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E.P.R. STUDIES OF THE PHASE TRANSITIONS IN β -PHASE VANADIUM BRONZES $\text{Na}_x\text{V}_2\text{O}_5$ (*)

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Résumé. — La phase β des bronzes de vanadium $\text{Na}_x\text{V}_2\text{O}_5$ a été étudiée par R.P.E. Nous avons mis en évidence deux transitions dans le comportement magnétique de ces composés quasi-unidimensionnels, une à $T = 150$ K, l'autre à $T = 20$ K. Nous les interprétons comme des transitions vers un ordre tridimensionnel. Ces transitions sont favorisées par l'ordre chimique à longue portée existant dans $\text{Na}_x\text{V}_2\text{O}_5$ pour $x = 1/3$.

Abstract. — The β phase vanadium bronzes $\text{Na}_x\text{V}_2\text{O}_5$ have been studied by E.P.R. Two transitions in magnetic behaviour are identified, one at $T = 150$ K, the other at $T = 20$ K. They are interpreted as three-dimensional ordering transitions in these quasi-one-dimensional compounds. The transitions are made possible by the long range chemical order existing in $\text{Na}_x\text{V}_2\text{O}_5$ at $x = 1/3$.

The β phase vanadium bronzes are oxides of formula $\text{M}_x\text{V}_2\text{O}_5$ [$\text{M} = \text{Na}, \text{Cu}, \text{Li} \dots$] for which recent studies of the physical properties have shown one dimensional conductive properties similar, for instance, to platinum KCP salts [1]. In particular the optical characteristics of $\text{Na}_{0.33}\text{V}_2\text{O}_5$ in the range 0.9μ to 3.4μ are those of a quasi-one-dimensional metal, with a plasma energy of 0.9 eV [2]. In this compound, conductivity measurements show a strongly anisotropic conductivity, typically $\sigma_{\parallel}/\sigma_{\perp} \sim 130$ at $T = 300$ K [3]. The conductivity anisotropy has also been observed for $\text{Cu}_x\text{V}_2\text{O}_5$ in E.P.R. measurements by Sperlich *et al.* [4]. We present here an E.P.R. study of $\text{Na}_x\text{V}_2\text{O}_5$ - β . Qualitative differences are found with results reported for $\text{Cu}_x\text{V}_2\text{O}_5$ - β , although the two oxides are structurally similar.

The β -phase of $\text{M}_x\text{V}_2\text{O}_5$ has monoclinic symmetry [5]. In this structure there are three types of vanadium sites labelled $\text{V}_1, \text{V}_2, \text{V}_3$ by Wadsley [5], which are present in equal numbers and organized in double-chains running parallel to the monoclinic \mathbf{b} -axis; these sites have an oxygen environment which can be nearly bipyramidal (V_3), or more octahedral (V_1, V_2). The metal ions M are accommodated in

tunnels which also run parallel to the monoclinic \mathbf{b} -axis.

It has been observed in N.M.R. experiments [6] that the metallic nuclei in the $\text{M}_x\text{V}_2\text{O}_5$ - β structure do not present any Knight-shift; consequently the metallic atoms M have lost their outer electron. The electrons fall into vanadium d-levels to form V^{4+} centres of spin $1/2$, which can be studied by E.P.R. The characteristics of the signal are similar to those of the single V^{4+} centres in V_2O_5 . In the vanadium bronzes one observes the single paramagnetic site. The g tensor is nearly axial, the axis being approximately along the direction of the shortest vanadium-oxygen distance [5]. The principal values are $g \simeq 1.91$ and $g \simeq 1.97$ at $T = 28$ K. These are temperature dependent, as discussed below. These V^{4+} centres are responsible for the conductive properties.

Single crystals with typical dimensions $10 \times 3 \times 3 \text{ mm}^3$ and with different values of the sodium concentration x were prepared by the Bridgman method. The value of x was determined by electron microprobe analysis. When the sodium concentration in the melt, x_L , was 0.33 , the resulting solid had the same sodium concentration, i.e. this value corresponds to the congruent melting composition, in agreement with previous reports [7]. This composition corresponds to one sodium atom per six vanadium atoms. Values of x_L less than 0.33 produced crystals with values of x intermediate

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between x_L and 0.33. However, crystals prepared from melts having x_L greater than 0.33 always resulted in solids having $x = 0.33$ to within the experimental precision of 0.01. Nevertheless, the low temperature E.P.R. properties of these samples were significantly different from those prepared with $x_L = 0.33$, as discussed below.

