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W. Brückner, U. Gerlach, W. Moldenhauer, H.-P. Brückner, B. Thuss, et al.. METAL-NONMETAL TRANSITION IN Fe- AND Al-DOPED VO₂. Journal de Physique Colloques, 1976, 37 (C4), pp.C4-63-C4-68. 10.1051/jphyscol:1976410 . jpa-00216524

HAL Id: jpa-00216524

<https://hal.science/jpa-00216524>

Submitted on 4 Feb 2008

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METAL-NONMETAL TRANSITION IN Fe- AND Al-DOPED VO₂

W. BRÜCKNER, U. GERLACH, W. MOLDENHAUER, H.-P. BRÜCKNER,
B. THUSS (*), H. OPPERMANN, E. WOLF and I. STORBECK

Akademie der Wissenschaften der DDR,
Zentralinstitut für Festkörperphysik und Werkstofforschung, 8027 Dresden, G. D. R.

Résumé. — Les propriétés structurales, électriques, thermo-électriques et magnétiques sont déterminées dans des monocristaux des systèmes $V_{1-x}Fe_xO_2$ ($x = 0 \dots 0.035$) et $V_{1-x}Al_xO_2$ ($x \approx 0.007$) préparés par transport chimique avec $TeCl_4$. Les phases M 1, T, M 2 et R apparaissent. Les diagrammes de phases de $V_{1-x}Me_x^{3+}O_2$ (Me = Fe, Al, Ga, Cr) avec la transition semi-conducteur-semi-conducteur $T \rightarrow M 2$ et la transition semi-conducteur-métal $M 2 \rightarrow R$ sont comparés. Les propriétés électriques et thermo-électriques des systèmes étudiés dans les phases semi-conductrices sont déterminées par la mobilité très faible des trous dans la bande 3 d du V pour assurer la neutralité de charge lors de la substitution de Me^{3+} . Cette mobilité est anisotrope et elle conduit particulièrement à l'anisotropie du pouvoir thermo-électrique.

Abstract. — The structural, electric, thermoelectric and magnetic properties were studied on monocrystals of the systems $V_{1-x}Fe_xO_2$ ($x = 0 \dots 0.035$) and $V_{1-x}Al_xO_2$ ($x \approx 0.007$) produced by chemical transport with $TeCl_4$. The phase M 1, T, M 2 and R arise. The phase diagrams of $V_{1-x}Me_x^{3+}O_2$ (Me = Fe, Al, Ga, Cr) with the semiconductor-semiconductor transition $T \rightarrow M 2$ and the semiconductor-metal transition $M 2 \rightarrow R$ are compared. The electric and thermoelectric properties of the systems investigated in the semiconducting phase are determined by the very low mobility of the holes formed in the V-3 d electron system for charge neutrality after the substitution of Me^{3+} . This mobility is anisotropic and leads particularly to the anisotropy of the thermoelectric power.

1. Introduction. — Doped VO₂ is being comprehensively investigated (see e. g. [1]) owing to its importance in clarifying the electronic and crystallographic properties of vanadium dioxide in connection with the semiconductor-metal transition. Doping with 3-valent ions has gained special interest because several semiconducting, crystallographic differing phases M 1, T and M 2 arise. The investigations include Cr^{3+} [2, 3], Ga^{3+} [4], and recently also Fe^{3+} [5-8], and Al^{3+} [9, 10]. This contribution is concerned with our results of electric, thermoelectric, magnetic and structural studies carried out on the systems $V_{1-x}Fe_xO_2$ and $V_{1-x}Al_xO_2$. The characteristic point about these studies was that monocrystalline samples were used.

2. Preparation. — As already described for the systems $V_{1-x}Ga_xO_2$ [4] and $V_{1-x}Al_xO_2$ [10], the monocrystals $V_{1-x}Fe_xO_2$ and $V_{1-x}Al_xO_2$ were prepared by chemical transport with $TeCl_4$ in sealed quartz ampoules at temperatures around 1 000 °C. The initial mixtures, consisting of high-pure oxides $V_2O_3/V_2O_5/Me_2O_3$ (Me = Fe, Al) and with a summary composition $V_{1-x}Me_xO_{2.00-2.02}$, were annealed in vacuum. The homogeneous starting products were

