

An NMR Analysis of Transitions in VO₂:Al*

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The nuclear magnetic resonance (NMR) spectra of ⁵¹V in V_{1-x}Al_xO₂ (0 ≤ x ≤ 0.038) has been determined as functions of Al concentration and temperature. The results which are in agreement with differential thermal analysis (DTA), dc electrical conductivity and 6328 Å optical reflectance, indicate that the temperature vs Al concentration phase diagram is similar to that previously proposed for Cr-doped VO₂. Comparison of the asymmetry parameters (η) in the electric field gradient and the quadrupole coupling constants (ν_Q) show that there exist three distinct phases below the semiconductor to metal (SM) transition temperature. At low Al concentrations ($x < 0.02$) and low temperatures, the structure may be identified as that of the semiconducting phase of pure VO₂ (Phase I). The *T*-phase previously reported in pure VO₂ is shown to be the phase occurring just below the SM transition temperature (Phase III). A previously unreported phase (Phase II) exists for $x > 0.02$ at temperatures between Phases I and III regions.

Introduction

The study of impurity-doped vanadium dioxide is of great interest because it is expected to lead to a better understanding of the semiconductor to metal (SM) transition which occurs at 340°K (1). This transition represents a conductivity change of almost five orders of magnitude. Examples of the effects of impurities on the transition are illustrated in Fig. 1, where the conductivities of tungsten and aluminium-doped VO₂ are compared with that of the pure material. Tungsten is representative of a class of impurities like Mo, Nb, Mn, etc., which lowers the transition temperature (T_t) (2-8). The conductivity in the low temperature phase is raised resulting in a smaller discontinuity at the transition. In contrast, aluminium belongs to another class of impurities like Cr, Ga, Ge, etc., which raise T_t (6-13). No remarkable change in the conductivity of the semiconducting phase is observed. The lower conductivity in the metallic phase may be attributed to the

development of cracks during the SM transition (14). In general, intermediate crystal phases are stabilized by this class of impurities (7-12). Such effects could be used to explain the minor semiconductor to semiconductor transitions observed in Al-doped VO₂ below T_t . This is shown in the inset of Fig. 1. The minor transition involves a decrease of the conductivity by a factor of a half without any apparent change in the activation energy. Measurements on Cr, Zr and Ti impurities show the same behavior.¹ Similar results have been reported earlier for Ti-doped VO₂ (15). This minor transition is greatly broadened in polycrystalline samples and overall results differ from those previously reported for Cr-doped VO₂ (9).

Various theoretical models have been proposed to explain the SM transition in VO₂ but none have been satisfactory, particularly with regard to the mechanisms of impurity effects (16-18). Only Goodenough has attempted to include these effects in a consistent model (7). He recognized that there are inherently

¹ A discussion of these and other experiments mentioned here will be given in a later publication.

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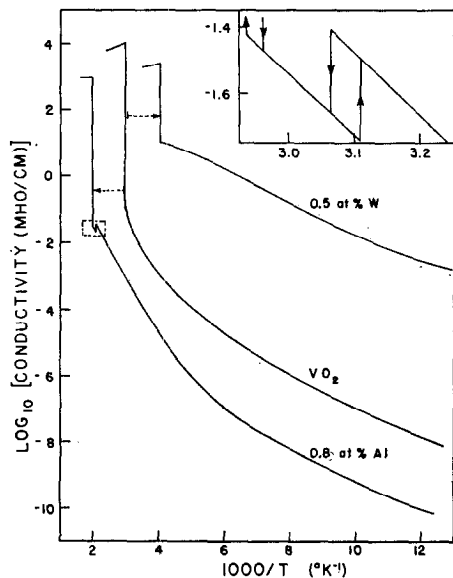


FIG. 1. Temperature dependence of the dc conductivity of pure and doped (aluminium and tungsten) VO_2 . Curves for Al and W dopings are shifted by one unit along the $1000/T$ axis as indicated by dashed arrows. The inset shows details of the minor semiconductor to semiconductor transition in Al-doped VO_2 .

two components in the transition in pure VO_2 . One of these corresponds to the shift of the vanadium ions inside their respective oxygen octahedron giving rise to an antiferroelectric type anomaly at T_f . The other component is the formation of homopolar bonds between vanadium ion pairs at T'_f . In pure VO_2 , T_f and T'_f are equal but the addition of impurities such as Cr, Al and Fe lowers T'_f , such that two distinct transitions may be experimentally observed. The minor transitions observed in the Al class of impurities would appear to agree with this interpretation. However, it was subsequently pointed out that at least two other phases exist below T_f in $\text{V}_{1-x}\text{Cr}_x\text{O}_2$ for $x < 0.05$ (10). Since Al impurities have been found to have similar effects on the SM transition as Cr, we would expect to see similar crystal phases induced in the $\text{V}_{1-x}\text{Al}_x\text{O}_2$ system. X-ray crystallographic analysis is difficult because of the minute differences between the crystal structures of the various phases (10). However, we have found that nuclear mag-

netic resonance (NMR) using the ^{51}V nucleus is a sensitive tool to differentiate between them. This technique yields values of the nuclear quadrupole coupling constant (ν_Q), the asymmetry parameter (η) of the electric field gradient (efg) and the principal values of the chemical shift tensor ($\sigma_1, \sigma_2, \sigma_3$) at the vanadium site. The asymmetry parameter is a measure of the site symmetry of the vanadium nuclear site. These parameters are sensitive to crystal and electronic structures surrounding the vanadium nucleus and small relative shifts in the atomic positions can be detected.

