bors. Similarly, considerations of electronegativity differences, which would imply that oxygen be negatively charged, seem not to be relevant: For our configuration even a small charge on the oxygen would be inconsistent with the observed work-function change of 0.3 eV. It was this fact that led Hagstrum and Becker[7] to postulate a structure in which nickel is coplanar with oxygen, allowing charge transfer without a dipole moment. However, such a model was found incompatible with the LEED data. It would seem that for an understanding of surface chemistry some modification of traditional chemical concepts will be required.

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Specific-Heat Anomalies in the Systems (Ti, V)₂O₃†

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A model for the Ti, V_2O_3 electronic d levels is proposed and shown to account satisfactorily for observed anomalous low-temperature specific heats in the system. In the (Ti, V)₂O₃ systems, in particular, empty V d levels lie so far below the conduction band as to penetrate the host valence band a short way.

Sjöstrand and Keesom[1] have measured the specific heat of a number of samples of Ti_2O_3 doped with varying amounts of vanadium. In the temperature range from a few tenths of a degree Kelvin to 20 K, they have discovered a remarkable anomaly. In this range, the specific heat exceeds expected values by as much as 3 orders of magnitude. Furthermore, after an initial steep, linear rise, this excess specific heat levels off and becomes almost independent of temperature.

In a series of publications, Sjöstrand and Keesom[1-3] have offered a "one-dimensional" band structure characteristic of the pure host material as a model for the origin of the anomaly. The "one-dimensional" model fits the specific-heat data extremely well. A similar model had been used for describing anomalies in the V_3Si system by Labbé and Friedel.[4] However, as has been argued elsewhere,[5,6] a one-dimensional band can only be found in a three-dimensional lattice as an approximation to an highly anisotropic three-dimensional band. The structural characteristics of V_3Si lead naturally to extreme anisotropy while those of Ti_2O_3 do not. The existence of one-dimensional bands in the Ti_2O_3 structure would thus be as anomalous and difficult to understand as the curious specific-heat behavior it has been invoked to explain. Also, such a model predicts corresponding anomalies and anisotropies in other phenomena such as transport where, however, they have not been observed.[5] A final puzzle is that each V ion seems to contribute only 0.12 of the 3 degrees of freedom we would expect (or 0.4 of the single degree expected in one dimension).

We thus take the position that the success of the "one-dimensional" hypothesis, although strik-

ing, is fortuitous, and seek an alternative explanation of the specific-heat data in accord with the three-dimensional nature of the Ti_2O_3 corundum lattice. To this end, we examine the data to see precisely what is required of a model.

The data of Keesom and Sjöstrand on a variety of V-doped Ti_2O_3 samples are shown in Fig. 1. The normal lattice specific heat, obtained from studies of undoped samples, has been subtracted. The anomalous C_p is a steep, linear function of T at low T; the slope of the rising portion varies inversely with vanadium content. In the neighborhood of a characteristic temperature T_c, the curves become level, C_p remaining nearly constant for higher temperatures. The apparent T_c is roughly proportional to the square of the V content, $\mathfrak{N}$, and the initial slope varies inversely with $\mathfrak{N}$, so the saturation value of C_p is proportional to vanadium doping. The curves are terminated where the lattice specific heat becomes dominant.

The large saturation value, $\sim 10^2$ mJ/mole Ti, absolutely demands a model with a large number of degrees of freedom, comparable to and linear in the number of V ions introduced. The steep initial rise likewise absolutely requires a high density of states per degree of freedom. The constant region up to 20 K requires an excitation spectrum for each degree of freedom extending with undiminished density to many times the characteristic energy of saturation, $k_B T_c$.

All these features could be obtained from a standard three-dimensional host band holding dopant-introduced carriers. The high density of states required by the anomalies, however, would make the host-band effective mass turn out to be about 2000 free-electron masses, a figure which is inconsistent with the high mobilities observed in pure Ti_2O_3.[7] This model would also be inconsistent with transport data[6,8] and recent ultrasonic measurements[9] as well as high-temperature specific-heat measurements in the transition region[10] around 500 K. Most of these objections apply with equal force to the one-dimensional model as well.

