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Abstract. The magnetic susceptibility of phases with block type structures in the Nb_2O_{5-2x} system, with $0 \leqslant x \leqslant 0.083$, has been determined by the Faraday method in the temperature region 77–400 K. The samples consisted of crystals of composition $Nb_{28}O_{70}$ (Nb_2O_5), $Nb_{53}O_{132}$ ($NbO_{2.491}$), $Nb_{25}O_{62}$ ($NbO_{2.480}$), $Nb_{47}O_{116}$ ($NbO_{2.468}$), $Nb_{22}O_{54}$ ($NbO_{2.454}$) and $Nb_{12}O_{29}$ ($NbO_{2.417}$). It is shown that the observed paramagnetic behaviour cannot be explained within the framework of classical Debye–Langevin behaviour or by Pauli paramagnetism. Instead, a Van Vleck type analysis of the magnetic susceptibility data gives evidence for the occurrence of bipolaron/single-polaron states at lower degrees of reduction ($x < 0.05$), in agreement with previous interpretations of electrical and optical properties. The quasi-metallic state for $x \geqslant 0.05$ reveals localized electrons, as suggested earlier.

1. Introduction

There exist several Nb_2O_{5-2x} phases, with $0 \leqslant x \leqslant 0.083$, that possess block-type structures (Norin and Magneli 1960, Norin 1963, 1965, 1966, Gatehouse and Wadsley 1964, Norin et al 1966, Gruehn and Norin 1967, 1969, Nimmo and Anderson 1972). These structures consist of blocks of $n \times m$ corner-sharing NbO_6 octahedra in the cross a–b section, indefinitely extended by corner-sharing in the direction of the unit-cell c axis. The blocks are interconnected by edge-sharing octahedra, yielding two sets of columns: one with its base at $z = 0$ and the other at $z = 0.5$ ($c/2$). The structure of H–Nb_2O_5 is outlined in figure 1. Periodical intergrowth of equally or differently sized $n \times m$ blocks determines the oxygen content of the phases. Each NbO_6 Octahedron contains one Nb atom, and additional tetrahedrally coordinated Nb atoms are found in the square tunnels formed at the corners of four interconnected blocks, at $z = c/4$ and $3c/4$, for all phase compositions except for $x = 0.083$ ($Nb_{12}O_{29}$).

In this article we describe the magnetic properties of six different Nb_2O_{5-2x} phases: $Nb_{12}O_{29}$ ($NbO_{2.417}$), $Nb_{22}O_{54}$ ($NbO_{2.454}$), $Nb_{47}O_{116}$ ($NbO_{2.468}$), $Nb_{25}O_{62}$ ($NbO_{2.480}$), $Nb_{53}O_{132}$ ($NbO_{2.491}$) and H–Nb_2O_5. In this study, as well as in the previous one dealing with the electrical and optical properties of these phases (Rüscher et al 1988), we have utilized single crystals prepared by transport reaction as described by Hussain et al (1986). These studies have revealed that:

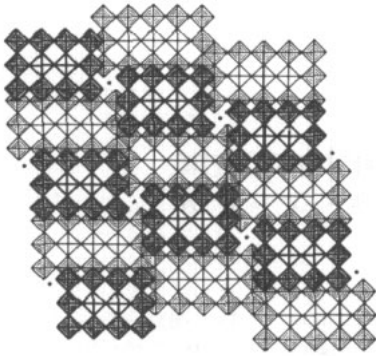(i) The conductivity increases with increasing x values, i.e. degree of reduction.

Figure 1. The structure of H–Nb$_2$O$_5$.

(ii) Below 250 K the temperature dependence of the conductivity changes from semiconductor to quasi-metallic behaviour with increasing x value, the compounds with $x \leqslant 0.01$ being semiconducting. Thus Nb$_{53}$O$_{132}$ exhibit an apparent activation energy of 0.01 eV.

(iii) Above 250 K, the temperature dependence of the conductivity approximates $T^{-3/2}$ behaviour for all the compounds.

(iv) A broad absorption band is found in the near-infrared spectral range, with $hw_{max} \approx 0.7$ eV, which extends asymmetrically into the visible range. The integrated intensity of this band increases with increasing degree of reduction up to $x \approx 0.05$ at $T = 293$ K.

