



**HAL**  
open science

## Observation of one-dimensional metallic optical properties of Na $0.33\text{v}2\text{o}5$

D. Kaplan, A. Zylbersztein

► **To cite this version:**

D. Kaplan, A. Zylbersztein. Observation of one-dimensional metallic optical properties of Na  $0.33\text{v}2\text{o}5$ . Journal de Physique Lettres, 1976, 37 (5), pp.123-125. 10.1051/jphyslet:01976003705012300 . jpa-00231253

**HAL Id: jpa-00231253**

**<https://hal.science/jpa-00231253v1>**

Submitted on 4 Feb 2008

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Classification  
 Physics Abstracts  
 8.812 — 8.273

## OBSERVATION OF ONE-DIMENSIONAL METALLIC OPTICAL PROPERTIES OF $\text{Na}_{0.33}\text{V}_2\text{O}_5$

D. KAPLAN and A. ZYLBERSZTEJN

Laboratoire Central de Recherches Thomson-C.S.F., 91401 Orsay, France

(Reçu le 17 décembre 1975, révisé le 23 février 1976, accepté le 26 février 1976)

**Résumé.** — Nous avons mesuré la réflectivité en incidence quasi-normale sur des monocristaux du bronze de vanadium  $\text{Na}_{0.33}\text{V}_2\text{O}_5$ , entre  $0,9 \mu$  et  $3,4 \mu$ . La réflectivité  $R_{\parallel}$  pour la polarisation le long de l'axe  $b$  présente un seuil plasma, comme dans un métal, alors que la réflectivité  $R_{\perp}$  en polarisation perpendiculaire ne présente que peu de structure.

**Abstract.** — We have measured the near-normal incidence reflectivity of single crystals of the vanadium bronze  $\text{Na}_{0.33}\text{V}_2\text{O}_5$ , in the range  $0.9 \mu$ – $3.4 \mu$ . The reflectivity  $R_{\parallel}$  for light polarized along the  $b$ -axis exhibits a plasma edge, as in a metal, whereas the reflectivity  $R_{\perp}$  for the perpendicular polarization is relatively featureless.

We report in this paper optical reflectivity measurements performed on the vanadium bronze  $\text{Na}_{0.33}\text{V}_2\text{O}_5$ . This material belongs to the family of the so-called  $\beta$ -phase vanadium bronzes [1]. The symmetry of the  $\beta$ -phase is monoclinic, the vanadium ions being located on a system of chains running parallel to the  $b$ -axis. One can distinguish bipyramidal-site chains and octahedral-site chains. This arrangement results in a tunnel structure (along the  $b$ -axis) which accommodates the sodium ions [2]. It is known from the absence of an NMR Knight shift on the metal atoms that their outer electron has been transferred to the vanadium d-states [3]. These d-electrons are clearly identified by electron spin resonance (ESR) [4]. Because of the chain-like structure of the  $\beta$ -phase, one could ask whether it should exhibit quasi-one dimensional properties. Indeed, a very large conductivity anisotropy had been reported in  $\text{Na}_{0.33}\text{V}_2\text{O}_5$  by Ozerov [5] with a conductivity along the  $b$ -axis  $\sigma \simeq 20 (\Omega \times \text{cm})^{-1}$  and a conductivity perpendicular to the  $b$ -axis  $\sigma \simeq 0.03 (\Omega \times \text{cm})^{-1}$ . More recently an anisotropic ESR line shape has been observed in  $\text{Cu}_x\text{V}_2\text{O}_5 - \beta$  [6], the resonance line being characteristic of a good conductor for the microwave electric field oriented along the  $b$ -axis. Our reflectivity data show that  $\text{Na}_{0.33}\text{V}_2\text{O}_5$  behaves as a quasi-one dimensional metal in the near infrared, in a manner analogous to KCP [7], TTF-TCNQ [8] or  $(\text{SN})_x$  [9].

The compound  $\text{Na}_{0.33}\text{V}_2\text{O}_5$  was prepared by allowing a mixture of  $\text{V}_2\text{O}_5$  and  $\text{Na}_2\text{CO}_3$  to react in an open platinum crucible at  $750^\circ\text{C}$  for 15 hours. Crystal-

line material was obtained by slow cooling ( $2^\circ\text{C}$  per hour) in a strong temperature gradient ( $\simeq 70^\circ\text{C}/\text{cm}$ ). X-ray measurements identified the crystals as being single crystals of  $\text{Na}_{0.33}\text{V}_2\text{O}_5$ . The sodium content was determined to be  $x = 0.335 \pm 0.015$  by electron microprobe and flame spectroscopy analysis. A few crystals were large enough for reflectivity measurements: a flat surface containing the  $b$ -axis, with a minimum area of  $3 \times 3 \text{ mm}^2$ , was obtained by appropriate cutting and mechanical polishing.