We present here a model which fits the specific-heat data and is consistent with all other Ti_2O_3 properties; a set of otherwise empty localized levels associated with the vanadium ions lies so far below the Ti_2O_3 host conduction band as to penetrate a short way into the host valence band. The resulting density of states is shown in Fig. 2. The Fermi level at $T = 0$ lies in the band of impurity states a short way from its lower edge. As the impurity band penetrates the valence band, electrons in the valence band empty into the unfilled impurity states. This provides a few electrons in the nearly empty vanadium band and a few holes in the top of the nearly full host valence band. These light holes account for the normal transport properties of the system, including the positive Hall coefficient seen previously.[11] The initial steep rise in C_p as a function of T is due to the very high state density in the impurity
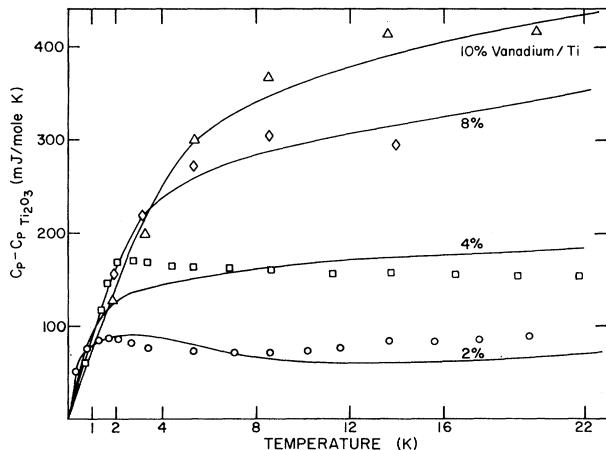

FIG. 1. Excess (over pure Ti_2O_3) specific heats of V-doped samples. Solid lines, theory obtained from the present model. Symbols, representative data points. (Data are available at much closer intervals.) On the linear, low-temperature portions, the model and the data coincide exactly, and no data are shown to avoid crowding.
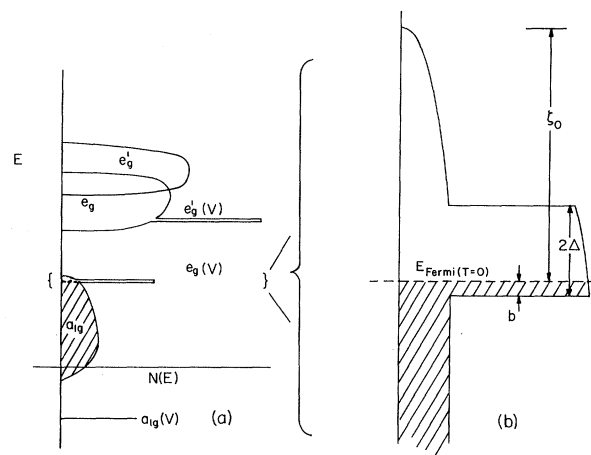

FIG. 2. Proposed density of d states of V-doped Ti_2O_3. (a) General structure proposed by Van Zandt, Honig, and Goodenough with V states added according to the present model; (b) expansion of the region around the Fermi level.

band. At a temperature T_c corresponding to the degree of filling of the impurity band, the impurity-band electrons become more like a nondegenerate gas, hence the specific heat tends to assume a constant, DuLong-Petit value characteristic of the number of electrons shifted from the valence band to the impurity band. This feature of the model accounts for the relatively small number of electrons per vanadium ion (0.12). At still higher temperature characteristic of the entire width of the vanadium band, the electrons become uniformly distributed through the vanadium band and cannot be further energized; the specific heat tends to fall to zero. Finally, the holes in the host valence band contribute a portion to C_p linear in T, but with a relatively smaller slope because of the much larger valence bandwidths and consequently reduced density of states.

The model requires four parameters for complete characterization: (1) the effective mass of the host valence band, m^*, (2) the degree of penetration of the vanadium band into the valence band, ζ_0, (3) the total number of vanadium band states, c, and (4) the width of the vanadium band, 2Δ. Of the four, m^* is least precisely determined by the experiments. (We used a parabolic, three-dimensional, valence band.) At the "high"-temperature end of the curves of Fig. 1, the anomalous C_p is rising again. This rise is the effect of the hole contribution and is more steep with increasing m^*. We adjust m^* to match this rise, but this is the range of T where the phonon contribution becomes dominant and thus where the experimental excess C_p is least accurate. ζ_0 is determined by the "saturation" value of the flat portion of the curves; $(\zeta_0 m^*)^{3/2}$ is proportional to the number of vanadium band electrons and valence band holes. c must be a constant multiple of the vanadium concentration. As we shall argue presently, the constant is 4. Δ is determined by the slope of the steep initial rise since the vanadium band density of states varies inversely with the bandwidth. For simplicity of calculation we took the vanadium band density of states to be constant across the band, as indicated in Fig. 2. We could introduce further parameters by complicating the shapes of bands involved, or allowing the parameters to become functions of temperature; four, however, is the absolute minimum required by the model.

