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Specific Heat and Paramagnetic Susceptibility of Stoichiometric and Reduced Rutile (TiO_2) from 0.3 to 20 K*

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The specific heat of rutile (TiO_2) has been measured between 0.3 and 20 K in different magnetic fields, and for various degrees and types of reduction. In addition, the paramagnetic susceptibility has been measured below 4.2 K for three reduced samples. The parameters which characterize the specific heat of the stoichiometric boule include a Debye Θ at $T=0$ of 778 K, an optical mode of Einstein frequency 83 cm^{-1}, and an impurity of 1.08 ppm Fe^{3+}. The specific heat of all reduced samples indicates that there is a narrow intrinsic conduction band lying below the wider conduction band seen above 30 K. The electrons in this band have a density-of-states effective mass of $190m_e$. The specific heat of a vacuum-reduced sample in zero field and two magnetic fields is reproduced by a model which has 1.1×10^{18} cm^{-3} impurity-related spin-degenerate levels 1.8×10^{-4} eV below the narrow band. In the more highly reduced samples, the defects are not impurity-related. Below 1.2 K, the specific heats and magnetic susceptibility of highly reduced rutile are characteristic of a paramagnetic ion with two energy levels about 10^{-4} eV apart. Hydrogen reductions result in interaction between the ions. The activation energy to the band is about 5×10^{-4} eV for rutile reduced highly without the use of hydrogen, but no activation energy is evident for hydrogen-reduced material. A decrease in the specific heat near 20 K is not understood. It may be explained as being due to a decrease in the lattice specific heat with reduction. It also may be due to electrons approaching the top of the band which then narrows with increasing temperature because of small polaron effects.

I. INTRODUCTION

STOICHIOMETRIC and reduced rutile (TiO_2) has been the subject of many different types of investigation, reviews of which were given by Frederikse[1] in 1961 and Grant[2] in 1959. Stoichiometric rutile is an insulator with an intrinsic energy gap generally agreed to be greater than 3 eV. Upon reduction to TiO_{2-x}, it becomes an n-type semiconductor with properties dependent upon both the amount and method of reduction. Above 30 K the conduction properties have been interpreted in terms of polaron band conduction[3] or standard band conduction in one[4] or two[5] bands. Below 30 K, the properties measured indicate some sort of narrow band conduction. This has been suggested to be either polaron band conduction[6] or some type of impurity band conduction.[7,8] None of the experiments performed could distinguish between these two types of conduction. The defects introduced by reduction have long been a source of controversy, and are variously thought to be either titanium ions or oxygen vacancies, or both, or combinations of these defects with impurities in the lattice.[9,10] Many experiments, e.g., electron spin resonance,[11] thermal conductivity,[12] etc., indicate that the nature of the defect is dependent upon the method of reduction.

In this article the results of measurements of the low-temperature specific heat of stoichiometric, vacuum-reduced, hydrogen-reduced, and Ti-powder-reduced rutile, as well as the paramagnetic susceptibility of some of the reduced samples, will be given and discussed. It is hoped that these results will be helpful in clarifying the type of conduction and nature of the defects in rutile reduced by different methods and to different degrees. Section II contains the experimental details of the measurements, while Secs. III and IV contain the results and discussions for stoichiometric and reduced rutile, respectively. The only previous measurements of the specific heat of stoichiometric and reduced rutile below 20 K were those of Keesom and Pearlman,[13] which extended down to 1.2 K. The magnetic susceptibility of stoichiometric rutile has been previously measured[14] down to 4.2 K while one hydrogen-reduced sample has been measured[15] as low as 1.25 K.

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[1] H. P. R. Frederikse, J. Appl. Phys. **32**, 2211 (1961).

[2] F. A. Grant, Rev. Mod. Phys. **31**, 646 (1959).

[3] V. N. Bogomolov, E. K. Kodinov, and Yu. A. Firsov, Fiz. Tverd. Tela **9**, 3175 (1967) [English transl.: Soviet Phys.—Solid State **9**, 2502 (1968)].

[4] G. A. Acket and J. Volger, Physica **32**, 1680 (1966).

[5] J. H. Becker and W. R. Hosler, Phys. Rev. **137**, A1872 (1966).