The reflectivity experiments were performed with a spectrometer of the Strong type [10]. Where the product  $R_{\parallel} R_{\perp}$  of the individual reflectivities of two samples is determined at an incidence of  $9^\circ$ . The measurements can be done at any fixed temperature between 77 K and room temperature, in the wavelength range  $0.9 \mu$ – $13.4 \mu$ ; the detector is a lead sulphide cell cooled to liquid nitrogen temperature. Between  $0.9 \mu$  and  $2 \mu$  polarized light was used (Polaroid filter # HR), sample 1 being a  $\text{Na}_{0.33}\text{V}_2\text{O}_5$  specimen and sample 2 a calibrated copper mirror. At longer wavelengths two samples of  $\text{Na}_{0.33}\text{V}_2\text{O}_5$  were used, sample 1 serving as a partial polarizer for sample 2. By performing four sequences of measurements one can obtain both  $R_{\parallel}$  and  $R_{\perp}$ , defining  $R_{\parallel}$  (resp.  $R_{\perp}$ ) as the reflectivity for an incident light linearly polarized parallel (resp. perpendicular) to the  $b$ -axis. Let  $(x, y)$  be a system of orthogonal directions in a plane parallel to the reflecting surfaces of samples 1 and 2: the arbitrarily polarized incident light intensity

can always be written as  $I_0 = (I_x + I_y)$ , and the reflected light intensity is given by

- (a)  $I_a = R_{\perp}^2 I_x + R_{\parallel}^2 I_y$  when  $\mathbf{b}_1 \parallel \mathbf{b}_2 \parallel \mathbf{x}$ ,  
 (b)  $I_b = R_{\parallel} R_{\perp} (I_x + I_y)$  when  $\mathbf{b}_1 \parallel \mathbf{x}$ ,  $\mathbf{b}_2 \parallel \mathbf{y}$ ,  
 (c)  $I_c = R_{\parallel}^2 I_x + R_{\perp}^2 I_y$  when  $\mathbf{b}_1 \parallel \mathbf{b}_2 \parallel \mathbf{y}$ .

The four measurements of  $I_0$ ,  $I_a$ ,  $I_b$ ,  $I_c$  uniquely determine the four unknowns  $I_x$ ,  $I_y$ ,  $R_{\parallel}$  and  $R_{\perp}$ . The reflectivity components  $R_{\parallel}$  and  $R_{\perp}$  obtained in this way at room temperature are plotted versus wavelength in figure 1. It is seen that  $R_{\parallel}$  is typical of a metal exhibiting a plasma edge, whereas  $R_{\perp}$  is flat and structureless, indicative of the absence of optical transitions in the investigated energy range. This anisotropic behaviour of the reflectivity clearly indicates the quasi one-dimensional metallic character of  $\text{Na}_{0.33}\text{V}_2\text{O}_5$  in the near infrared. The anisotropy seems to vanish at higher energies (Fig. 2), which is consistent with the observation of an isotropic reflecting power under a polarizing microscope.

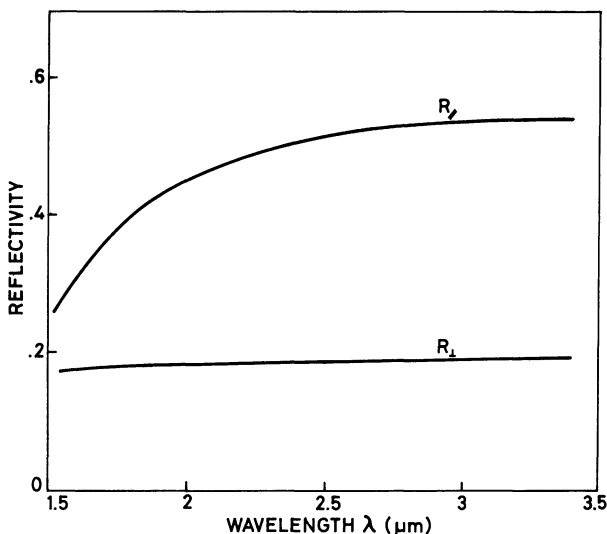


FIG. 1. — Reflectivity of  $\text{Na}_{0.33}\text{V}_2\text{O}_5$  as measured by the two samples method (see text).