then formed at reversed transport gradient (temperature T_2 at the resolution zone smaller than the temperature T_1 at the crystallization zone). Transport was carried out at temperatures of $T_2 = 1\ 100$ °C to $T_1 = 900$ °C with a transport agent concentration of approximately 7 mg $TeCl_4$ /ml over a period of three to four days. In both transport systems only the $V_{1-x}Me_xO_2$ phase having an oxygen content at the upper phase limit of the vanadium dioxide ($VO_{2.002 \pm 0.002}$ [11, 12]) was obtained on the growth zone, although a limited solubility of the dopant in VO₂ was observed at $V_{1-x}Al_xO_2$, similar to $V_{1-x}Ga_xO_2$. In the system $V_{1-x}Fe_xO_2$ crystals of up to about $x = 0.035$ were grown on the crystallization zone at Fe_2O_3 weighed-in contents of up to 10 mol %. The entire range of solubility of aluminium was not studied in the system $V_{1-x}Al_xO_2$. Only samples having a weighed-in concentration of 1.2 and 5 mol % Al_2O_3 were produced where crystals having a content of about $x = 0.006$ and $x = 0.008$, respectively, grew on the crystallization zone. The transport rates decreased from about 12 mg/h (for $x_{Fe} = 0.01$) to about 4 mg/h (for $x_{Fe} = 0.03$) with the rising doping level, and this was accompanied with a reduction of the crystal size.

The Fe and Al contents were determined by activation analysis, while the content of oxygen (stoichio-

(*) Technische Universität Dresden, Sektion Physik, 8027 Dresden, G. D. R.

metry) was determined thermogravimetrically. The tellurium content of the crystals was analyzed and amounted to $< 1\ 000$ ppm. Figure 1 shows a few crystals of Fe-doped (a) and Al-doped (b) VO_2 .

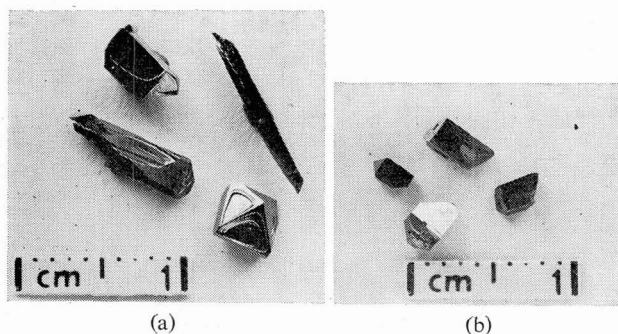


FIG. 1. — Single crystals of $\text{V}_{1-x}\text{Fe}_x\text{O}_2$ (a, $x = 0.03$) and $\text{V}_{1-x}\text{Al}_x\text{O}_2$ (b, $x = 0.007$).

3. Experiments. — The transition temperatures between the phases T-M 2 and M 2-R were determined by establishing the holding point of a small, powdered sample with an embedded copper-constantan thermocouple while heating or cooling. To establish the transition temperature between the phases M 1 and T the splitting of the pseudo-(110)-rutile-reflection in the monoclinic and triclinic low-temperature phases was determined with powdered monocrystals by the X-ray diffractometer HZG 3 using Cu-K_α radiation.

The resistivity was measured preferably in the direction of the pseudo-rutile-a-direction with the help of four tungsten probes sprung-mounted at a spacing of about 0.3 mm on the pseudo-(111)-rutile face.

In order to determine the thermoelectric power the monocrystals were clamped between copper blocks where a temperature difference of about 5 K was maintained.

The magnetic susceptibility was measured by the Faraday method in a LINSEIS apparatus on a larger number of monocrystals (isotropic mean value). The measurements carried out on individual crystals revealed no significant anisotropy.

More detailed information on the experimental conditions was given in an earlier paper of ours [12].