To obtain the spin susceptibility, we made a Lorentzian fit of the V^{4+} resonance line (E.P.R.) measured at 10 GHz as has been described in more detail previously [8]. Thin samples (thickness $\sim 50 \mu$) and a geometry with the microwave electric field perpendicular to the \mathbf{b} axis were used. Other geometries were avoided because of the high conductivity [3] or high dielectric constant [9] parallel to the \mathbf{b} axis (chain axis) which yield asymmetrical lines.

In discussing our experimental results we distinguish between three temperature regions :

a) $T > 150$ K. — This range has been the subject of a previous publication [8]. The susceptibility has a Curie Weiss law $\chi \propto C/(T + \theta)$ behaviour in all our samples (Fig. 1), the value of the Curie constant C corresponding to a density of spins 1/2 equal to the sodium density, with an absolute precision of 25%. This is in agreement with a complete transfer of electrons from sodium to vanadium orbitals.

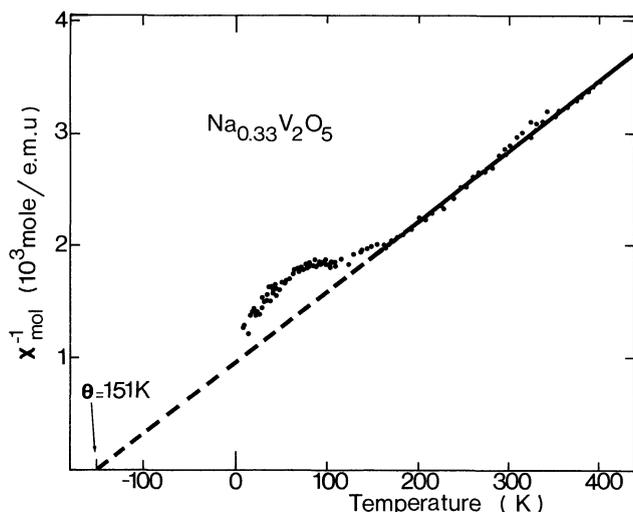


FIG. 1. — The inverse E.P.R. susceptibility versus temperature for a sample of $\text{Na}_{0.33}\text{V}_2\text{O}_5$ prepared from a melt having $x_L = 0.33$. The straight line is a Curie-Weiss fit to the data above 150 K.

The experimental Weiss temperature θ is 150 K [10] for $x = 0.33$. In this temperature range the linewidth ΔH varies little with temperature. This constancy of ΔH between 150 K and 300 K has also been observed by Sperlich *et al.* [4] in $\text{Cu}_x\text{V}_2\text{O}_5$ with a comparable absolute value in this range of x values (Fig. 2).

b) $30 \text{ K} < T < 150 \text{ K}$. — Below 150 K in $\text{Na}_x\text{V}_2\text{O}_5$ the susceptibility starts to deviate from Curie-Weiss behaviour (Fig. 1). More noticeably, the linewidth