We have compared the experimental variation of  $R_{\parallel}$  in the plasma edge region to a simple Drude calculation. In this model, the dielectric function  $\epsilon_{\parallel}(\omega)$  parallel to the  $b$ -axis is given by the expression,

$$\epsilon_{\parallel}(\omega) = \epsilon_{\infty} \left[ 1 - \frac{\omega_p^2}{\omega \left( \omega + \frac{i}{\tau} \right)} \right] \equiv \epsilon_1 + i\epsilon_2 \quad (1)$$

where

$$\omega_p^2 = \frac{Ne^2}{\epsilon_0 \epsilon_{\infty} m_{\parallel}^*} \quad (2)$$

$\epsilon_{\infty}$  is the residual relative dielectric constant at high frequency,  $\tau$  is the electronic relaxation time,  $\omega_p$  is the plasma frequency,  $N$  is the electron density, and  $m_{\parallel}^*$  is the optical effective mass along the  $b$ -axis.

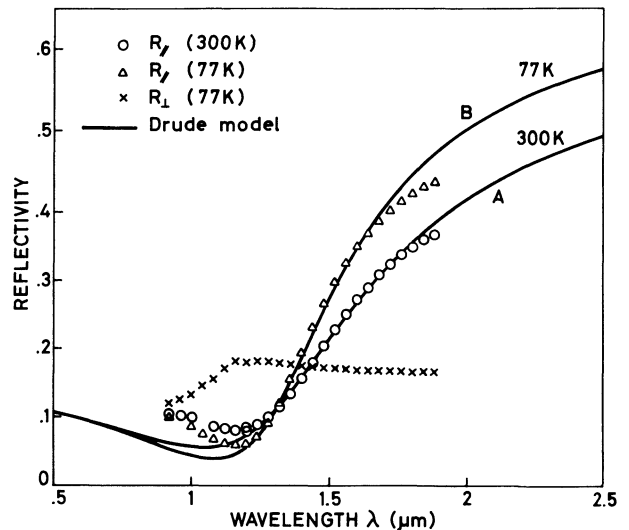


FIG. 2. — Reflectivity of  $\text{Na}_{0.33}\text{V}_2\text{O}_5$  in the region of the plasma edge. Symbols are experimental points and the solid curves are obtained from a Drude model (see text).

In terms of the real and imaginary parts of  $\epsilon$ , the reflectance is given by,

$$R = \frac{1 + |\epsilon| - [2(|\epsilon| + \epsilon_1)]^{1/2}}{1 + |\epsilon| + [2(|\epsilon| + \epsilon_1)]^{1/2}} \quad (3)$$

where  $|\epsilon| = (\epsilon_1^2 + \epsilon_2^2)^{1/2}$ . Application of formula (1) to the anisotropic case has been discussed by Bright *et al.* [8].

Curve A of figure 2 shows a fit to the experiment at 300 K, taking values of  $\epsilon_{\infty} = 4.5$ ,

$$\omega_p = 1.44 \times 10^{15} \text{ s}^{-1},$$

and  $\tau = 1.35 \times 10^{-15}$  s. Curve B of figure 2 shows a similar fit at 77 K, with  $\epsilon_{\infty}$  and  $\omega_p$  the same as above, and  $\tau = 1.90 \times 10^{-15}$  seconds. The fit is adequate in the 1.2  $\mu$ -1.7  $\mu$  wavelength range, i.e. in the region where the reflectivity exhibits a rapid variation with wavelength. Although this is admittedly a limited range, we believe our interpretation in terms of a plasma edge to be correct for the following reasons : (i) an oscillator fit to the data would predict a reflectivity maximum at long wavelength, in contrast to the observed monotonic increase of  $R_{\parallel}$  (see Fig. 1); (ii) in this model, only the electronic relaxation time is expected to vary with temperature, as found experimentally.