4. Results. — First of all we shall give some details on the phase diagrams, although the measurements of the electric and magnetic properties described further on were also used to determine the phase transitions. Guinier diagrams have confirmed that the monoclinic phases M 1 and M 2, the triclinic phase T, and the tetragonal phase R (rutile type) arise in both systems $\text{V}_{1-x}\text{Fe}_x\text{O}_2$ and $\text{V}_{1-x}\text{Al}_x\text{O}_2$. At first these different phases were studied and described on Cr-doped VO_2 [13, 2]. Figure 2a shows the phase diagram for $\text{V}_{1-x}\text{Fe}_x\text{O}_2$ established during heating. The slope of the phase limits are: $\Delta T_i(\text{M } 1 \rightarrow \text{T})/\Delta x \approx -450 \text{ K}/0.01$ and $\Delta T_i(\text{T} \rightarrow \text{M } 2)/\Delta x = -32 \text{ K}/0.01$ for $x \leq 0.02$. The transition temperatures during heating (\uparrow) and

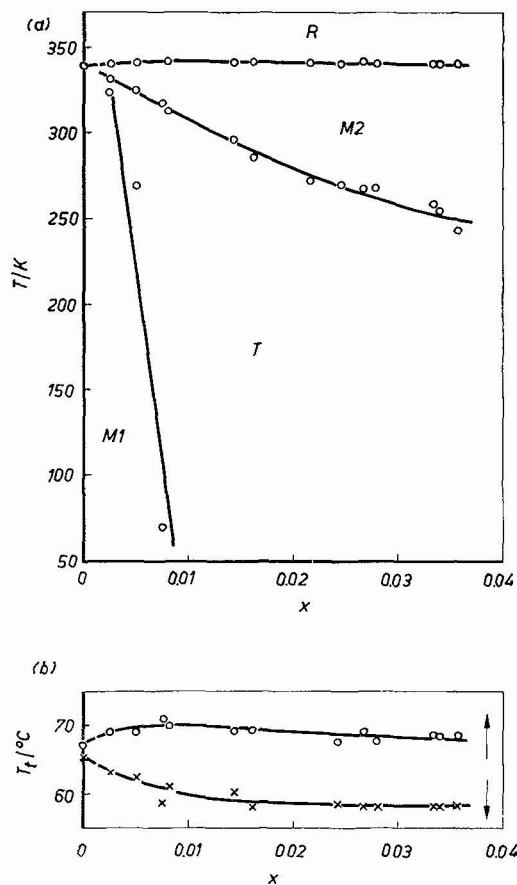


FIG. 2. — Phase diagram (a) and semiconductor-metal transition temperature (b) of $\text{V}_{1-x}\text{Fe}_x\text{O}_2$.

cooling (\downarrow) are shown in figure 2b for the semiconductor-metal transition $\text{M } 2 \rightarrow \text{R}$. For small x values (up to $x \approx 0.01$) T_t (\uparrow) rises to about $70 \text{ }^\circ\text{C}$, and then drops down again to $68 \text{ }^\circ\text{C}$. We were able to confirm this behaviour by measurements on a few sintered samples and on samples which are with certainty at the upper limit of the homogeneity range by a special oxidation treatment. Shortly before this paper Kosuge *et al.* [8] carried out measurements on powder samples and published the phase diagram of $\text{Fe}_x\text{V}_{1-x}\text{O}_2$ in the range $0 \leq x \leq 0.25$ which conforms for small x with our results. We want to add that the T-phase appears on the sample with $x = 0.0025$ in the temperature range of $51 \text{ }^\circ\text{C}$ to $59 \text{ }^\circ\text{C}$ because the presence of this phase in a similar sample in [8] could not be definitely established. Doping produces a hysteresis of about 10 K for the M 2-R transition.

The complete phase diagram of $\text{V}_{1-x}\text{Al}_x\text{O}_2$ cannot be given on the basis of our measurements on monocrystals. Studies on a few sintered samples have indicated, however, that the phase diagram of $\text{V}_{1-x}\text{Al}_x\text{O}_2$ has great quantitative similarity with $\text{V}_{1-x}\text{Ga}_x\text{O}_2$ [4].

The temperature dependence of the resistivity ρ during the first heating cycle is shown in figure 3. Doping with Fe and Al maintains a resistivity jump of about 4 orders of magnitude at the semiconductor-

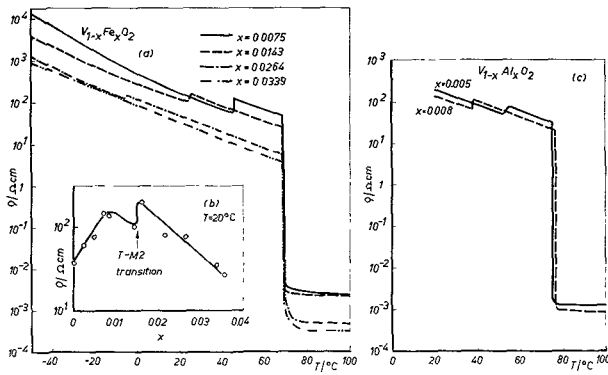


FIG. 3. — Resistivity of $V_{1-x}Fe_xO_2$ (a, b) and $V_{1-x}Al_xO_2$ (c) in dependence on temperature and concentration.

