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Low-temperature specific heat and magnetic susceptibility of nonmetallic vanadium bronzes

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A linear γT term is observed in the low-temperature specific-heat behavior of the nonmetallic vanadium-oxide bronzes of sodium and copper. The low-temperature magnetic susceptibility is equally anomalous and points to a singlet or diamagnetic ground state. It is postulated that the V^{4+} centers in these bronzes form near-neighbor pairs or bipolarons through deformation-induced attraction. The tunneling of these bipolarons between pairs of sites gives rise to the linear term of the specific heat. The progessive breaking up with temperature of the singlet bipolarons provides a natural explanation of both the magnetic susceptibility as well as of the electrical conductivity.

I. INTRODUCTION

The anomalous low-temperature linear temperature dependence (γT) of the specific heat of nonmetallic glassy and amorphous solids was first reported by Zeller and Pohl[1] and later in greater detail by Stephens.[2] It has been established that the same kind of linear dependence obtains for metallic spin glasses,[3] and it has also been recognized that such γT behavior may be quite universal as a common feature of all disordered materials. The theory of Anderson[4] *et al.* and of Phillips[5] establishes this common feature as due to the possibility that tunneling modes in glasses are the low-lying excitations capable of providing for the linear specific heat or for other anomalous thermal properties. We point out in this communication that a large γT term in the specific heat is observed in a great variety of nonmetallic vanadium bronzes. These are nonstoichiometric compounds[6] of formula $M_xV_2O_5$ where M is an alkali metal, Ag or Cu, and $x \approx 0.3-0.6$. We propose that the ground states of these bronzes are singlet bipolarons (phonon-induced electron pairs) and a tunneling motion of these bipolarons between almost equivalent sites produces the anomalous specific heat at low temperatures. We will show that magnetic-susceptibility as well as electrical-resistivity data are consistent with the bipolaron picture, and this may indeed be a general feature of a variety of transition-metal bronzes. In Sec. II, the experimental results are described; they include specific-heat, magnetic-susceptibility, and electrical-conductivity data. In Sec. III the data are analyzed on the basis of the bipolaron model: in Sec. III A, the bipolaron model is presented, while in Secs. III B–III D, the specific-heat, magnetic-susceptibility, and the electrical-conductivity data are confronted with the bipolaron idea.

II. EXPERIMENTAL RESULTS

Single crystals of the vanadium bronzes were made by heating mixtures of Na_2CO_3 or Ag_2CO_3 with V_2O_5 (Vanadium Corporation of America, purified grade). The mixtures were taken in a platinum dish through the following 72-h programmed heating and cooling cycle: 30 h at 720 °C, cooling at 0.6 °C min^{-1} to about 650 °C, then to 550 °C at about 0.1 °C min^{-1}, and finally to room temperature under the natural cooling rate of the furnace (2 to 3 °C min^{-1}). After being leached with hot 6*N* aqueous NH_3 to separate the bronzes from the dish, the samples were washed, dried, and ground to a fine powder. X-ray photographs showed patterns of only β-vanadium bronze structure. For analysis, the bronzes were dissolved in hot sulphuric acid. Vanadium was determined by potentiometric titration with Ce^{4+} after reduction to V^{4+} with SO_2. Sodium was determined by flame photometry; silver by electrodeposition.

The low-temperature heat capacity was measured with an apparatus as described previously.[7] A cylindrical sample fitted with a well for a germanium thermometer and wound with a heating coil is suspended in a copper cryostat. Exchange gas is maintained between the sample and the copper can until the sample is at the desired starting temperature, i.e., 4.2 or 1.5 °K. After evacuation of the exchange gas, current is passed through the heating coil at constant power input while the temperature of the sample is recorded. At the same time, an independent heating coil wound on the copper can supplies heat at a servo-commanded rate to maintain the surrounding copper wall at the same temperature as the rising temperature of the sample. The temperature-time readout is converted to heat capacity data by an IBM 7094.

Six different bronzes, $Na_{0.25}V_2O_5$, $Na_{0.28}V_2O_5$,

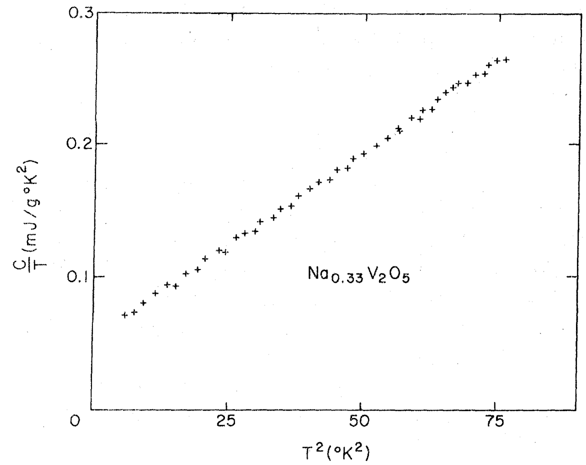

FIG. 1. Low-temperature specific heat.