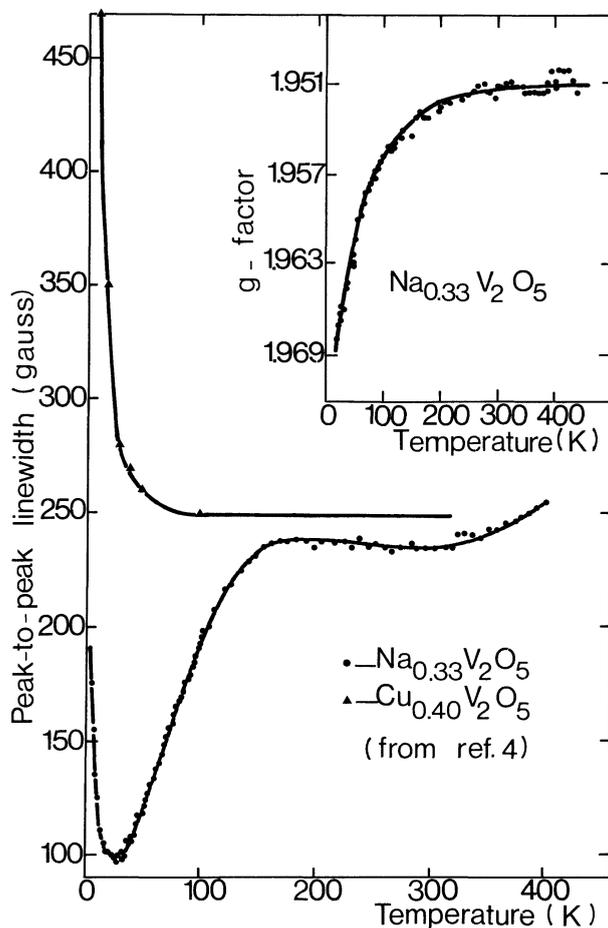


FIG. 2. — The linewidth and (inset) g -factor as a function of temperature for the same sample as in figure 1. The magnetic field is oriented at 16°C from the g_L direction. The linewidth data of Sperlich *et al.* (ref. [4]) on $\text{Cu}_{0.40}\text{V}_2\text{O}_5$ are shown for comparison.

starts to decrease sharply (Fig. 2). A similar change is observed in the g -value, which is constant above 150 K and starts to decrease below this temperature (Fig. 2). This change of behaviour is suggestive of a second order phase transition at 150 K.

This behaviour is in contrast with that reported for $\text{Cu}_x\text{V}_2\text{O}_5$ [4], in which no particular anomaly at 150 K was seen.

c) $T < 30 \text{ K}$. — This temperature range is characterized by extremely important variations in behaviour among samples. In $\text{Na}_x\text{V}_2\text{O}_5$ prepared with a nominal concentration in the melt $x_L = 0.33$, the linewidth begins to increase with decreasing temperature similarly to that for $\text{Cu}_x\text{V}_2\text{O}_5$ (Fig. 2). The susceptibility has a complex behaviour (Fig. 3), increasing slower than a simple Curie law. In contrast samples prepared with high sodium concentrations ($x_L > 0.33$) in the melt show a completely different behaviour (Fig. 3). A transition occurs at $T = 20 \text{ K}$: in a 1 K range the spin susceptibility measured by the integrated E.P.R. signal decreases to zero; during this decrease the line broadens and shifts rapidly.

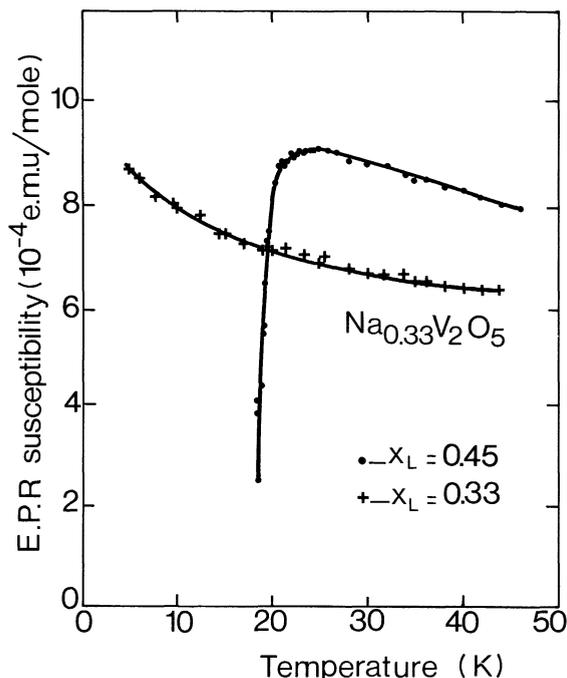


FIG. 3. — The behaviour of the E.P.R. susceptibility at low temperatures for two samples of $\text{Na}_x\text{V}_2\text{O}_5$ - β , both having $x = 0.33$ in the solid but prepared with different melt sodium concentrations x_L .

In summary, the results in $\text{Na}_x\text{V}_2\text{O}_5$ differ from those in $\text{Cu}_x\text{V}_2\text{O}_5$ mainly by the observation of two transitions, one of second order type at $T=150$ K, and the other at 20 K, which is only observed in samples of composition $x = 0.33$ prepared with an excess of sodium in the melt. The first transition is principally observed in the linewidth and g -factor, with no drastic change in the susceptibility; for the second transition, the main experimental fact is the disappearing of the E.P.R. line.