[6] H. P. R. Frederikse, W. R. Hosler, and J. H. Becker, in *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Publishing House of The Czechoslovak Academy of Sciences, Prague, 1961), Paper R7, p. 868.

[7] R. R. Hasiguti, N. Kawamiya, and E. Yagi, in *Proceedings of the International Conference on the Physics of Semiconductors, Paris, 1964* (Dunod Cie, Paris, 1965), p. 1225.

[8] J. H. Becker and W. R. Hosler, J. Phys. Soc. Japan Suppl. **18**, 152 (1963).

[9] L. A. K. Dominik and R. K. MacCrone, Phys. Rev. **156**, 910 (1967); **163**, 756 (1967), and references therein.

[10] R. N. Blumenthal, J. Baukus, and W. M. Hirthe, J. Electrochem. Soc. **114**, 172 (1967).

[11] P. F. Chester, J. Appl. Phys. **35**, 3414 (1964); and Westinghouse Scientific Paper No. 908C 901-P 3 (unpublished).

[12] W. R. Thurber and A. J. H. Mante, Phys. Rev. **139**, A1655 (1965).

[13] P. H. Keesom and N. Pearlman, Phys. Rev. **112**, 800 (1958), hereafter referred to as KP.

[14] F. E. Senftle, T. Pankey, and F. A. Grant, Phys. Rev. **120**, 820 (1960).

[15] J. M. Honig and P. H. Keesom, Purdue University, Semiconductor Research Quarterly Report, 1955 (unpublished).

TABLE I. Parameters of reduced samples.

	RH1	RH2	RH2A	RV3	RTi5	RH6	RH7
Reduction	900 C, 2 h vac+ 900 C, 12 h vac+ 950 C, 2 h hydrogen	1000 C, 7.5 h hydrogen	a piece of RH2	1000 C, 1 wk vacuum	1000 C, vacuum with Ti powder	1000 C, 2 h hydrogen	1000 C, 4 h+ 1000 C, 6 h hydrogen
Weight Loss	$4\times10^{-3}\%$+ $4\times10^{-3}\%$+ 0.74%	1.18%		$8\times10^{-3}\%$	0.36%	0.12%	0.23%+ 0.11%
Number of electrons per cm^3	3.6×10^{19}	5.7×10^{19}	4.4×10^{19}	1.1×10^{18}	3.3×10^{19}	1.0×10^{19}	4.9×10^{19}
Number of paramagnetic centers per cm^3		9.0×10^{19}	7.0×10^{19}		6.9×10^{19}	1.4×10^{19}	
Level separation, a	$\approx$0.9 K	$\approx$0.9 K	$\approx$0.9 K	($\Delta E=2.1$ K)	1.3 K	$\approx$1.3 K	
A (K/Oe^2)		$\approx8\times10^{-9}$	$\approx8\times10^{-9}$		4.5×10^{-9}	$\approx4.5\times10^{-9}$	
Position of low-range maximum	0.50 K	0.47 K	0.48 K	0.80 K	0.53 K	0.62 K	
Mass of sample (in g)	7.711	9.569	1.708	7.876	7.527	91.316	52.878
Resistivity (ohm-cm)							
295 K	0.043			4.2	0.12		
77 K	2.3			1.65	0.43		
4.2 K	$>10^6$			$>10^7$	$>10^6$		

II. EXPERIMENTAL

A. Sample Preparation

The rutile used was obtained from Linde with the exception of boule RH7, which was obtained from National Lead. Three different types of reduction processes were employed. The method of reduction of the various samples is indicated in Table I, together with other parameters. The labeling of the samples, H, V, and Ti, indicates the method of reduction.

Sample RV3 was cut from the end of the boule used for the stoichiometric measurement. It was prepared by heating in a vacuum of approximately 5×10^{-5} Torr in a clean carbon boat. The vacuum pump was liquid nitrogen trapped to minimize contamination. RV3 had small weight loss, no large cracks, and a uniform gray color. The hydrogen-reduced samples were placed in a clean carbon crucible in an induction furnace. They were heated in flowing hydrogen and cooled to room temperature in about 2 h with the hydrogen flow continued. Strong reduction in hydrogen resulted in large cracks in the crystal. The reduction in hydrogen was not completely uniform, as evidenced by variations in the blue-black color over the surface and by the difference between the specific heats of RH2 and RH2A (RH2A was a piece of RH2). To attempt to gain a large reduction without hydrogen, sample RTi5 was prepared at the National Bureau of Standards by heating stoichiometric rutile and finely divided Ti powder in an evacuated Vycor capsule. This sample had some cracks and a uniform gray-black color.