$Na_{0.33}V_2O_5$, $Na_{0.40}V_2O_5$, $Ag_{0.33}V_2O_5$, and $K_{0.20}V_2O_5$ were examined. Figure 1 shows typical results. In all cases, the data can be well described by the standard relation $C=\gamma T+DT^3$, where γ and D are obtained from the intercept and slope, respectively, of the plots C/T against T^2. The slope D is related to the lattice spectrum through the characteristic Debye temperature Θ_D, by the relation $D=1944\, n/\Theta_D^2$ where D is in millijoules $\text{mole}^{-1}\,K^{-4}$ and n is the number of formula units of the empirical formula.

In Table I, we have tabulated the experimentally measured γ, D, and Θ_D's for our samples. A linear low-temperature specific heat for copper-vanadium bronzes was observed by Casalot[8] and has been briefly reported.[9] More recently, in semiconducting $Li_{1+x}Ti_{2-x}O_4$ Johnston *et al.*[10] have also observed a linear term. These two sets of data are also included in Table I. In some of our samples, a Schottky-like anomaly[11] below 3 K is observable, however our data do not go down sufficiently low in temperature to permit us to analyze this extra contribution. As can be seen from Table I, the γ term is extremely large, and had the samples been metallic would have corresponded to about several states per electron volt per vanadium atom, at the Fermi level.

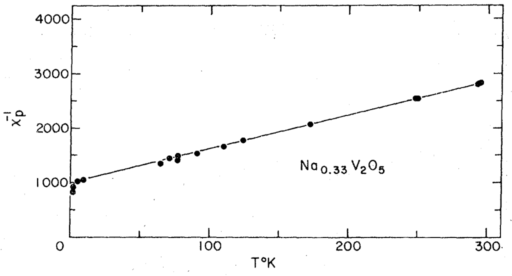

FIG. 2. Inverse magnetic susceptibility [(emu/mole)$^{-1}$] vs temperature (K).

Extensive data are available on magnetic-susceptibility measurements on the Na-vanadium bronzes[12] down to 1.5 °K; typical results are shown in Fig. 2. The inverse susceptibility shows an apparent Curie-Weiss behavior at the higher temperatures, often falling sharply below the Curie-Weiss line at the lower temperatures. The same general pattern is also observed in the copper-vanadium bronzes[9] as well as in $Li_{1+x}Ti_{2-x}O_4$.[13] (In the susceptibility plot of Fig. 2, the following two major corrections have been made: a core diamagnetic term[14] of -70×10^{-6} emu/mole and a temperature-independent paramagnetic term of $+112\times10^{-6}$ emu/mole, for the under-lying V_2O_5 lattice. This last value was measured by Sohn[15] for stoichiometric single-crystal spec pure V_2O_5.)

Single-crystal electrical conductivity for $Na_{0.33}$ vanadium bronzes was measured by Perlstein[16] and is shown in Fig. 3. $\text{Log}_{10}\sigma$ vs $1/T$ plots show semiconducting behavior at all temperatures, with

TABLE I. Low-temperature specific-heat coefficients of nonmetallic β-vanadium bronzes. $C=\gamma T+DT^3$.

Composition	γ (millijoules $g^{-1}K^{-2}$)	D (millijoules $g^{-1}K^{-4}$)	Debye temp. Θ_D (K)	Density of tunneling states ($cm^{-3}\,eV^{-1}$), N_0	Reference
$Na_{0.25}V_2O_5$	0.06	3.3×10^{-3}	181	4.8×10^{22}	this work
$Na_{0.28}V_2O_5$	0.05	3×10^{-3}	189 [a]	4.00×10^{22}	
$Na_{0.33}V_2O_5$	0.052	3×10^{-3}	189	4.00×10^{22}	
$Na_{0.40}V_2O_5$	0.03	1.4×10^{-3}	277.8	2.4×10^{22}	
$K_{0.20}V_2O_5$	0.08	1.7×10^{-3}	252	6.4×10^{22}	
$Ag_{0.33}V_2O_5$	0.037	3×10^{-3}	189	4.93×10^{22}	
$Cu_{0.30}V_2O_5$	0.19	5.44×10^{-3}	110 [a]	1.46×10^{23}	8
$Cu_{0.40}V_2O_5$	0.29	4.2×10^{-3}	125	2.23×10^{23}	
$Cu_{0.55}V_2O_5$	0.15	5.25×10^{-3}	105 [a]	1.15×10^{23}	
$Cu_{0.60}V_2O_5$	0.12	6.56×10^{-3}	100 [a]	9.2×10^{22}	
$Li_{1.2}Ti_{1.8}O_4$	$\frac{3.6\text{ mJ}}{\text{mole K}^2}$	$\frac{0.05\text{ mJ}}{\text{mole K}^4}$	650 ± 40		10

[a] In these samples above ~7 K, Θ_D seems to jump abruptly by a factor ~ 1.3 to higher value.