The electrical and optical properties for $x \leqslant 0.05$ could consistently be described in terms of polaron theory. The Austin and Mott (1969) description of small polarons, stating that $hw_{max} \leqslant 4E_a$ and $E_a \approx (1/r_p - 1/R_p)$ (e_p = polaron radius, R_p = average distance between the charge carriers), seems to be roughly obeyed for $x \leqslant 0.01$. The surprising observation that the polaron absorption increases up to $x = 0.05$ although quasi-metallic behaviour sets in at $x \approx 0.02$ can be understood in terms of the polarons being highly correlated or of the carriers consisting of a mixture of bipolarons and single polarons for $0.02 \leqslant x \leqslant 0.05$. Finally the threshold value at $x \approx 0.05$ of the integrated intensity of the polaron absorption suggests that the quasi-metallic behaviour for compounds with $x > 0.05$ is due to superimposed quasi-free electrons, as previously found for WO$_{3-x}$ with $x > 0.1$ (Salje and Güttler 1984).

In this article we describe the magnetic properties of the various Nb$_2$O$_{5-2x}$ phases. From polaron–polaron correlation and polaron–free electron interactions one would expect strong deviation from classical Debye–Langevin behaviour and/or from Pauli paramagnetism. We are going to show that the observed paramagnetic properties can be explained within the framework for a transition from the bipolaron/single-polaron state to the quasi-metallic state with increasing x.

2. Experiment

Needle-shaped crystals of maximum sizes up to $2 \times 0.2 \times 0.2$ mm^3, of the compositions Nb$_{12}$O$_{29}$ (NbO$_{2.147}$), Nb$_{22}$O$_{54}$ (NbO$_{2.454}$), Nb$_{47}$O$_{116}$ (NbO$_{2.468}$), Nb$_{25}$O$_{62}$ (NbO$_{2.480}$), Nb$_{53}$O$_{132}$ (NbO$_{2.491}$) and Nb$_{28}$O$_{70}$ (NbO$_{2.500}$) have been prepared by a transport reaction

Table 1. Structural data for the Nb_2O_{5-2x} phases of concern in this study. The homogeneity ranges given are those determined by Schäfer *et al* (1969). The number of Nb^{4+} ions per cm^3 (N_{th}) has in each case been calculated with use of the unit cell volume, V_N, of the ideal composition. T denotes occurrence of tetrahedrally coordinated Nb atoms in the structure.

Composition	Block-type structure	O/Nb ratio	Homogeneity range	V_N ($Å^3$)	N_{th}
$Nb_{12}O_{29}$	3×4	2.417	2.471	47.71	3.5×10^{21}
$Nb_{22}O_{54}$	$3 \times 3 + 3 \times 4 + T$	2.454	2.448–2.454	47.69	1.9×10^{21}
$Nb_{47}O_{116}$	$3 \times 3 + 2(3 \times 4) + T$	2.468	2.464–2.467	47.97	1.3×10^{21}
$Nb_{25}O_{62}$	$3 \times 4 + T$	2.480	2.472–2.478	47.60	0.8×10^{21}
$Nb_{53}O_{132}$	$2(3 \times 4) + 3 \times 5 + T$	2.491	2.484–2.485	48.38	0.4×10^{21}
$Nb_{28}O_{70}$	$3 \times 4 + 3 \times 5 + T$	2.500	2.500–2.489	48.40	0

technique using $HgCl_2$ as the transporting agent. A detailed description of the preparatory route used and of the determination of the degree of reduction, i.e. x in Nb_2O_{5-2x}, is given by Hussain *et al* (1986). It has previously been shown that these phases are stoichiometric or have very limited homogeneity ranges with respect to the Nb/O ratio (Schäfer *et al* 1969). These ranges, together with some structural data and the calculated numbers of Nb^{4+} ions per cm^3 for the various phases are given in table 1.

The magnetic susceptibility of about 20–30 mg of as-grown crystals of each composition was determined by the Faraday method. The field strength was $H = 0.7 \times 10^7$ A m^{-1}, and the resolution of the weight measurements both with and without magnetic field was better than 5 μg. The set up was calibrated with $CoHg(SCN)_4$ and the measurements were carried out in the temperature region 77–400 K. Each measured point represents the average of three switch on–switch off cycles of the magnetic field at a fixed temperture, and data were recorded for increasing T. Successive runs of the same samples showed the reproducibility of the measurements to be better than 1%. The crystals had a good statistical distribution of orientation within the sample holder, i.e. we were not able to measure any anisotropic susceptibility by different modes of packing.