Hydrogen-reduced material has a low thermal conductivity and high specific heat. The resultant low thermal diffusivity can cause errors in determination of the specific heat due to excessively long thermal equilibrium times. To decrease these equilibrium times, RH1 and RH2 were cut into two flat slabs each. Between the slabs was placed a third slab of high purity Ge with the heater wire on its periphery. The facing surfaces were polished and coated with a thin layer of Apiezon "N" grease. This "sandwich" construction eliminated difficulties with thermal equilibrium times except with the lowest temperature measurements in a magnetic field. The sandwich construction was not used on RH2A because of its small size, nor was it needed on RV3, RTi5, or RH6 because of their higher thermal diffusivity. RH7 was not measured in a temperature range where there were excessive thermal equilibrium times.

B. Measurement Techniques

The specific-heat measurements were made using a heat pulse method. Early specific-heat measurements on RH1 and RH2 used constantan heater wire, while later Pt-9%W wire was employed. The thermometer and heater were glued with Glyptal enamel. In the 0.3 to 4.5 K range, Ge resistance thermometers made in this laboratory were used for the specific-heat measurements. They had low heat capacity, but were not reproducible and had to be calibrated after each run. The calibrations were based on the 1958 He^4 temperature scale above 1.2 K and the 1962 He^3 scale between 0.5 and 1.2 K. Below 0.5 K the calibration was accomplished by the measurement of the paramagnetic susceptibility of a sphere of ferric ammonium sulphate granules. The effect of a magnetic field on the longitudinally mounted thermometers was found to be approximately quadratic in H and linear in $1/T$ with the magnetoresistance positive below and negative above 1.5 K. As the paramagnetic susceptibility could not be measured in the presence of a magnetic field, the thermometer calibrations below 0.5 K in a field are based on extrapolations of higher-temperature corrections to the zero-field calibrations.

The thermometer used for the 4 to 20 K measurements was an encapsulated commercial Ge resistance thermometer calibrated by the manufacturer[16] against secondary standards traceable to the National Bureau of Standards provisional scale of 1965. This calibration was used in calculating the specific heat in the 4 to 20 K range. The thermometer was compared several times with the He^4 vapor pressure and showed no detectable deviation from the calibration. Also, the specific heats measured with this thermometer and a thermometer made in this laboratory agreed to well within the expected errors in the region of overlap. The calibration in the 11 to 20 K range was compared with the hydrogen vapor pressure and agreed to better than 0.1% in T, which was within the uncertainty of the ortho-para ratio of the liquid hydrogen used. All calibrations were broken up into suitable overlapping regions and $1/T$ was expanded in powers of $\log R$ up to the cubic term using a least-squares computer method.

The addenda correction was made below 4.5 K by using the published values for the specific heats of the various constituents. For the 4 to 20 K region the actual heat capacity of the addenda, i.e., the thermometer, heater wire, lead-in wires, and a fixed quantity of Glyptal, was measured. The same addenda was then used except for minor variations in the amount of Glyptal for all of the 4 to 20 K measurements.

The systematic error in the specific heat due to inaccuracies in the calibrations, addenda corrections, heater resistance and current, and timing errors should not exceed 2% at the extreme temperatures, except for the magnetic field values below 0.5 K. These latter values may have greater errors due to the extrapolated calibration, longer thermal equilibrium time, and greater electrical noise. The intermediate temperature data should have less than 1% systematic error. Due to the large amount of data recorded, most points shown on the graphs are averages of two or more measured points.