metal transition. At the semiconductor-semiconductor transition $T \rightarrow M2$ ρ increases by a maximum factor of 2 (at T_t ($T-M2$) ≈ 50 °C) without a noticeable change of the activation energy of ≈ 0.35 eV (between 20 and 60 °C). It can be seen that in the system $V_{1-x}Fe_xO_2$ the resistivity jump at the transition $T \rightarrow M2$ decreases with increasing x , and practically disappears at $x = 0.034$. In the metallic range the resistivity is about 10^{-3} Ω cm. The measured differences for the various samples are not typical and are probably due to crystal imperfections (particularly cracks arising at the semiconductor-metal transition). The concentration dependence of the room temperature resistivity for $V_{1-x}Fe_xO_2$ is shown in figure 3b. The drop above $x \approx 0.01$ by nearly one order of magnitude is noticeable. The jump at $x \approx 0.015$ is caused by the change of the stable phase from $M2$ to T at room temperature (see Fig. 2).

The results of the measurement of the thermoelectric power S (measured against copper) are shown in figure 4. Figure 4a gives for $V_{1-x}Fe_xO_2$ and a

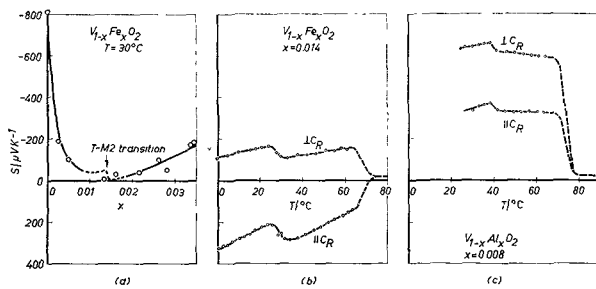


FIG. 4. — Thermoelectric power of $V_{1-x}Fe_xO_2$ (a, b) and $V_{1-x}Al_xO_2$ (c) in dependence on concentration and temperature for different crystallographic directions (c_R -pseudo rutile c axis).

measuring temperature of 30 °C the isotropic mean value of S which was established as the mean value of several crystals and of several directions. A remarkable fact is the change to more positive values (decrease of the negative thermopower) by doping with Fe in comparison with pure VO_2 . Above $x \approx 0.01$ the thermoelectric power rises again to more negative values. The jump at $x \approx 0.015$ is

expected because of the change of the stable phase at 30 °C (as at the ρ (20 °C) curve in figure 3b).

Measurements of the anisotropy of the thermoelectric power carried out on some larger crystals of the system $V_{1-x}Fe_xO_2$ have indicated (see Fig. 4b) that the thermoelectric power parallel to the pseudo-rutile- c -direction (c_R) is larger (more positive) by 200 to 400 μ VK⁻¹ than perpendicularly to this axis. It also acquires positive values, e. g. for $V_{0.986}Fe_{0.014}O_2$ in figure 4b. With the phase transition $T \rightarrow M2$ a discontinuity of the thermoelectric power of about 50 to 100 μ VK⁻¹ to more positive values arises, essentially without a change of the slope $\Delta S/\Delta T$, which is negative for Fe-doped VO_2 . Above the semiconductor-metal transition the thermoelectric power in the doped samples behaves just as pure VO_2 and amounts to about $-20 \dots -25$ μ VK⁻¹. The dotted parts of the curves of figures 4b and 4c correspond to the results measured on other crystals of the same concentration x .