3. Results and discussion

The molar magnetic susceptibilities of the compounds under investigation are given in figure 1. All compounds exhibited paramagnetic behaviour. The susceptibilities of $NbO_{2.500}$ and $NbO_{2.491}$ were found to be temperature independent. For the other compounds, both the susceptibility at a given temperature and the temperature dependence of the susceptibility increase with increasing degree of reduction, i.e. with increasing concentration of Nb^{4+} ions present. The increase of χ_m at 100, 200 and 300 K with the degree of reduction (x in Nb_2O_{5-2x}) is illustrated in figure 2. According to figure 2, it seems that the susceptibility saturates for the compounds with $x \geq 0.05$. The compositional variation of the susceptibility is so large that any influences not related to x, such as impurity effects, diamagnetic contributions of the Nb and O ions and small deviations from the ideal stoichiometry (see table 1), can be neglected.
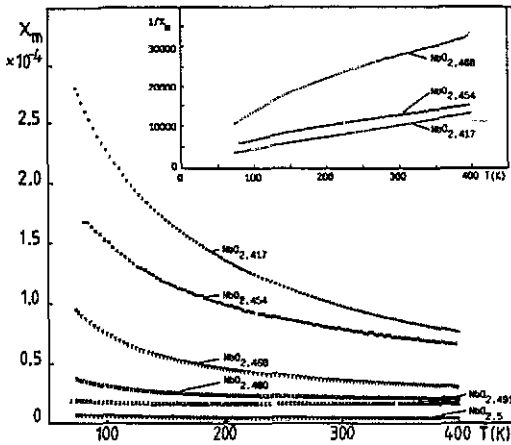
Figure 2. The molar magnetic susceptibility, χ_m in emu mol^{-1}, plotted as a function of the temperature, T, for Nb$_{28}$O$_{70}$ (NbO$_{2.500}$), Nb$_{53}$O$_{132}$ (NbO$_{2.491}$), Nb$_{25}$O$_{62}$ (NbO$_{2.480}$), Nb$_{47}$O$_{116}$ (NbO$_{2.468}$), Nb$_{22}$O$_{54}$ (NbO$_{2.454}$) and Nb$_{12}$O$_{29}$ (NbO$_{2.417}$). The inset shows the temperature dependence of $1/\chi_m$ for NbO$_{2.417}$, NbO$_{2.454}$ and NbO$_{2.468}$.

As the compounds with $x \geq 0.02$ exhibited quasi-metallic behaviour one would expect them to exhibit Pauli paramagnetism, which can be estimated from the formula:

$$X_p = g(E_F)\mu_B^2 N_a/N \tag{1}$$

where $g(E_F)$ = the density of states at the Fermi energy, μ_B = the Bohr magneton, $N_a = 6.023 \times 10^{23}$ (Avogadro number) and N = the total carrier concentration. We have calculated X_p values for the various compounds and plotted them in figure 2, assuming the concentration of free electrons (N) to be equal to the number of Nb^{4+} ions present in each compound (N_{th} in table 1). A further assumption is an isotropic Fermi distribution, implying that:

$$g(E_F) = m^*/h\pi^2 (3N\pi)^{1/3}. \tag{2}$$

In the calculations, the effective mass, m^*, has been set equal to one. As seen in figure 3, our measured data are clearly at variance with the calculated ones, implying that we should eliminate Pauli paramagnetism from further considertion.

The temperature dependence of the susceptibility of all compounds except Nb$_{12}$O$_{29}$ (NbO$_{2.417}$) and Nb$_{22}$O$_{54}$ (NbO$_{2.454}$), could be fitted to the equation:

$$X_m = C/T + B \tag{3}$$

with $C = N_a\mu_B^2 \langle(\mu_p)^2\rangle/3k$ and B equal to the temperature-independent paramagnetic contribution as seen in figure 3 where $f(T)$ defined as

$$f(T) = \chi_m T3k/(N_a\mu_B^2) \tag{4}$$

is plotted against the temperature.