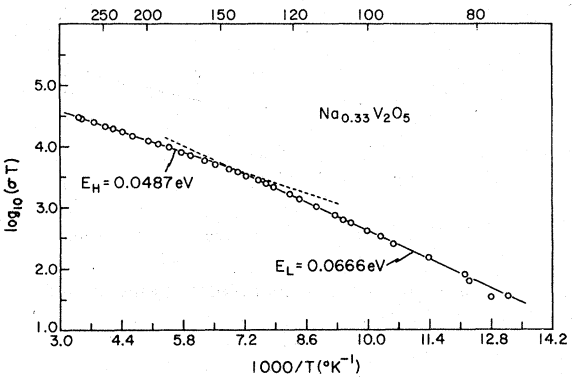

FIG. 3. Log_{10} electrical conductivity vs $1/T$ of single crystal $\mathrm{Na_{0.33}V_2O_5}$.

two activation energies for conduction, a low-temperature activation energy of 0.07 eV, and, above ~100 °K, a smaller activation energy of ~0.06 eV. The same general behavior has also been observed by Casalot *et al.*,[9] for the copper-vanadium bronzes.

III. ANALYSIS OF RESULTS ON A BIPOLARON MODEL

We propose that the ground states of the nonmetallic vanadium bronzes are bipolarons or singlet Heitler-London pairs of near-neighbor V^{4+} ions stabilized through local lattice deformation. Pure and stoichiometric vanadium pentoxide is slightly paramagnetic (temperature-independent) and insulating ($3d^0$ configuration of the V^{5+} ions, empty conduction band corresponding to V*d* orbitals) with a band gap of about 2.3 eV,[17] separating the filled oxygen band, from the empty *d* band. The interstitial alkali metals, or Ag, or Cu act as donors. Published ESR investigations[18] of variously doped V_2O_5 give evidence that these extra electrons brought in by the donors do not remain in the conduction band but are localized as V^{4+} centers. This is consistent with earlier work on the NMR of Li-vanadium bronzes[19] which showed lack of a Knight shift for the lithium, indicating that Li is totally ionized. Since Na has a lower ionization potential than Li, one expects this to be true also of the Na-vanadium bronzes. The ESR work on Na-vanadium bronzes[20] shows that, indeed, the resonating centers are V^{4+}, $S=\frac{1}{2}$, $3d^1$ cations, whose concentrations correspond to that of the interstitial metal atoms.[21] The fundamental question that we shall ask ourselves is whether these $S=\frac{1}{2}$ spin centers remain at $T=0$ as localized isolated spins or condense out as singlet $S=0$ pairs of near-neighbor V^{4+} cations. We shall show that such pairing occurs, if the lattice is soft enough to allow sufficient local deformation to overcome the near-neighbor Coulomb repulsion of two V^{4+} centers. The resultant attractive interaction provided between two spins through phonons is reminiscent of superconductivity and can be viewed as localized Cooper pairs. It has been clearly demonstrated by Schlenker *et al.*[22] that these bipolarons are the ground state of $\mathrm{Ti_4O_7}$, and, as they break up with temperature, it leads from nonmetal to metal transition in this compound. $\mathrm{Ti_4O_7}$ provides a model case of bipolaron formation, which was previously analyzed.[23] The fundamental interest of this kind of ground state originates from the conjecture of Anderson[24] that a collection of $S=\frac{1}{2}$ centers in a solid will tend to go at $T=0$ to a system of mobile or "liquid pairs" of singlet bonds. Anderson carried this idea further,[25] from the observation of lack of paramagnetic centers in amorphous chalcogenides, to postulate the formation of bipolarons in these materials due to local lattice deformation, leading to an attractive on-site interaction energy between two spins (negative correlation energy U_{eff}) and a singlet state. The bipolarons that we postulate, as the ground state of the vanadium bronzes, differ from Anderson bipolarons in that the pairing between two $S=\frac{1}{2}$ spins is not an on-site pairing but an inter-site one. We shall show that these Heitler-London bipolarons will in general lie energetically way below the Anderson bipolarons.

A. Bipolaron model

We shall consider the simplest case of two electrons between two sites *a* and *b*, each site having one single nondegenerate orbital. Adapting the single-site Anderson Hamiltonian[25] to the two-site case, we can write

$$H = H_e + H_l + H_{e-l}\,, \tag{1}$$

where H_e, H_l, and H_{e-l} are electron, lattice, and electron-lattice terms. These are given, respectively, by

$$H_e = \sum_{i=a,b} \epsilon_0 n_{i\sigma} + \sum_{i,j=a,b} T^0_{ij} c^*_{i\sigma} c_{j\sigma} + U \sum_{i=a,b} n^{\uparrow}_i n^{\downarrow}_i + \mathcal{V} \sum_{i,j=a,b} n_{i\sigma} n_{j\sigma'}\,,$$

where ϵ_0 are the unperturbed site energies, T^0_{ij} is the usual hopping integral, U is the on-site Coulomb repulsion between an up and a down spin, $\mathcal{V}$ is the intersite Coulomb repulsion, between two electrons on near-neighbor sites *a* and *b*, $n_{i\sigma}$ is the occupation operator of spin σ, and c^*, c are the usual creation and destruction operators for fermions.

The lattice term is represented through

$$H_l = \tfrac{1}{2}\beta x_{ab}^2, \qquad (1b)$$

where β is the stiffness constant of the lattice and x_{ab} is the local deformation of the bond a-b, equivalent to $x_{ab} = [(R_{ab} - R_{ab}^0)/R_{ab}^0]$, R_{ab} being the length of the bond $a-b$. The electron-lattice coupling term is written simply as

$$H_{e-l} = \lambda(n_{a\sigma} + n_{b\sigma'})x_{ab}, \qquad (1c)$$

where λ is a coupling constant.