The experiments were performed on samples with a variety of vanadium concentrations. We obtained a reasonable fit to the various curves by letting ζ_0 and Δ be linear functions of the concen-

tration; with $m^* = 3.5m_0$, $\zeta_0 = (240 + 85n)$ K and $\Delta = (-20 + 15n)$ K. n is the relative vanadium content in percent. These relations should not be regarded as anything but rough characterizations, however. Particularly at the lower concentrations, the vanadium levels apparently have a more complex structure than we have assumed. The parameter c is, of course, strictly linear in V concentration, and the host-band effective mass m^* is constant.

Figure 2(a) shows the general scheme of d bands in Ti_2O_3 as proposed by Van Zandt, Honig, and Goodenough.[12] Shown as well are proposed d impurity levels of vanadium ions in the Ti_2O_3 host. The lowest-lying a_{1g} states are filled by the two d electrons of V^{3+} ion. The next highest d levels are of e_g symmetry and are doubly orbitally degenerate. Together with the spin degeneracy, this provides the four states per V ion mentioned earlier. These e_g states are so tightly bound to the V ion as to fall below the upper edge of the a_{1g} valence band. This model is also clearly consistent with the suggestion of Honig et al.[11] concerning the origins of the positive Hall coefficient of V-doped Ti_2O_3.

The calculation of the specific heat from this model is elementary and will not be discussed here. The results are shown as solid curves in Fig. 1. The model provides a satisfactory explanation of the anomalies, although some details are not reproduced. It is clear that by including various refinements as discussed above, the fit to the data could be much improved. This discussion provides a model for the anomalies, but as a theory it is incomplete. We have offered no explanation for the concentration dependence of ζ_0 and Δ. The model suggests further that there should be a correspondingly enormous electronic susceptibility anomaly which we shall discuss elsewhere.

It is possible to construct a similar model for a corresponding anomaly in the specific heat of V_2O_3 doped with Ti.[13] In this system, the specific-heat anomaly is of similar magnitude at low T, but does not show the saturation behavior. As we have just discussed at length, the saturation behavior of $(Ti, V)_2O_3$ occurs because otherwise empty levels of V penetrate the host valence band. To eliminate the saturation, therefore, we need only consider partially filled levels of Ti penetrating a V_2O_3 host band. V^{3+} ion has two d electrons which we accounted for by assuming a_{1g} vanadium level below the Ti_2O_3 valence band. Ti^{3+}, by contrast, has only a single d electron.

Because of spin degeneracy, any level into which it goes will be partially filled. Thus we may apply this model to $(V, Ti)_2O_3$ by assuming that the lowest Ti level, whatever its symmetry, slightly penetrates the V_2O_3 host valence or conduction band, whatever their symmetries.

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Thermoelectric Power of Tetrathiofulvalinium Tetracyanoquinodimethane*

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Measurements of the thermopower of the organic conductor tetrathiofulvalinium tetracyanoquinodimethane have been made in the region 10–300°K. At high temperatures ($T > 140°K$) the samples are metallic showing increased electron correlations as the temperature is lowered to about 56°K. At this point the thermopower is zero and a discontinuity marks the transition to the insulating state.

In a recent Letter Coleman et al.[1] reported the observation of a high conductivity maximum in the organic charge-transfer salt tetrathiofulvalinium tetracyanoquinodimethane (TTF-TCNQ). The magnitude and temperature dependence were interpreted in terms of superconducting fluctuations preceding a transition to a Peierls insulating ground state. The extraordinary conductivity maximum has been observed in only a few of the many samples tested. The remaining samples show a qualitatively similar conductivity, but with much smaller maxima of magnitude varying from 5 to 25 times the room-temperature value, in general agreement with the results of Ferraris et al.[2]

The structure of TTF-TCNQ[3] consists of alternating chains of TCNQ anions and TTF cations, creating strong anisotropy in the electronic properties and a quasi–one-dimensional conductivity similar to many of the other highly conducting TCNQ salts.[4] The one-dimensional chains are extremely sensitive to imperfections, defects, and impurities as a conductivity measurement on a highly conducting chain would be limited by the resistance of any interruptions. It is therefore plausible that the measurement of an extremely high conductivity would only be observed in near-perfect crystals. The thermoelectric power, however, is a *zero-current* transport measurement and would not be limited by breaks in the chains assuming that most of the temperature drop occurred across the unbroken regions