Following van Vleck (1965), B in (3) denotes the temperature-independent paramagnetism resulting from excitations from states with energetical separations exceeding kT, $\delta E \gg kT$, i.e. high frequency elements. B can be determined from the slopes of the $f(T)$ versus T full curves in figure 3. In our case the high-frequency excitations could

Table 2. Composition, degree of reduction (x) and calculated and observed number of magnetons for various phases in the Nb_2O_{5-2x} system, with $0 \leqslant x \leqslant 0.083$. The μ_{obs} values are obtained by linear extrapolation to 0 K of the data given in figure 4. The μ_{obs} values for $Nb_{12}O_{29}$ and $Nb_{22}O_{54}$ are estimated since linear extrapolation is not possible.

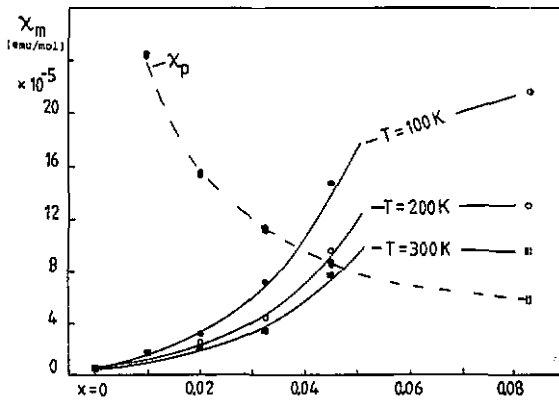| Composition	Degree of reduction x in Nb_2O_{5-2x}	μ_{calc}	μ_{obs}
$Nb_{12}O_{29}$	0.083	0.693	$\cong 0.2$
$Nb_{22}O_{54}$	0.046	0.525	$\cong 0.1$
$Nb_{47}O_{116}$	0.032	0.438	0.045
$Nb_{25}O_{62}$	0.020	0.346	0.010
$Nb_{53}O_{132}$	0.009	0.232	<0.005
$Nb_{28}O_{70}$	0.000	0.000	<0.005

Figure 3. The molar magnetic susceptibility (χ_m) at 100, 200 and 300 K plotted as a function of the degree of reduction x in the system Nb_2O_{5-2x}. The Pauli susceptibilities (χ_p) calculated according to equations 1 and 2 (see text) are also given. The curves are given as guides for the eyes.

arise from phonon-assisted hopping of polarons. In the van Vleck picture, the $f(T = 0\ K)$ quantity results from low-frequency elements (normal states) with $\delta E \leqslant kT$ of permanent moments. The permanent moments (μ_p) can be calculated according to:

$$\mu_{calc} = g[J(J+1)2x]^{1/2} \qquad g = 2 \text{ and } J = \tfrac{1}{2}. \tag{5}$$

Assuming that each Nb^{4+} ion contributes one moment, and neglecting spin-orbit coupling effects one obtains the μ_{calc} values given in table 2. The μ_{obs} values give in the same table are extrapolations to $T = 0$ of the $f(T)$ versus T curves in figure 3. Consistently $\mu_{obs} \ll \mu_{calc}$, which can be understood within the framework of the bipolaron picture. The increasing number of effective magnetons, μ_p, with increasing temperature means breaking of bipolaron states. The observation that $\mu_{obs} \neq 0$ at 0 K is then due to saturation of the bipolaron-order parameter (Rüscher *et al* 1990).
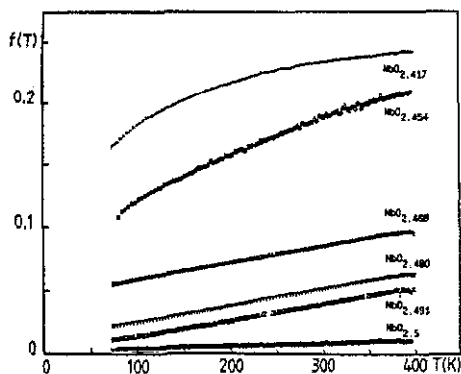
Figure 4. A plot of $f(T) = \chi_m T 3k/(N_a \mu_B^2)$ versus temperature, T, for $Nb_{28}O_{70}$ ($NbO_{2.500}$), $Nb_{53}O_{132}$ ($NbO_{2.491}$), $Nb_{25}O_{62}$ ($NbO_{2.480}$), $Nb_{47}O_{116}$ ($NbO_{2.468}$), $Nb_{22}O_{54}$ ($NbO_{2.454}$) and $Nb_{12}O_{29}$ ($NbO_{2.417}$).