As Anderson[26] pointed out, this is a low-frequency approximation but contains the essential physics of the problem. Eliminating x_{ab} from (1b) and (1c) we get

$$x_{ab}^0 = (-\lambda/\beta)(n_{a\sigma} + n_{b\sigma'}). \qquad (2a)$$

Substituting it back in (1b) and (1c), we obtain

$$H_l + H_{e-l} = (-\lambda^2/2\beta)(n_{a\sigma} + n_{b\sigma'})^2. \qquad (2b)$$

We can now write for the full effective Hamiltonian

$$H_{\text{eff}} = \sum_{a,b} \epsilon n_{a,b,\sigma} + \sum_{a,b} T_{ab} c_{a\sigma}^* c_{b\sigma} + U_{\text{eff}} \sum_{i=a,b} n_i^{\uparrow} n_i^{\downarrow} + \mathcal{V}_{\text{eff}} \sum_{i,j=a,b} n_{i\sigma} n_{j\sigma'}, \qquad (3)$$

where

$$\begin{aligned} &\epsilon = \epsilon_0 - \lambda^2/\beta, \\ &U_{\text{eff}} = U - 2\lambda^2/\beta, \quad \mathcal{V}_{\text{eff}} = \mathcal{V} - 2\lambda^2/\beta, \\ &T_{ab} = T_{ab}^0 \exp(-\lambda^2/2\beta\omega_0), \end{aligned} \qquad (3a)$$

ω_0 being the frequency of vibration of the atoms $(\omega_0^2 = \beta/m)$. We note in Eq. (3), that every term of the Hamiltonian (1) has been profoundly modified due to interaction with the lattice. The bare electron has now become a polaron, λ^2/β being the polaron binding energy corresponding to the undeformed state energy ϵ_0. T_{ab} is the new overlap integral reduced from bare electron overlap due to phonon overlap factor; this is the Holstein reduction factor[27] and is an extremely sensitive function of temperature, going down rapidly as temperature rises. U_{eff} is the bare Mott-Hubbard repulsion term reduced through the electron-phonon coupling term $2\lambda^2/\beta$. Similarly $\mathcal{V}_{\text{eff}}$ is the intersite Coulomb repulsion enormously reduced from its bare value. These last two terms raise the possibility of negative (attractive) correlation energies in a strongly, electron-lattice coupled system, provided $2\lambda^2/\beta > U > \mathcal{V}$. For the two-electron two-site Hamiltonian (3), we can have the exact solutions for the eigenfunctions and the eigenvalues. These are enumerated below in the order of increasing energy:

$$\begin{aligned} \epsilon_\alpha &= 2\epsilon + \mathcal{V}_{\text{eff}} + \tfrac{1}{2}(U_{\text{eff}} - \mathcal{V}_{\text{eff}}) - \tfrac{1}{2}[(U_{\text{eff}} - \mathcal{V}_{\text{eff}})^2 + 16T_{ab}^2]^{1/2} \\ &\sim 2\epsilon + \mathcal{V}_{\text{eff}} - 4T_{ab}^2/(U_{\text{eff}} - \mathcal{V}_{\text{eff}}), \\ &\qquad \text{for } U_{\text{eff}} - \mathcal{V}_{\text{eff}} \gg 4T_{ab}. \end{aligned} \qquad (4a)$$

This is the bipolaronic ground-state singlet

$$\begin{aligned} |\alpha\rangle \to \{&\phi_a(r_1)\phi_b(r_2) + \phi_a(r_2)\phi_b(r_1) \\ &+ \tfrac{1}{4}[x + (x^2+16)^{1/2}][\phi_a(r_1)\phi_a(r_2) + \phi_b(r_1)\phi_b(r_2)]\} \\ &\times (|\alpha_1\rangle|\beta_2\rangle - |\alpha_2\rangle|\beta_1\rangle), \end{aligned} \qquad (4b)$$

where r_1, r_2 are the electron coordinates of electrons 1 and 2 with spin-function $\alpha_1\beta_2$, etc., and $x = (U - \mathcal{V})/T_{ab}$ provides for the amount of admixture of the ionic state $\phi_a(r_1)\phi_a(r_2) + \phi_b(r_1)\phi_b(r_2)$ to the pure covalent state of the first term of Eq. (4b). Next, we have the triplet state

$$\epsilon_\beta = 2\epsilon + \mathcal{V}_{\text{eff}}, \qquad (4c)$$

with its eigenfunction triplet

$$\left.\begin{matrix} \beta_0 \\ \beta_1 \\ \beta_{-1} \end{matrix}\right\} \to [\phi_a(r_1)\phi_b(r_2) - \phi_a(r_2)\phi_b(r_1)] \times \left\{\begin{matrix} (|\alpha_1\rangle|\beta_2\rangle + |\alpha_2\rangle|\beta_1\rangle) \\ |\alpha_1\rangle|\alpha_2\rangle \\ |\beta_1\rangle|\beta_2\rangle \end{matrix}\right. . \qquad (4d)$$

This is followed by the singlet Anderson bipolaron

$$\epsilon_\gamma = 2\epsilon + U_{\text{eff}}, \qquad (4e)$$

with eigenfunction

$$|\gamma\rangle = [\phi_a(r_1)\phi_a(r_2) - \phi_b(r_1)\phi_b(r_2)] \times (|\alpha_1\rangle|\beta_2\rangle - |\alpha_2\rangle|\beta_1\rangle). \qquad (4f)$$

We note the purely ionic nature of the wave function $|\gamma\rangle$.