The thermoelectric power for Al-doped VO_2 (Fig. 4c) is anisotropic in the same manner as for Fe-doped VO_2 , except that the values at the same x are not so markedly shifted to the positive. Discontinuities, usually to more positive values, were measured at the phase transition $T \rightarrow M2$, but jumps to more negative values were also measured on two samples with T_t ($T-M2$) of about 50 °C. Probably, this undefined behaviour is the reason why Villeneuve *et al.* [10] could not establish a change of the thermoelectric power at the phase transition $T \rightarrow M2$ for their

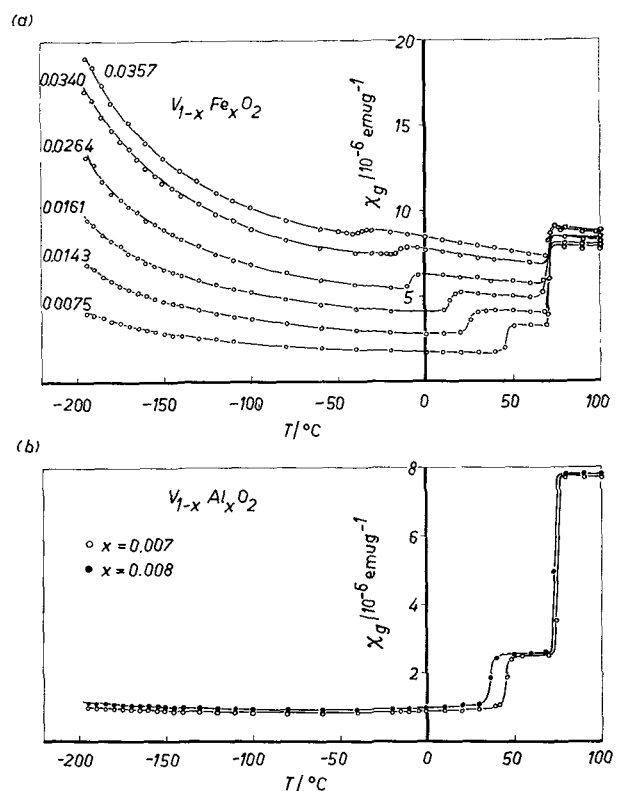


FIG. 5. — Temperature dependence of the magnetic susceptibility of $V_{1-x}Fe_xO_2$ and $V_{1-x}Al_xO_2$ (parameter x).

$V_{0.387}Al_{0.013}O_2$ sample. Thermopower measurements of Ga-, Fe- and Al-doped VO_2 will be described and discussed in detail in a subsequent paper.

The temperature dependence of the magnetic susceptibility is shown in figure 5. Two phase transitions can be clearly seen, $T \rightarrow M2$ at the lower temperature and $M2 \rightarrow R$ at the higher temperature. All samples shown in figure 5 remained in the T-phase down to nitrogen temperature, as was indicated by X-ray investigations. The pronounced paramagnetism in the semiconducting phase of $V_{1-x}Fe_xO_2$ is due to the contribution of the Fe^{3+} ions having a moment of $5.92 \mu_B$. The contribution, which must be attributed to the VO_2 lattice-electron system, is concealed in this system, while it arises unfalsified in the system $V_{1-x}Al_xO_2$.

5. Discussion. — In order to maintain the neutrality of the lattice the substitution of one Fe^{3+} or Al^{3+} ion must result in the formation of one V^{5+} ion and thus a hole in the V-3 d band. This hole can be either bound to the Me^{3+} (formation of a $Me^{3+}-V^{5+}$ pair), or mobile in the metal sublattice and then contribute to the conductivity. The predominant bonding in $Me^{3+}-V^{5+}$ pairs, as they are present in the lattice, can be excluded because of the paramagnetism of Al-doped VO_2 (in the T phase), as was already discussed with Ga-doped VO_2 [4]. The conductivity values without strong changes in the semiconducting state compared with pure VO_2 mean that the mobility of the holes must be very small. The electric transport contribution of the holes, however, cannot be neglected, as is clearly proved by the occurrence of positive values of thermoelectric power. The anisotropy of S with more positive values in the c_R direction means that the holes in the chains parallel to the c_R direction have a greater mobility than perpendicularly to this axis.

In the system $V_{1-x}Fe_xO_2$ the resistivity at room temperature decreases above $x \approx 0.01$ and the thermoelectric power goes to more negative values. This must be considered as a rise of the conductivity contribution of the mobile electrons, where the rise is mainly due to an increase of the electron concentration and not of the mobility. This behaviour is unexpected. It points to changes in the band structure or to a portion of interstitial metal ions. The latter would correspond to a very small shift of the upper phase boundary to oxygen deficiency with Fe-doping, resulting in the production of additional electrons [12]. The decrease of $T_i(M2-R)$ above $x \approx 0.01$ is doubly connected with this because the creation of electrons and holes in VO_2 indicates opposite behaviour regarding the semiconductor-metal transition temperature [14].