We now discuss limitations of the Drude theory in the present case. The most important one concerns the magnitude of the bandwidth  $B$  in relationship with the plasma energy  $\hbar\omega_p$ . We assume that the conduction band is a one-dimensional tight binding band with a dispersion relation of the form

$$E = \frac{B}{2} (1 - \cos ka). \quad (4)$$

From formula (2) and (4), using an average effective mass given by

$$(m_{\parallel}^*)^{-1} = \hbar^{-2} k_F^{-1} \int_0^{k_F} \frac{\partial^2 E}{\partial k^2} dk \quad (5)$$

where  $k_F$  is the Fermi wavevector, one obtains the following relation between the plasma frequency and the bandwidth

$$B = 2 \frac{\hbar^2 \omega_p^2}{a^2} \left( \frac{Ne^2}{\epsilon_0 \epsilon_{\infty}} \right)^{-1} \frac{k_F a}{\sin k_F a}. \quad (6)$$

As discussed by Goodenough [11] the occupied vanadium d states are associated with one third of the vanadium sites in the structure. For the composition  $\text{Na}_{0.33}\text{V}_2\text{O}_5$  the corresponding band is one quarter filled so that  $k_F a = \pi/4$ . Taking

$$N = 3.7 \times 10^{21} \text{ cm}^{-3},$$

$a = 3.61 \text{ \AA}$  [2] and the experimental value

$$\omega_p = 1.44 \times 10^{15} \text{ s}^{-1}$$

one gets from (6)  $B = 1.0 \text{ eV}$ , to be compared with  $\hbar\omega_p = 0.9 \text{ eV}$ . In the vicinity of the plasma edge photon energies are comparable to the bandwidth so that deviations from a simple Drude law are expected. Furthermore at energies above 1 eV interband transitions may contribute to the optical properties.

An additional limitation arises from the fact that the d.c. conductivity is not metallic but shows rather a semiconductor-like activated temperature dependence, with a characteristic activation energy in the range 4.8 to  $6.7 \times 10^{-2} \text{ eV}$  [12]. At the moment it not clear whether this behaviour is due to a Peierls gap [13] or to electron localization by correlations, disorder or small polaron formation [14]. In any case one expects a frequency dependent conductivity as one goes from optical frequencies to d.c. One may assume that the material will behave like a metal for photon energies much larger than the observed activation energies, which yields a condition  $\lambda \ll 20 \mu$ , reasonably well fulfilled in our case. This limitation of the Drude model should thus be less serious than the previous one.

In conclusion, although a simple Drude theory is here of limited applicability, the reflectance of the  $\beta$ -phase vanadium bronze  $\text{Na}_{0.33}\text{V}_2\text{O}_5$  in the near infrared, for light polarized along the  $b$ -axis, can be described in terms of a plasma edge. This material is a one-dimensional conductor, which behaves as a semiconductor at d.c. and as a metal at optical frequencies. This is very similar to what has been reported for KCP [7], or for TTF-TCNQ [8] below the metal-insulator transition temperature.

We wish to thank J. L. Pinsard and D. Saux for technical assistance, and Pr. J. Bok for a valuable discussion. We also thank Mrs. N. Sol for measuring the sodium content in our samples.

### References

- [1] HAGENMULLER, P., *Prog. Solid State Chem.* **5** (1971) 71.
- [2] WADSLEY, A. D., *Acta Crystallogr.* **8** (1955) 695.
- [3] GENDELL, J., COTTS, R. M. and SIENKO, M. J., *J. Chem. Phys.* **37** (1962) 220.
- [4] SIENKO, M. J. and SOHN, J. B., *J. Chem. Phys.* **44** (1966) 1369.
- [5] OZEROV, R. P., *Sov. Phys.-Crystallogr.* **2** (1957) 219.
- [6] SPERLICH, G., LAZÉ, W. D. and BANG, G., *Solid State Commun.* **16** (1975) 489.
- [7] KUSE, D. and ZELLER, H. R., *Phys. Rev. Lett.* **27** (1971) 1060.
- [8] BRIGHT, A. A., GARITO, A. F. and HEEGER, A. J., *Phys. Rev. B* **10** (1974) 1328.
- [9] PINTSCHOVIVUS, L., GESERICH, H. P. and MÖLLER, W., *Solid State Commun.* **17** (1975) 477.
- [10] BENNETT, H. E. and KOEHLER, W. F., *J. Opt. Soc. Am.* **50** (1960) 1.
- [11] GOODENOUGH, J. B., *J. Solid State Chem.* **1** (1970) 349.
- [12] PERLSTEIN, J. H. and SIENKO, M. J., *J. Chem. Phys.* **48** (1968) 174.
- [13] See, for example, *Low Dimensional Cooperative Phenomena*, ed. H. J. Keller (New York, Plenum Press), 1975.
- [14] See, for example, MOTT, N. F., *Metal Insulator Transitions* (Taylor and Francis, London) 1974.