The highest eigenenergy is the antibonding singlet orbital corresponding to (4a) and is given by

$$\epsilon_\delta = 2\epsilon + \mathcal{V}_{\text{eff}} + \tfrac{1}{2}(U_{\text{eff}} - \mathcal{V}_{\text{eff}}) + \tfrac{1}{2}[(U_{\text{eff}} - \mathcal{V}_{\text{eff}})^2 + 16T_{ab}^2]^{1/2}. \qquad (4g)$$

The antibonding wave function is

$$\begin{aligned} |\delta\rangle = \{&\phi_a(r_1)\phi_b(r_2) + \phi_a(r_2)\phi_b(r_1) \\ &+ \tfrac{1}{4}[x - (x^2+16)^{1/2}] \\ &\times [\phi_a(r_1)\phi_a(r_2) + \phi_b(r_1)\phi_b(r_2)]\} \\ &\times (|\alpha_1\rangle|\beta_2\rangle - |\alpha_2\rangle|\beta_1\rangle). \end{aligned} \qquad (4h)$$

The four sets of energies with typical electron

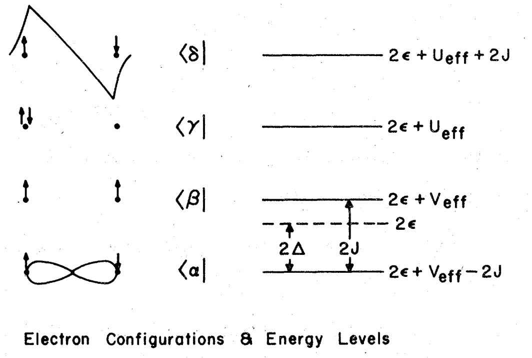

FIG. 4. Two-electron configurations and their energies. Ground state is the bonding singlet orbital, followed by the triplet state (β), and the singlet ionic state (γ), the highest being the antibonding singlet orbital (δ). The dashed line refers to the energy of two widely separated single polarons.

configurations are shown in Fig. 4. We see that because $U \gg \mathcal{V}$ the Anderson bipolaron will be least likely, except in cases of isolated impurity centers which do not have a near neighbor to give rise to the Heitler-London singlet bipolaron. This latter is stabilized as long as either $\mathcal{V}_{\text{eff}}$ is negative or if $2J > \mathcal{V}_{\text{eff}}$ where $2J$ is the singlet-triplet exchange energy given by, from Eq. (4a) and (4c),

$$2J = 4T_{ab}^2/(U_{\text{eff}} - \mathcal{V}_{\text{eff}}). \tag{5}$$

In Fig. 4, the completely dissociated bipolaron (i.e., two widely separated polarons) have energy 2ϵ, shown by the dotted line, and we have drawn the figure with a small positive $\mathcal{V}_{\text{eff}}$, so that the triplet state lies above the energy of the two separated polarons. If $\mathcal{V}_{\text{eff}}$ becomes negative the triplet state would become more stable than the separated polarons. We note from the figure that the energy to dissociate the ground-state singlet bipolaron is 2Δ where, from Eq. (4a),

$$2\Delta = 2J - \mathcal{V}_{\text{eff}}. \tag{6}$$

We note from Eqs. (3a), (5), and (6) the enormous role that the lattice must play if a singlet state is to be achieved; because the superexchange Eq. (5) term is generally small ($T_{ab} < \mathcal{V}_{\text{eff}} < U_{\text{eff}}$), one needs a greatly reduced intersite repulsion term to give an eventual attractive interaction between two spins on near-neighbor sites. The two basic ingredients to achieve the singlet ground state are that the lattice has to be soft, to allow a large coupling constant λ, and the initial wave function of the isolated electron must be sufficiently localized (either due to narrow bandwidth or disorder) to permit a large λ (or Frank-Condon shift). Both the Na- and the Cu-vanadium bronzes have relatively small Debye temperatures ~150 K. They are also highly disordered, due to random potentials of the alkali atoms. We believe that in such systems the essential conditions are met to give rise to a singlet ground state from $S = \frac{1}{2}$ spin centers. We will analyze the specific-heat, magnetic-susceptibility, and electrical-conductivity data on the postulated singlet ground state.

