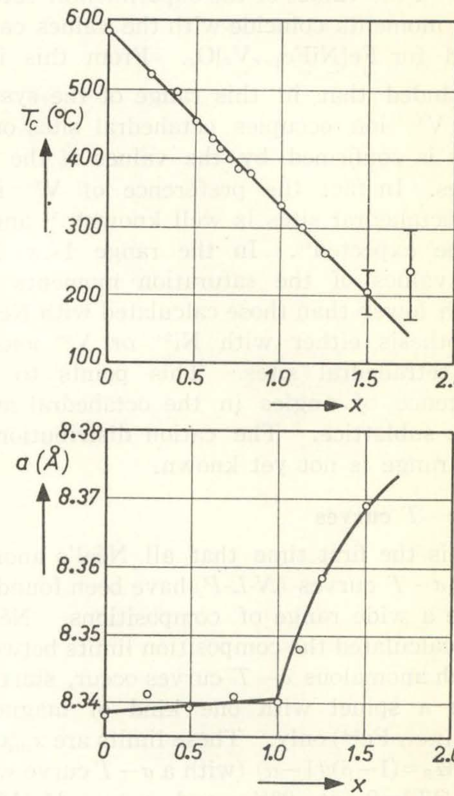

Fig. 4. Curie temperatures and cell edges for the system $NiFe_{2-x}V_xO_4$.

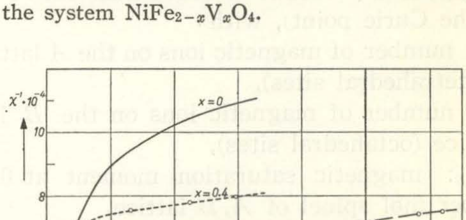

Fig. 5. Reciprocal susceptibility per gram vs reduced temperature for the system $NiFe_{2-x}V_xO_4$.

the Néel values. Another argument for the presence of trivalent ions is found in the saturation moments (Fig. 3).

b. Saturation moments

It is seen from Fig. 3 that in the range $0<x<1$ the values of the experimental saturation moments coincide with the values calculated for $\underset{\rightarrow}{Fe}[\underset{\leftarrow}{Ni}\underset{\leftarrow}{Fe}_{1-x}\underset{\leftarrow}{V}_x]O_4$. From this it is concluded that in this range of the system the V^{3+} ion occupies octahedral sites only. This is confirmed by the values of the cell edges. In fact the preference of V^{3+} ions for octahedral sites is well known[2),3)] and is to be expected[4)]. In the range $1<x<1.75$ the values of the saturation moments are much lower than those calculated with Néel's hypothesis either with Ni^{2+} or V^{3+} ions in the tetrahedral sites. This points to the existence of angles in the octahedral magnetic sublattice. The cation distribution in this range is not yet known.

c. $\sigma-T$ curves

It is the first time that all Néel's anomalous $\sigma-T$ curves (*N-L-P*) have been found in quite a wide range of compositions. Néel[5)] has calculated the composition limits between which anomalous $\sigma-T$ curves occur, starting from a spinel with one kind of magnetic ions (i.e., Fe^{3+}) only. These limits are $x_A/x_B=M_A/M_B=(1-\beta)/(1-\alpha)$ (with a $\sigma-T$ curve with $\partial^2 M_s/\partial T^2=0$ at 0°K) and $x_A/x_B=M_A/M_B=(1+\beta)/(1+\alpha)$ (with a $\sigma-T$ curve with $\partial M_s/\partial T=0$ at the Curie point), with

x_A: number of magnetic ions on the *A* lattice (tetrahedral sites),

x_B: number of magnetic ions on the *B* lattice (octahedral sites),

$M_{A,B}$: magnetic saturation moment at 0°K per mol spinel of *A*, *B* lattice,

α: ratio of the *AA* and *AB* interactions,

β: ratio of the *BB* and *AB* interactions.

α and β are negative for antiferromagnetic interactions. The latter limit corresponds with an anomalous $\chi^{-1}-T$ curve also. Our experimental $\chi^{-1}-T$ curve for $x=0.5$ looks like the one predicted by Néel.