For the paramagnetic susceptibility measurements another commercial encapsulated Ge resistance thermometer[16] was used. It was calibrated several times against the He^4 and He^3 vapor pressures and the paramagnetic salt thermometer and was found reproducible. The paramagnetic susceptibility measurements were carried out by measuring the mutual inductance between a primary and two oppositely wound secondaries, one of which surrounded the central part of the sample.[17] For this arrangement, the mutual inductance can be shown to be linearly related to the susceptibility of the sample. A 17-Hz commercial mutual inductance bridge[17,18] and a 130-Hz Hartshorn bridge built in this lab were used. The primary was wound on a Bakelite tube using 5625 turns of 0.0076-cm-diam Nb wire. As the first samples to be measured were the slabs already used in the specific-heat determinations, the two sections of the secondary were wound on a rectangular core of braced Bakelite sheet. Each section contained 2063 turns of 0.005-cm Formvar insulated Cu wire with layers of the wire separated by Mylar sheet and covered with a G. E. 7031 varnish-toluene-alcohol mixture. The thermometer was glued with 7031 varnish on the sample outside of the secondary windings or with gray Glyptal on the top of the rectangular core. Measurements on the sample with the thermometer in the different positions gave equivalent results. The mutual inductance of the system with no sample was temperature-independent below 1.2 K. For thermal equilibrium, helium exchange gas was used. The error in the paramagnetic susceptibility measurements is mostly due to the uncertainty in the measurement of the mutual inductance and is indicated in Fig. 8.

In order to convert the measured mutual inductances to susceptibilities, the coils were calibrated by replacing the rutile samples with a crystal of cerous magnesium nitrate (CMN) cut to the same dimensions (approximately 1.6×0.6×2.5 cm long). The effective demagnetizing factor of the CMN crystal was found to be 0.23 and is probably due to the confining effect of the superconducting primary on the return flux[19] and the effect of the surrounding vacuum can as well as sample geometry. The measured mutual inductance is composed of a temperature-dependent term due to the temperature dependence of the sample susceptibility plus a temperature-independent term. The latter term changes from experiment to experiment due to slight shifts in the geometry of the coils and their surroundings. Therefore, only the temperature-dependent values of the magnetic susceptibility can be determined by this method.

All measurements were performed in a He^3 cryostat.[20] Temperatures much above 4.2 K were obtained by gluing a heater wire to the outside of the inner can. The inner can was pumped for several hours at room temperature before the specific-heat runs, eliminating any problems with the adsorption of gas on the sample surface. A superconducting solenoid wound on the outer can with Cu-plated Nb-25% Zr wire provided the magnetic fields. As would be expected in a material with paramagnetic centers, all reduced samples cooled when the magnetic field was reduced and heated when the field was increased. Demagnetization was used in some cases to attain the lowest temperature reached in

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[16] CryoCal Inc., P. O. Box 10176, Riviera Beach, Fla. 33404.

[17] W. L. Pillinger, P. S. Jastram, and J. G. Daunt, Rev. Sci. Instr. **29**, 159 (1958).

[18] Cryotronics, Inc., High Bridge, N. J.

[19] A. C. Anderson, W. R. Roach, and R. E. Sarwinski, Rev. Sci. Instr. **37**, 1024 (1966).

[20] G. M. Seidel and P. H. Keesom, Rev. Sci. Instr. **29**, 606 (1958).

the specific-heat runs. As there was no way of calibrating the thermometers much below 0.3 K and true adiabatic demagnetization was impossible due to the eddy current heating induced in the Cu and brass of the cryostat, no study of the adiabatic demagnetization of rutile was attempted.

Four terminal potentiometrically measured resistances were taken for some of the samples. The contacts to the samples were attached with In solder. Difficulty in measuring resistances was found with the highly reduced material due to the numerous large and small cracks. The orientation of some of the rutile crystals was determined by x-ray diffraction.

III. STOICHIOMETRIC RUTILE

A. Specific Heat between 0.3 and 4 K

Since stoichiometric rutile is an insulator with a high Debye temperature Θ_D, the specific heat C below 4 K might be expected to be strictly proportional to the cube of the temperature T. Graphs of C versus T^3 in this temperature range seem to yield straight lines, which, however, extrapolate to positive intercepts at 0 K (see Fig. 1 and also KP). Closer examination of the data in the low range, Fig. 2, shows a Schottky contribution to the specific heat below the 1.2 K limit of the previous investigation of KP. This Schottky term can be understood as resulting from the transitions between the three Kramers doublets of Fe^{3+} located at substitutional cation positions in the lattice. The splittings between these levels are known from electron paramagnetic resonance[21] and so the only adjustable parameter is the concentration of substitutional Fe^{3+}. Using an iterative method, the data for the measured sample of stoichiometric TiO_2 is best fit by the Schottky term for a concentration of 1.08 ppm substitutional Fe^{3+} ions plus a cubic term with a coefficient of 12.4 μJ/mole K^4. Using the relation