B. Specific heat

If we have a strictly two-level system, with energies $\epsilon_1 = 0$ and $\epsilon_2 = \delta$, the specific heat will be given by[28]

$$C = k_B \frac{(\delta/k_B T)^2 \exp(\delta/k_B T)}{[1 + \exp(\delta/k_B T)]^2}. \tag{7}$$

For $k_B T > \delta$, this gives rise to the so-called Schottky anomaly $C = k_B(\delta/2k_B T)^2$. If however the system is quite random, then one will expect a certain distribution of δ, such that all values of δ are equally likely up to some limit δ_0. In such a case, one obtains the heat capacity linear with T, up to $k_B T < \delta_0$. This analysis was first proposed for dilute magnetic alloys by Marshall[29] and is at the heart of the two-level tunneling-mode argument of Anderson[4]–Halperin-Varma-Phillips[5] (AHVP) for glassy systems. The nature of the centers executing the tunneling motion in the AHVP model remains unspecified and highly ambiguous. If we consider that the nonmetallic vanadium bronzes are bipolaronic glasses, then we can imagine, as in Fig. 5, a typical bipolaron and its tunneling motion, as indicated by the arrows. In the absence of disorder, such a "rattlesnake" tunneling motion of the bipolaron along the V chains could give rise to certain bipolaron band conductivity. In the presence of disorder, one has a typical two-level tunneling system, the initial and the final configurations separated by certain energy $\delta_0 > k_B T$. The configuration of the two sets of V chains had been worked out for $\mathrm{Na}_{0.33}\mathrm{V}_2\mathrm{O}_5$ by Wadsley,[30] and we presume the bipolaron to form preferentially on

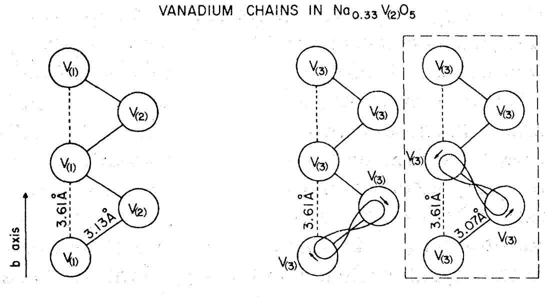

FIG. 5. Two vanadium chain configurations along the b axis. Right-hand chain shows two alternate configurations of the bipolaron on the $\mathrm{V}_{(3)}$ chain.

the chain with the shortest V – V distance. Recently Phillips[31] has shown that the Anderson bipolarons cannot give rise to tunneling motion, and hence to the linear term in the specific heat, because of the inherent difficulty of two electrons on the same site tunneling out of it at the same time. No such difficulty exists for the Heitler-London bipolaron, as shown in Fig. 5, for it suffices for only one electron of the pair to tunnel, causing the bipolaron to flip flop between two equivalent configurations. It is quite obvious that beyond a critical concentration of bipolarons, tunneling motion within a chain would be impeded, causing the linear term to drop in magnitude, which is what is seen experimentally at the higher sodium or copper concentrations. In point of fact, not all the bipolarons can participate in the tunneling process. This is seen by examining the density of the tunneling states ($\mathrm{eV}^{-1}\,\mathrm{cm}^{-3}$), as tabulated in the next-to-last column of Table I. This density is arrived at by the use of the AHVP[4,5] formulation of γ,

$$\gamma = \tfrac{1}{12}\pi^2 n_0 k_B^2 , \tag{8}$$

where n_0 is the density of tunneling states. If we assume that $\delta_0 \approx k_B T \approx 10^{-4}$ eV, this gives us $\sim 10^{19}$ states/cm^3 executing the tunneling motion. Only one out of a thousand bipolarons is thus able to absorb a phonon and tunnel. In order to convert the γ of Fig. 1, we have used a mass density of 2.5 g/cm^3 for the bronzes. This reduced number probably reflects a steric hindrance, imposed by the fact that for a bipolaron to tunnel there must be an empty site nearby on the same chain, and thus one ought to expect in the γ term, as a function of concentration, a maximum. The number n_0 ($\sim 10^{22}$ per cm^3 per eV) gives us an approximate value of the density of states at the tail of the bipolaron band at the Fermi level. We may note that in the absence of disorder or tailing, the density of states at the Fermi level would be zero, the Fermi-level remaining pinned in the middle of the single-particle excitation gap 2Δ of Eq. (6).

C. Magnetic susceptibility

The magnetic susceptibility behavior of these bronzes is very characteristic, as we can see in Fig. 2, the inverse susceptibility showing an apparent Curie-Weiss behavior at the higher temperatures, with a deviation from the Curie-Weiss line as the temperature is lowered. This behavior can be explained by supposing one has at least two contributions to the magnetic susceptibility, one of the majority, host V^{4+} spin ($N \sim 10^{22}/\mathrm{cm}^3$, $S=\frac{1}{2}$) with antiferromagnetic interaction and, at lower temperatures, the usual paramagnetic impurity contribution of the form C/T. But what is disturbing in such an explanation is the singular and remarkable fact that even in such large spin concentrations, the host spins do not seem to order antiferromagnetically at all, down to the lowest temperatures of measurement (1.5 K for the Na bronzes, 0.5 K for $\mathrm{Li}_{1+x}\mathrm{Ti}_{2-x}\mathrm{O}_4$). One can get an idea of the average magnetic moment by replotting the data in the manner used by Van Vleck[32]:

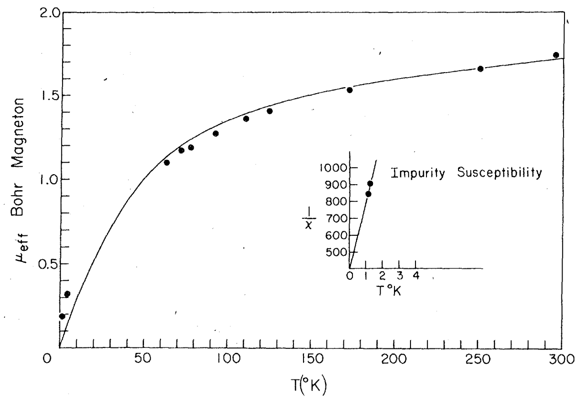

FIG. 6. Effective Bohr magneton per atom vs temperature; circles are the experimental points. Inset shows the Curie law for the impurity susceptibility.

$$\bar{\mu} = (\chi 3kT/N\mu^2)^{1/2} , \tag{9}$$

where $\bar{\mu}$ is the average magnetic moment, χ the measured susceptibility, and μ the Bohr magneton. This plot is seen in Fig. 6 as a function of temperature for the $\mathrm{Na}_{0.33}\mathrm{V}_2\mathrm{O}_5$ sample. The figure would indicate that the majority spins are entering, as the temperature is lowered, to some form of nonmagnetic, zero-spin state. It is only towards 300 K and upwards that the effective magnetic moment seems to approach the $S=\frac{1}{2}$ spin only value ($g[S(S+1)]^{1/2}$) of $\sim 1.8\mu_B$, corresponding to a localized V^{4+} center.

In order to analyze the bulk susceptibility data further, it is essential that one takes out the impurity contribution. If we suppose that the low-temperature deviation from the Curie-Weiss behavior is uniquely due to paramagnetic impurities, one can draw a C_{imp}/T line, for the low-temperature points, this is seen in the inset of Fig. 6 for the $\mathrm{Na}_{0.33}\mathrm{V}_2\mathrm{O}_5$ sample. The data indicate a Curie constant $C_{\mathrm{imp}} = 0.001$. Since the dominant paramagnetic impurity is Fe^{3+}, using $S=\frac{5}{2}$ gives us an impurity concentration of about 0.05mol%. This corresponds to about 10^{18} impurities/cm^3 which is what we have in the sample. We note that such a paramagnetic impurity concentration would be adequate to give us also the Schottky anomaly in the specific heat, seen in some samples.

We shall now analyze the rest of the bulk susceptibility, on the bipolaron model. Let us suppose that at $T = 0$ we have the singlet bipolarons and that they break up progressively as the temperature is raised. Each bipolaron needs an energy 2Δ (Fig. 4) to become two separated localized spins, or, one needs an energy Δ per single-particle excitation. We shall suppose that the triplet state is way above in energy and does not contribute to susceptibility except for virtual excitation, providing for the temperature-independent Van Vleck susceptibility χ_{VV}.[33] The total susceptibility can be written as a thermal average

$$\chi(T) = \chi_{VV} p(T) + \chi_p(T)[1 - p(T)], \tag{10}$$

where $p(T)$ is the probability that an electron has remained in the paired singlet state and $1 - p(T)$ is the probability that the electron has been excited. In Eq. (10), $\chi_p(T)$ is the paramagnetic susceptibility of localized spins given for N electrons/mole, by

$$\chi_p(T) = Ng^2 S(S+1)\mu^2/3kT \tag{10a}$$

and χ_{VV} is the Van Vleck term given for N singlet pairs, by

$$\chi_{VV} = 8N\beta^2/2J. \tag{10b}$$

The simplest derivation of $p(T)$ can be obtained by referring to Fig. 7 for the two-level system, where Δ is the energy necessary to create one nonpaired localized spin. The probability of the single-particle excitation is then $\exp(-\Delta/kT)$, to give us

$$p(T) = \frac{1 - \exp(-\Delta/kT)}{1 + \exp(-\Delta/kT)} = \tanh(\Delta/2kT). \tag{11}$$

The susceptibility (10) is then

$$\chi(T) = \chi_{VV} \tanh(\Delta/2kT) + \frac{C}{T}[1 - \tanh(\Delta/2kT) , \tag{12}$$

where

$$C = \frac{M\mu^2 g^2 S(S+1)}{3k}.$$

M is the number of donor ions per mole, assuming each donor gives one electron, $S = \frac{1}{2}$. In Eq. (12) it is extremely difficult to obtain an *a priori* evaluation of χ_{VV}, as we do not know the singlet-triplet spacing $2J$. In Ti_4O_7,[22] it is found to be small: 2×10^{-14} emu/mole; it is probably even smaller in the vanadium bronzes. We have evaluated Eq. (12) for the case

$$\chi_{VV} = 1.4 \times 10^{-4}, \quad \Delta/k = 100 \text{ K}.$$

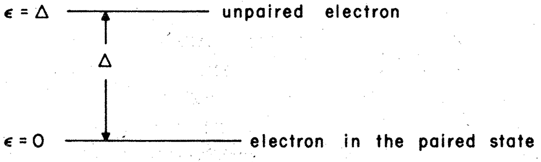

FIG. 7. Ground and the excited state of a electron; excited state refers to a broken pair.