Experimental Results

Phase transitions may be detected by small changes occurring in the NMR spectra as functions of temperature during heating and cooling. The temperature intervals during heating where these transitions occur are shown in Fig. 2. The mean heating transition temperatures taken from measurements of dc conductivity, differential thermal analysis

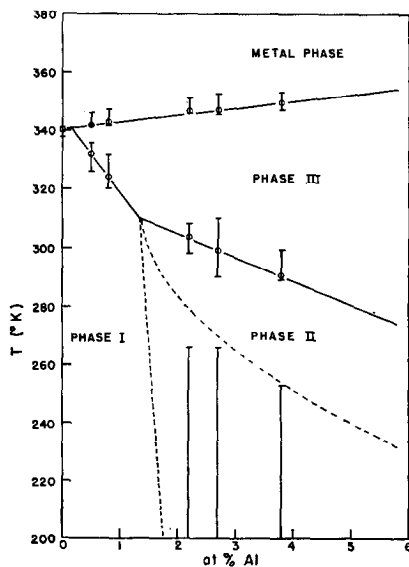


FIG. 2. Transition temperature vs composition diagram for $\text{V}_{1-x}\text{Al}_x\text{O}_2$. Bars are temperature intervals where transitions are observed in NMR. Open circles are mean transition temperature as measured by dc conductivity, differential thermal analysis, and 6328 Å optical reflectance. The multiphase region between dashed curves extend to 77°K.

(DTA), and 6328 Å optical reflectance are included in the diagram. Thermal hysteresis of the order of a few degrees is observed. At 280°K, the NMR spectra for two samples containing 0.5 and 0.8 at% Al are similar to that of pure VO₂ below T_i . This region is labelled Phase I in Fig. 2. As the temperature is increased, the spectrum changes to one with a smaller quadrupole splitting and at still higher temperatures, the transition to the corresponding metallic phase of pure VO₂ is finally observed. The intermediate phase is labelled Phase III. For Al concentrations greater than 2 at%, the same sequence of transitions to Phase III and the metallic phase is observed on increasing temperature. However, the spectra at 280°K are different from that of pure VO₂ and as the temperature is decreased, a very broad transition is observed to one which may be identified with the pure VO₂ spectrum. At 77°K, this transition is still surprisingly incomplete. The latter intermediate structure is called Phase II. It is evident from the diagram that the minor semiconductor to semiconductor transitions observed in dc conductivity may be identified with the transitions from Phases I and II to Phase III.

In order to demonstrate the differences

between the three phases observed below the SM transition, the respective NMR parameters were measured at $T = 285$ and 310°K. At these temperatures we expect to see transitions from Phase I to Phases II and III as the Al concentration is increased from 0.8 to 2.2 at%. The results are listed in Table I. Measurements made at room temperature (~300°K) and at 335°K (for 0.8 at% Al) are included for comparison. The values obtained for pure VO₂ are in good agreement with earlier polycrystalline and single crystal data (19-22).

In Fig. 3, η and ν_Q are plotted against Al concentration. An interesting result is that even in Phase I, the addition of Al appears to change ν_Q and η significantly. Instead of the abrupt change expected between 0.8 and 2.2 at% Al, a gradual change at low Al concentration is observed which appears to level off at 2.2 at%. Because of the larger experimental errors involved in the measurement of η , comparison of ν_Q seems to be a better means of differentiating between Phases I, II, and III. The room temperature values given in Table I show that 0.5 and 0.8 at% Al samples are in Phase I, 2.2 and 2.7 at% Al are in Phase II and 3.8 at% Al in Phase III. In addition, the 0.8 at% Al sample is verified to be in Phase III at 335°K.

Table I

Experimental values of nuclear quadrupole coupling constant ν_Q , asymmetry parameter (η) and principal value of chemical shift tensor ($\sigma_1, \sigma_2, \sigma_3$) for ⁵¹V in Al-doped VO₂.