A remarkable point at Fe-doped VO_2 is that the semiconductor-metal transition temperature $T_i(M2-R)$ does not exceed $70^\circ C$ compared with other $V_{1-x}Me_x^{3+}O_2$ systems, and above $x \approx 0.01$ it even

decreases again, while the semiconductor-semiconductor transition temperature $T_i(T-M2)$ declines uniformly in all systems (also Fe-doped VO_2). In all systems the slope amounted to

$$\Delta T(T-M2)/\Delta x \approx -35 \text{ K}/0.01$$

(see also [2, 4, 7, 8]). It follows that other factors are decisive for the stabilization of the phase M2 over R through Me^{3+} -doping than for the destabilization of the T-phase over the M2 phase with increasing x so that the behaviour of these phase boundaries is not rigidly linked to one another.

The magnetic properties of $V_{1-x}Al_xO_2$ are similar to those of Ga-doped VO_2 [4]. In the T phase the susceptibility can be resolved into $\chi = \chi_0 + \frac{C}{T}$ (Fig. 6b) with $\chi_0 \approx 0.75 \times 10^{-6} \text{ emug}^{-1}$, as is mea-

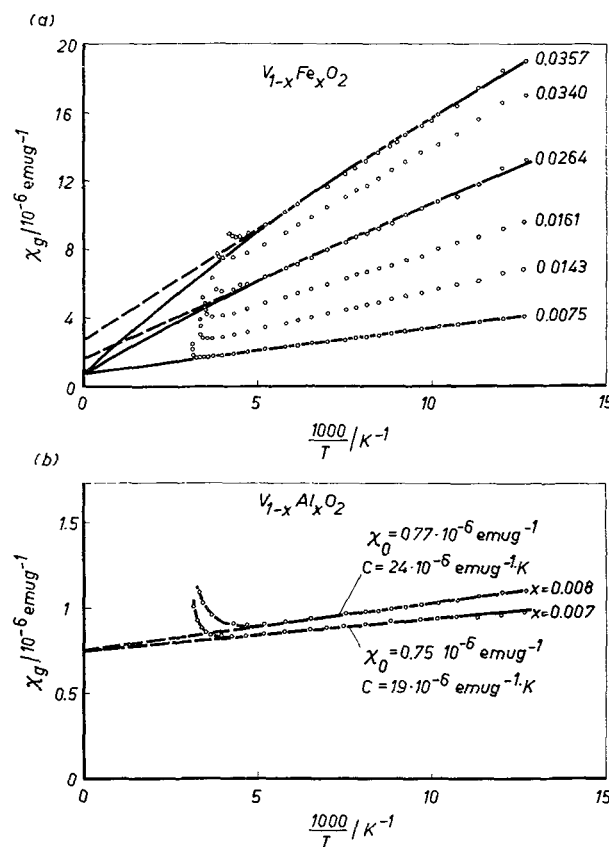


FIG. 6. — Magnetic susceptibility vs. reciprocal temperature of $V_{1-x}Fe_xO_2$ and $V_{1-x}Al_xO_2$ for the T-phase.

sured for pure VO_2 . The term C/T arises as result of $Al^{3+} - V^{4+}$ and $V^{4+} - V^{5+}$ pairs, each with $S = \frac{1}{2}$, whereas no moment is to be expected for $Al^{3+} - V^{5+}$ pairs. An estimate indicates that in the picture above rough the half of the holes are not encountered in $Al^{3+} - V^{5+}$ pairs in the temperature range 77 K-200 K. The same susceptibility of $\chi \approx 2.5 \times 10^{-6} \text{ emug}^{-1}$ as measured for the M2 phase in Al-doped VO_2 as in Ga-doped VO_2 [4]. Pouget *et al.* [3] have shown for $V_{1-x}Cr_xO_2$ that the

magnetic properties of the M 2 phase can be described by linear Heisenberg chains with antiferromagnetic interaction. This also applies to the Al-doped VO₂ and the Fe-doped VO₂ (see below) and underlines the discussion of Pouget *et al.* [3] as to the importance of the intra-atomic electron correlation.