Nearly all solid solution series in which anomalous $\sigma-T$ curves occur contain more than one kind of magnetic ions. Introducing certain approximations (that $\alpha=0$, that $g=2$ for all magnetic ions present and that the sublattice magnetizations vary with temperature according to a Brillouin function) it was possible to generalize Néel's calculations for the composition limits between which anomalous $\sigma-T$ curves occur to spinels with more than one kind of magnetic ions. The results are nearly the same as those given by Néel.

In a solid solution series in which all types of anomalous $\sigma-T$ curves occur, the saturation magnetization at 0°K always passes through zero, *i.e.*, the ratio of the sublattice magnetizations M_A/M_B grows from <1 to >1, starting from an inverse ferrite. *E.g.* for

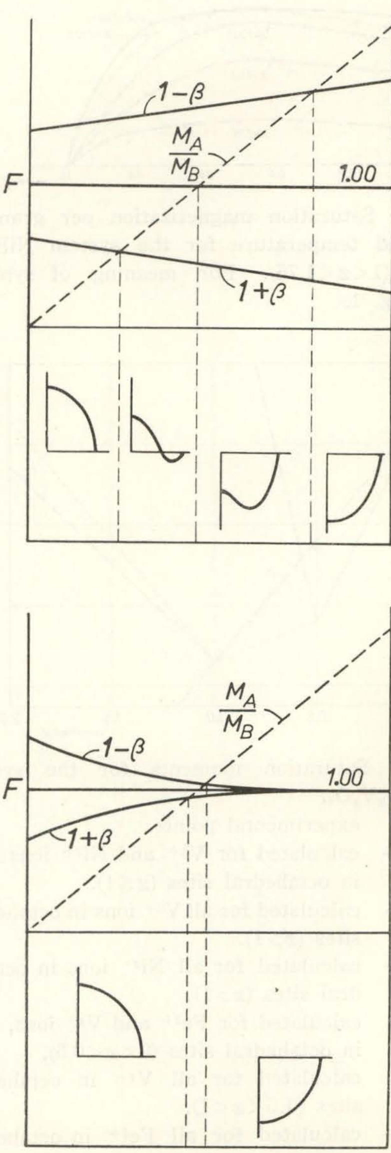

Fig. 6. See text.

$NiFe_{2-x}V_xO_4$ M_A/M_B has the values 0.69, 1.0 and 1.17 for $x=0$, $x=0.75$ and $x=1$ respectively. Remembering the limits between which anomalous curves occur, it is seen from Fig. 6 that in such a solid solution series *F-A* an increasing (or roughly constant) value of $|\beta|$ results in anomalous $\sigma-T$ curves in a wide region of compositions in the sequence *N, L, P* and that in the case of decreasing $|\beta|$ (solid solution series *F-B*) anomalous $\sigma-T$ curves can be expected in a small region of composition in the same sequence. If our approximations $\alpha=0$ or $g=2$ are not rigidly adhered to, a sequence *P, L, N* can be obtained for $|\beta|\sim 0$.

Table I shows that anomalous $\sigma-T$ curves occur in a wide composition region for ferrites with Cr^{3+} and V^{3+} substitutions and in a narrow composition region for those with Al^{3+} substitution (Fig. 7).

Table I. Range of anomalous $\sigma-T$ curves.

System	Curves $x=$	Sequence	Ref.
$NiFe_{2-x}Al_xO_4$	0.6−0.7	*P, L, N*	6)
$Li_{\frac{1}{2}}Fe_{5/2-x}Al_xO_4$	0.7−0.9	*P, L, N*	7)
$NiFe_{2-x}Cr_xO_4$	0.8−1.3	*N*	8)
$NiFe_{2-x}V_xO_4$	0.6−1.7	*N, L, P*	this work
$Li_{\frac{1}{2}}Fe_{5/2-x}Cr_xO_4$	0.9−1.8	*N*	6)

In the system $NiFe_{2-x}Al_xO_4$ the *AB* interaction will decrease with increasing x. From the small range of x in which anomalous $\sigma-T$ curves occur we can conclude, however, that β decreases also; this means that the *BB* interactions vanish with increasing x and that the Ni-Ni and Ni-Fe exchange interactions in the *B* sublattice are negligible. In the systems $NiFe_{2-x}V_xO_4$ and $NiFe_{2-x}Cr_xO_4$ anomalous $\sigma-T$ curves are found in a wide range of x, i.e., β increases with x. Now the *AB* interactions will certainly not decrease as strongly with x as in the case of Al^{3+} substitution, so that the *BB* interactions will be constant or increase with x. The Ni-Ni and Ni-Fe *BB* interactions were already found to be negligible, so there will be a certain negative *BB* interaction between V-V and Cr-Cr.