$$C_L = 5833(T/\Theta_D)^3 \text{ J/mole K}, \qquad (1)$$

where C_L is the lattice specific heat corresponding to 9 deg of freedom in the TiO_2 molecule, results in a Θ_D of 778±5 K. This value of Θ_D is in good agreement with the value of 775 K obtained[22] from the elastic constants measured at room temperature.

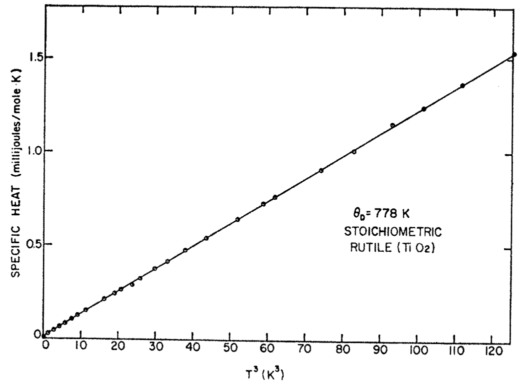

FIG. 1. The specific heat of the stoichiometric boule plotted versus T^3. The apparent intercept is 0.013 mJ/mole K.

As the apparent intercept of the C versus T^3 curve for this sample is about 5 times lower than that of KP, this sample evidently has a lower Fe^{3+} concentration. Mass spectrographic analysis[23] of vacuum-reduced pieces from the same boule as the stoichiometric samples gives an Fe concentration of 23 ppm, much greater than the 1.08 ppm of Fe^{3+} actually present, but electron spin resonance results[24] on stoichiometric TiO_2 before and after γ irradiation indicate that only a small percentage of the iron present in "pure" rutile is in the Fe^{3+} state, most of it being in the Fe^{2+} state. Fe^{2+} should have no effect on the specific heat at these temperatures. The same analysis gives a Cr concentration of 2–4 ppm. Chromium in the Cr^{3+} state has been found in rutile,[21] but the specific-heat results show no term due to 2–4 ppm Cr^{3+}. This leads to the conclusion that Cr, as well as Fe, enters the lattice in more than one valence state.

Other impurities in the piece of vacuum-reduced material were stated to be, in ppm, N 5, F 90, Mg 37, Al 88, Si 83, S 12, Cl 14, Zn 2, Sr 4, Ba 9, plus less than 2 ppm each of P, Sc, V, Mn, Co, Ni, Ga, Ge, As, Rb, Nb, Nd, Ta, and Pb. In rutile, 1 ppm = 0.96×10^{17} cm^{-3}.

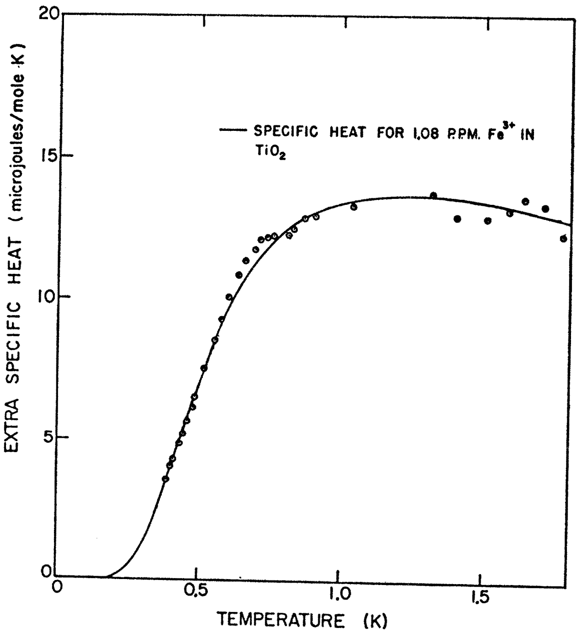

FIG. 2. The specific heat of the stoichiometric boule after the subtraction of $12.4T^3$ μJ/mole K (with T in K).