The magnetic susceptibility of V_{1-x}Fe_xO₂ vs. the reciprocal temperature is represented in figure 6a. The curves are fitted to a dependence of

$$\chi = \chi_0 + C/(T - \theta).$$

The established parameters θ , C and χ_0 are listed in table I.

One receives for $\theta \approx 0$, for χ_0 increasing values with rising concentrations, and for the Curie constants C values which are about 30 % below those to be expected as a result of the analyzed Fe³⁺ concentration ($C_{conc.}$ in table I). This discrepancy was also established by Pollert *et al.* [7]. If χ_0 is kept to the value for pure VO₂ ($= 0.75 \times 10^{-6} \text{ emug}^{-1}$), a reasonable fit is also obtained (see the full line curves in figure 6a; sum of error squares larger by about the factor 2 in comparison to the case with fitted χ_0). The Curie constants then conform satisfactorily with the expected values (see table I). The Curie-Weiss temperatures are negative and indicate an antiferromagnetic interaction between the V-ions. This does not come unexpectedly because antiferromagnetic interactions exist also in the M 2 phase. Magnetic measurements below 77 K could show whether this interpretation is correct. Using the χ_0 and the Curie contribution of the fit (2) with the fixed χ_0 , one receives for the M 2 phase at 60 °C for

$$\delta\chi = \chi - \left(\chi_0 + \frac{C}{T - \theta} \right)$$

the values that are listed in table I ($\approx 1.7 \times 10^{-6} \text{ emug}^{-1}$). Apart from a small dependence on the concentration the $\delta\chi$ conforms well for Ga-[4], Al-, Fe- and Cr-[3] doped VO₂ and amounts to about $1.7 \times 10^{-6} \text{ emug}^{-1}$. This indicates that the antiferromagnetic interaction J in the linear Heisenberg chains [4] is practically of the same magnitude, independent of the doping element, and amounts to $J \approx k.360 \text{ K}$.

A comparison of our results gained from V_{1-x}Fe_xO₂ and V_{1-x}Al_xO₂ samples, and the results from Ga- [4] and Cr- [2, 3] doped VO₂ show that on these systems containing substituted 3-valent ions there is a far-reaching similarity of the phase diagrams and of the electric, thermoelectric and magnetic properties. The characteristic point about these phases is the presence of holes in the V-3d electron system which determines to a major extent especially the electrical transport properties. In the presence of excessive electrons in VO₂ (e. g. due to doping with Mo⁶⁺ or due to nonstoichiometry) other behaviour arises [15, 14]. We are convinced that the holes in the VO₂ electron system also determine decisively the crystallographic modifications. The relations, however, are still unclear.

The phase boundaries in all systems with 3-valent doping elements, which produce the same hole concentration per x , goes quantitatively nearly conform. The question whether the hole concentration really determines the position of the phase boundaries should be studied by doping of VO₂ with the 2-valent Zn²⁺. Efforts to produce monocrystalline (by chemical transport) and polycrystalline V_{1-x}Zn_xO₂ samples have shown unfortunately that no ZnO can be dissolved in VO₂ and, therefore, no influence on the properties could be measured.

TABLE I

Parameters of the magnetic susceptibility of V_{1-x}Fe_xO₂

x	C _{conc} [10 ⁻⁶ emug ⁻¹ K]	Fit (1)			Fit (2)		δχ (60 °C) [10 ⁻⁶ emug ⁻¹]
		χ = χ ₀ + $\frac{C}{T - \theta}$			χ = 0.75 × 10 ⁻⁶ emug ⁻¹ + $\frac{C}{T - \theta}$		
		χ ₀ [10 ⁻⁶ emug ⁻¹]	C [10 ⁻⁶ emug ⁻¹ K]	θ [K]	C [10 ⁻⁶ emug ⁻¹ K]	θ [K]	
0.007 5	385	0.84	244	4.5	272	- 3.4	1.73
0.014 3	744	1.02	469	- 2.9	545	- 13.0	1.72
0.016 1	827	1.72	586	4.9	859	- 20.5	1.78
0.026 4	1 356	2.18	768	9.2	1 171	- 19.5	1.77
0.034 0	1 747	2.00	1 218	- 1.5	1 424	- 23.2	1.70
0.035 7	1 834	3.01	1 227	3.2	1 832	- 23.0	1.59

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