This interaction may be either of a direct type as suggested by Goodenough[9], or of a super-exchange type such as suggested by Kanamori[10].

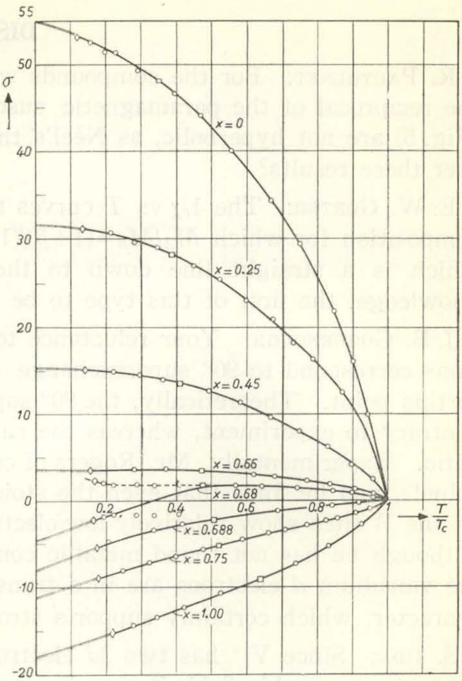

Fig. 7. Saturation magnetizations per gram vs reduced temperature for the system $NiFe_{2-x}Al_xO_4$ ($0\leqq x\leqq 1$).
○ experimental points.
◇ idem at liquid oxygen temperature.
□ idem at room temperature.

A paper giving a more detailed account of the present considerations is in preparation.

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DISCUSSION

R. PAUTHENET: For the compounds with $x=0.4$, $x=0.5$ and $x=0.6$, the variations of the reciprocal of the paramagnetic susceptibility as a function of the temperature (Fig. 5) are not hyperbolic, as Néel's theory predicts; have you an explanation to interpret these results?

E. W. GORTER: The $1/\chi$ vs T curves that do not look like hyperbolae occur near the composition for which $M_A/M_B=(1+\beta)/(1+\alpha)$, for which Néel predicts a $1/\chi$ vs T curve which is a straight line down to the Curie temperature. So these curves, to our knowledge, the first of this type to be reported, support Néel's theory.

J. B. GOODENOUGH: Your reluctance to comment on whether the strong V-V interactions correspond to 90° superexchange or cation-cation interactions invites a remark to this point. Theoretically, the 90° superexchange is anticipated to be ferromagnetic, contrary to experiment, whereas the cation-cation interactions would be antiferromagnetic. Experimentally, Mr. Rogers of our laboratory has been investigating vanadium spinels, and he finds that even the stoichiometric compounds that have only V^{3+} ions on the B sites show relatively low electrical resistivity and a small activation energy. Although he has not found metallic conductivity, his results definitely indicate that the vanadium d electrons are in a transition region between collective and localized character, which certainly supports strong cation-cation interactions.

S. IIDA: Since V^{3+} has two $3d$ electrons and the lowest orbital state should be degenerate in a cubic field, it may be probable that the orbital magnetic moment is not quenched on $16d$ sites. Is there any information on the magnitude of the magnetic anisotropy in these crystals and also on the induced anisotropy of them?

E. W. GORTER: We have measured the permeability versus temperature curve of $NiFe_{1.98}V_{0.02}O_4$ which shows a second hump near room temperature. This probably indicates a zero point of K_1. Single crystals are now being prepared.

J. B. GOODENOUGH: In answer to the question of Dr. Iida, I can report that preliminary measurements in our laboratory on polycrystalline materials of the anisotropy of vanadium spinels indicate that the V^{3+} ions contribute a large magnetic anisotropy, as would be anticipated from their electron configuration.