In discussing these results, we shall assume that the analysis by Goodenough of the β phase is correct: based on the atomic distances, Goodenough [11] concludes that the electrons occupy only the V_1 sites, which comprise one third of the total number of vanadium sites. At the concentration $x = 0.33$, half of these V_1 sites are occupied by an electron. We analyse the transitions we observe in terms of 3-dimensional ordering transition in this electronic system. Our model is the following.

a) **150 K transition.** — We propose this is a second order transition corresponding to positional ordering of the electrons. Above 150 K the electrons are randomly distributed among the V_1 sites. Below 150 K they start to occupy preferentially one side of each V_1 double-chains. This type of charge ordering transition is thought to occur for instance in Fe_3O_4 because of Coulombic intersite interactions (Verwey transition). Mott has suggested that a similar transition exists in $\text{Na}_x\text{V}_2\text{O}_5$ [12, 13]. One must note that besides Coulombic interactions other mechanisms can be present, for instance cooperative displacement

of the sodium ions. Under these conditions an energy gap will appear between electronic states on the two sides of the V_1 double-chains. Evidence for the opening of the gap exists in the thermopower [14] and dielectric constant [9] data.

b) **20 K transition.** — We believe this a 3-dimensional magnetic ordering transition among the V^{4+} magnetic ions which are completely positionally ordered at this low temperature.

We now discuss the implication of this model in the interpretation of our E.P.R. results. As the second order transition develops the occupied chain sites will become differentiated from the unoccupied chain sites because of Coulombic interaction and/or structural distortion. This is reflected in the observed variation of g value which occurs below 150 K. This suggests a structural differentiation between sites on occupied and non-occupied halves of the V_1 double-chains. This structural distortion could arise from vanadium and/or sodium displacements. Some additional evidence is available from thermopower measurements [14] which show a constancy of S above 150 K in agreement with a partially filled band. Also, measurements of the dielectric constant ϵ indicate a divergence near 150 K [9]. A detailed interpretation of the linewidth behaviour is not as straightforward. Ordinary theories [15] for 1-D magnetic systems with dipole-dipole interactions narrowed by an exchange term $J \sim 150$ K (100 cm^{-1}) yield linewidth estimates which are an order of magnitude too small. Also the angular dependence does not fit the predicted $(3 \cos^2 \theta - 1)$ behaviour with respect to the chain axis. We believe the broadening mechanism is due to an exchange anisotropy. This may come from virtual excitation of V^{3+} configurations for which the fine structure D can be as large as 50 cm^{-1} [16]. A detailed analysis [17] of the d-orbitals involved indicates that these virtual excitations are less important in the ordered configuration, thus explaining the decrease in linewidth below 150 K. The very rapid broadening and line shift of the E.P.R. is in agreement with the interpretation of the 20 K transition in terms of magnetic ordering. Preliminary static susceptibility measurements indicate an anisotropy appearing at this temperature [18].

As above, this transition is only observed in samples prepared with a sodium concentration in the melt x_L greater than 0.33, even though, there was no detectable difference in the sodium concentration in the solid from samples prepared from melts having $x_L = 0.33$. According to Wadsley [5], the composition $x = 1/3$ corresponds to saturation of the available sodium sites in the tunnels. We propose that only in those samples prepared with $x_L > 0.33$ is this saturation of sites actually achieved, and it is the resulting long-range chemical order which permits the 20 K magnetic ordering transition. Samples prepared from melts having $x_L = 0.33$ are, we believe, slightly substoichiometric in the solid,

and although this difference is not detectable by analytic methods the resulting chemical disorder is sufficient to suppress the 20 K transition. The slowly increasing susceptibility at low temperatures for these samples might be interpretable in terms of the disorder model of Theodorou and Cohen [19]. In $\text{Cu}_x\text{V}_2\text{O}_5$ the disorder is even more significant, since the copper ions are distributed among different possible sites : this probably suppresses even the positional order.

Preliminary measurements on $\text{Ag}_x\text{V}_2\text{O}_5$, in which the silver ions occupy the same sites as the sodium ions, show the same 150 K transition.

In conclusion we have found experimental evidence for electronic ordering transitions in the sodium vanadium bronzes, which we believe are made possible by the long range chemical order in these compounds.

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