Sample	T(°K)	ν_Q (MHz)	η	σ_1 (%)	σ_2 (%)	σ_3 (%)
VO ₂	285	0.480±0.018	0.475±0.053	-0.34	-0.32	-0.16±0.07
	300	0.487±0.006	0.485±0.042	-0.28	-0.32	-0.16±0.02
	310	0.500±0.020	0.491±0.050	-0.15	-0.32	-0.18±0.05
V _{0.995} Al _{0.005} O ₂	285	0.473±0.020	0.458±0.072	-0.34	-0.31	-0.16±0.04
	300	0.464±0.008	0.492±0.029	-0.32	-0.32	-0.11±0.01
	310	0.481±0.012	0.497±0.068	-0.22	-0.31	-0.19±0.02
V _{0.992} Al _{0.008} O ₂	285	0.453±0.022	0.547±0.056	-0.32	-0.29	-0.16±0.09
	300	0.452±0.007	0.529±0.049	-0.21	-0.31	-0.19±0.01
	310	0.450±0.009	0.595±0.045	-0.18	-0.33	-0.18±0.02
	335	0.339±0.008	0.680±0.020	-0.29	-0.27	-0.20±0.02
V _{0.978} Al _{0.022} O ₂	285	0.407±0.001	0.629±0.024	-0.21	-0.29	-0.17±0.02
	300	0.396±0.010	0.629±0.023	-0.18	-0.31	-0.16±0.03
	310	0.347±0.005	0.712±0.049	-0.24	-0.30	-0.20±0.01
V _{0.973} Al _{0.027} O ₂	285	0.387±0.012	0.609±0.040	-0.22	-0.29	-0.13±0.02
	300	0.385±0.007	0.659±0.033	-0.25	-0.29	-0.18±0.02
	310	0.357±0.003	0.710±0.009	-0.22	-0.31	-0.22±0.01
V _{0.962} Al _{0.038} O ₂	285	0.382±0.010	0.681±0.019	-0.21	-0.30	-0.14±0.01
	300	0.367±0.004	0.720±0.019	-0.22	-0.33	-0.18±0.01
	310	0.353±0.003	0.695±0.026	-0.22	-0.30	-0.23±0.01

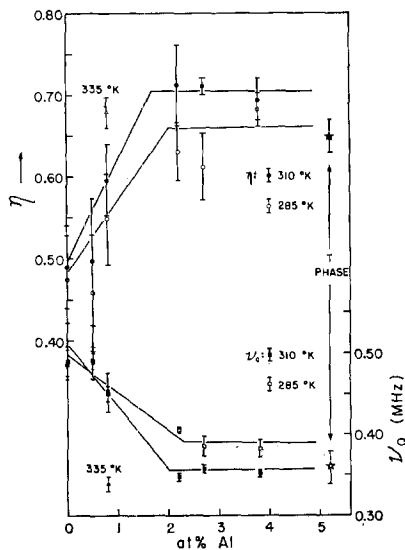


FIG. 3. Asymmetry parameter (η) of the electric field gradient and quadrupole coupling constant (ν_Q) vs composition for $V_{1-x}Al_xO_2$ at 285 and 310°K. Values obtained for 0.8 at% Al at 335°K and those quoted for T -phase are also shown. (See Ref. 22.)

Discussion

A transient T -phase has been reported earlier in NMR measurements in materials of doubtful purity (22). The values given for ν_Q and η were 0.36 ± 0.02 MHz and 0.65 ± 0.02 , respectively. These are shown in Fig. 3. Although η is closer to that of Phase II, ν_Q is the same as that of Phase III. Since values of ν_Q have been shown to be more reliable and since the temperature interval where the T -phase has been observed is just below T_t , it is reasonable to identify this transient phase with Phase III of our diagram.

It is difficult to interpret the gradual change of the efg observed in Phase I without more data in the intermediate composition range. If it is assumed that the addition of impurities like Al induces a local configuration similar to Phase III (or Phase II depending on the temperature), then the results appear more reasonable. As the impurity concentration is increased, more of the crystal will have the local configuration of Phase III. Because of the interaction of Phases III and I (or II), whether electronic or lattice type, the free energy would increase until a value is reached

where Phase III (or II) is more stable. This is probably the situation in the large multiphase region at low temperatures and high Al concentrations. In this case, the two phases involved are I and II. Phase II appears to be an intermediate and less stable phase because of the slight change observed in the efg on increasing Al concentration. It is reasonable to suspect that a critical point or another phase boundary exists at still higher impurity concentrations.

Except for the presence of a large multiphase region in the phase diagrams for VO₂:Al, the similarity with that previously given for Cr-doping is striking (10). Experiments with Ti and Cr impurities show that indeed the intermediate phase appearing below T_t is similar to Phase III. The stabilization of Phase III, or one similar to it, now seems to be a common property of these impurities. It would be of interest to see if the crystal structures of these phases are the same. In the Cr system, for instance, the proposed structure of the intermediate phase is characterized by half of the vanadium ion chains forming metal-metal pairs along the pseudorutile c -axis without twisting and the other half twisting without pairing (10). This is to be compared with that of pure VO₂ where all chains pair and twist. This implies that the effect of Cr is to reduce the tendency for pair formation. This effect is consistent with Goodenough's model where pair formation is associated with homopolar bonds (7). However, the increase in resistivity in the intermediate phase is contrary to predictions of the model. The electrons in Phase III appear to have a more localized character than in Phase I.

Conclusions

We have shown that NMR is a very useful tool in the study of multiple phase transitions occurring in doped VO₂ below the SM transition temperature. Single phase regions can be easily determined. However, concurrent structure determinations by X-ray crystallography are still necessary for a complete characterization of the different phases and transitions obtained.

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