The susceptibility of $Nb_{12}O_{29}$ follows the Curie–Weiss behaviour

$$\chi_m = C/(T - \theta) \tag{6}$$

with $\theta \approx 47$ K (see inset in figure 1). From the slope of $(\chi_m)^{-1} = f(T)$ curve we calculate C and deduce to $\langle(\mu_p)^2\rangle^{1/2}$ value of the order 0.5. The corresponding x value calculated according to (5) corresponds to $x \approx 0.042$, implying that for this phase composition, about 50% of all possible moment contribute to the susceptibility. Corresponding data for $Nb_{22}O_{54}$ (with $\theta \approx 120$ K) show that all Nb^{4+} ions introduce freely rotating moments. From structural considerations it seems plausible that one cannot introduce more than one Nb^{4+} ion possessing a freely rotating moment per block of 3×4 NbO_6 octahedra. Introducing more moments thus implies that the structural capability of hosting freely rotating moments is exceeded. This is in agreement with the observation that the integrated intensity of the optical absorption increases with increasing degree of reduction up to $x \approx 0.05$ (Rüscher *et al* 1988). The optical and magnetic properties of $Nb_{22}O_{54}$ ($NbO_{2.454}$) can thus be interpreted in terms of the concentration of polarons saturating around $x = 0.05$. When the degree of reduction, x, exceeds 0.05 quasi-free electrons start to appear. Accordingly in $Nb_{12}O_{29}$ ($NbO_{2.417}$) the principal charge carriers ought to consist of a mixture of polarons and quasi-free electrons.

4. Concluding remarks

The considerable reduction of the effective magnetic moments in the compounds described above can be understood in terms of these compounds possessing a mixture of bipolaron–single polaron states. Pair breaking occurs with increasing degree of reduction resulting in increasing $\langle(\mu_p)^2\rangle$ values as seen in figure 3. It has previously been shown that the extension of the wave function of the charge carriers is closely related to the size of the structural block unit (Ruscher *et al* 1988). This implies that when chemical reduction introduces more than one electron per block of 3×4 NbO_6 octahedra, as in $Nb_{12}O_{29}$, one would expect the appearance of quasi-free electrons. The magnetic as well as the electrical properties of $Nb_{12}O_{29}$ thus seem to be understandable in terms of superimposition of localized electrons (polarons) and free carriers.

Acknowledgments

References

Austin I G and Mott N F 1969 *Adv. Phys.* **18** 41
Gatehouse B M and Wadsley A D 1964 *Acta. Crystallogr.* **17** 1545
Gruehn R and Norin R 1967 *Z. Anorg. Allg. Chemie* **355** 176
Gruehn R and Norin R 1969 *Z. Anorg. Allg. Chemie* **367** 209
Hussain A, Reitz B and Gruehn R 1986 *Z. Anorg. Allg. Chemie* **535** 186
Nimmo K and Anderson J S 1972 *J. C. S. Dalton* 2328
Norin R 1963 *Acta. Chem. Scand.* **17** 1391
Norin R 1965 *Naturwissenschaften* **52** 300
Norin R 1966 *Acta. Chem. Scand.* **20** 871
Norin R, Carlson M and Elcqvist B 1966 *Acta Chem. Scand.* **20** 2892
Norin R and Magneli A 1960 *Naturwissenschaften* **47** 354
Rüscher C H, Rüffer N, Seiwert F J and Gruehn R 1990 *Physica* C **166** 158
Rüscher C H, Salje E and Hussain A 1988 *J. Phys. C: Solid State Phys.* **21** 3737
Salje E and Güttler B 1984 *Phil. Mag.* B **50** 607
Schäfer H, Bergner D and Gruehn R 1969 *Z. Anorg. Allg. Chemie* **365** 31
Van Vleck J H 1965 *The Theory of Electric and Magnetic Susceptibilites* 1st edn. (Oxford: Oxford University Press) p 181