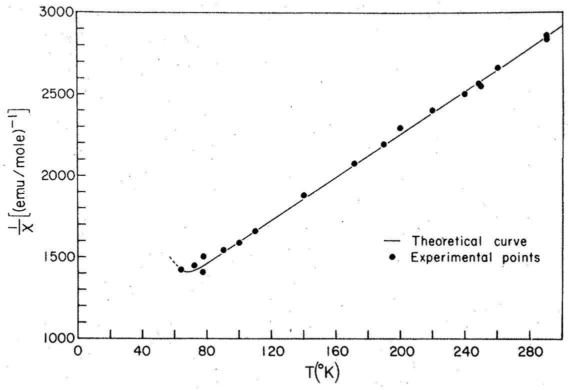

FIG. 8. Inverse magnetic susceptiblity (with impurity contribution subtracted) vs $1/T$: solid line, theoretical curve; dots, experimental points.

Figure 8 shows the results, evaluated for $T > 60$ K for which the experimental data points are available, for $Na_{0.33}V_2O_5$. The almost perfect fit with the experimental data is to be noted. The specific value of Δ has been chosen with an eye on the conductivity data. It is to be emphasized that no antiferromagnetic interactions need be invoked to explain the bulk susceptibility. In point of fact, extrapolation of the high-temperature inverse susceptibility to extract the Curie-Weiss Θ often gives ridiculous numbers[9] and is nonphysical. In Fig. 8, for the experimental points, the impurity contribution has been subtracted.

D. Electrical conductivity

We shall not dwell in any detail on the electrical-conductivity data (Fig. 3) of these bronzes. According to the bipolaron model developed above, the temperature T_C above which the activation energy goes from high to low value will correspond to $kT_C \sim \Delta$. The conductivity is by excitation of the localized polarons across the mobility edge to the d conduction band, as Mott[34] has suggested for the tungsten bronzes. It is transparent that the activation energy for conduction below T_C will contain the extra energy Δ necessary to create the single particles. In our analysis, we have supposed that Δ is a constant, but nothing prevents Δ from being temperature-dependent and allowing for a true phase transition, at $\Delta = 0$ at $T = T_C$. Unlike Ti_4O_7, we have no evidence of a phase transition in the vanadium bronzes. Although bipolaron tunneling and hopping would occur, the dominant conduction mechanism in these bronzes will be single-particle excitation to the mobility edge at all but the lowest temperatures.

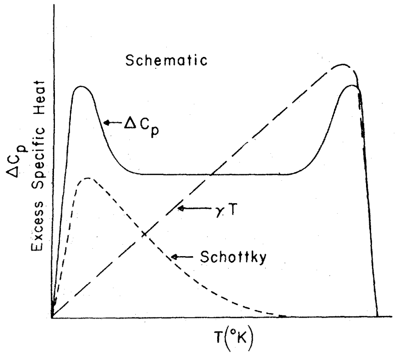

FIG. 9. Schematic extra low-temperature specific heat, when γT is comparable to the Schottky term. Lattice contribution not included in the figure.

IV. DISCUSSION

We have shown in Secs. III B–III D that the low-temperature, specific-heat, magnetic-susceptibility, and conductivity data of a variety of nonmetallic vanadium bronzes can be unified in a coherent whole on the basis of a singlet ground state of bipolarons or deformation-induced electron pairing. The most striking is the linear specific heat which is explained naturally as due to bipolaron tunneling. Sandin and Keesom[35] had reported earlier on the observation at low temperatures of an extra specific heat above the lattice T^3 term in reduced rutile TiO_{2-x}; their data show, however, the extra contribution to be independent of temperature. It is to be remarked that, if the paramagnetic (Ti^{3+}) centers go in reduced rutile at $T=0$ to singlet states, as in Ti_4O_7, the joint Schottky and the bipolaron γT term would explain the rutile data, as shown in Fig. 9. The Schottky line is the Eq. (7) of our Sec. III, and the γT term falls off beyond a temperature T when the tunneling ceases and merges into hopping or other multiphonon processes. The resultant double-humped specific-heat curve would obtain if the γ term (in reduced rutile, γ would be much smaller than in the bronzes, as x corresponds to $\sim 10^{19}$ Ti^{3+}/cm^3). There will be a large temperature segment where the extra specific heat will be flat, and this may be an alternative explanation for the rutile data.

The pairing interactions that we have proposed here for the vanadium bronzes is not without analogy with its more well-known siblings as seen in VO_2,[36] or V_4O_7.[37] Ragle,[38] as early as 1962, postulated their presence in order to explain his ESR data on reduced V_2O_5. More recently Bang and Sperlich[39] have actually laid down the evidence of this kind of pairing with their ESR data on $K_{0.3}MoO_3$ bronzes. How close the phonon-induced pairing phenomenon postulated here is to superconductivity can be gauged by the fact that, although $Li_{1+x}Ti_{2-x}O_4$ is semiconducting, $LiTi_2O_4$ is a superconductor with a $T_C = 12$ K.[40] The localized Cooper pairs that one has seen in Ti_4O_7,[23] and that we have invoked in these vanadium bronzes, may indeed be a genuine precursor to true superconductivity.

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