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[21] D. L. Carter and A. Okaya, Phys. Rev. **118**, 1485 (1960).

[22] R. A. Robie and J. L. Edwards, J. Appl. Phys. **37**, 2659 (1966).

[23] Kindly performed at the James Franck Institute, The University of Chicago.

[24] T. Purcell and R. A. Weeks, Bull. Am. Phys. Soc. **13**, 71 (1968); and T. Purcell (private communication).

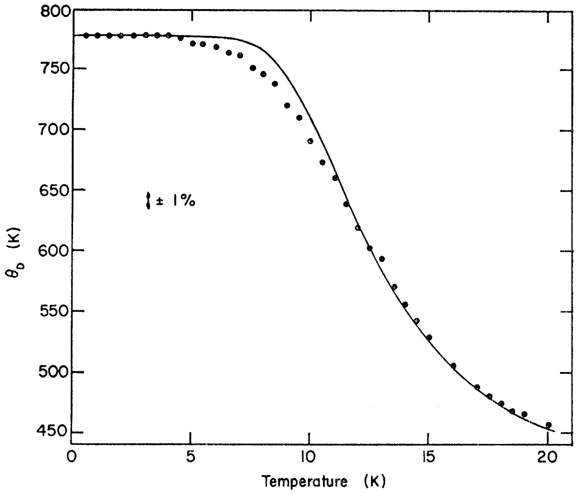

FIG. 3. The Debye temperature of stoichiometric rutile. The solid line was calculated using the Debye and Einstein terms described in the text.

B. Specific Heat between 4 and 20 K

Table II gives the experimentally found specific-heat values and the Θ_D subsequently determined by Eq. (1). The measured specific heat agrees well with higher temperature measurements[25] in the region of overlap. Taking the specific heat to be the sum of a Debye term for the acoustical modes of lattice vibration and Einstein terms for the optical modes, Pandey[26] finds agreement with the experimental specific heat above 20 K using observed and calculated frequencies. Below 20 K, most of the specific heat is due to the sum of a cubic Debye term and the Einstein term for the lowest-frequency optical mode. This mode is active in neither Raman nor the infrared, but has been calculated from Pandey's force-constant model to be 111 K (77 cm^{-1}). Excellent agreement with experiment is found if instead, it is taken to be 119 K (83 cm^{-1}) as shown in Fig. 3. This difference may be due to some neglected terms in the calculations of the force-constant model, changes in the force constants with temperature, and the intrinsic deficiencies of the Einstein model. Small contributions are also included from modes observed by infrared and Raman measurements at 206 K (143 cm^{-1}) and 272 K (189 cm^{-1}).[26] Even if the room-temperature value of 189 cm^{-1} decreases to about 165 cm^{-1} at low temperatures as predicted,[27] the effect on the specific heat below 20 K would be negligible. In this analysis it has been assumed that the specific heat due to the acoustical modes is proportional to T^3 up to 20 K or $\Theta_D/39$. Considering the good agreement between predicted and measured values so obtained, it does not seem fruitful to attempt to include T^5 and higher terms.

TABLE II. Specific heat and Debye temperature for stoichiometric rutile.

Temperature (K)	Specific heat (mJ/mole K)	Θ_D (K)
Below 4	($0.0124T^3$)	778
4	0.79	778
5	1.59	772
6	2.79	768
7	4.53	762
8	7.15	746
9	11.26	720
10	17.7	691
11	27.0	660
12	42.4	619
13	63.6	593
14	93.4	556
15	133	529
16	184	506
17	246	488
18	320	474
19	395	466
20	493	456

IV. REDUCED RUTILE

A. Results

When rutile is reduced, the specific heat is increased above the lattice term. The difference between the measured specific heat and the lattice specific heat will be called the extra specific heat. An overview of the extra specific heat in zero magnetic field is seen in Fig. 4. More details of the results will be given in the following discussions, but in general the results can be described as follows. The three different types of reduction have a maximum in the specific heat in the low range (0.3–1.0 K). In the midrange (1.0–5.0 K), the vacuum- and hydrogen-reduced samples all show a relatively constant value for the extra specific heat over most of this range, while the Ti-powder–reduced sample has a maximum somewhat above 2 K. However, in the high range (5–20 K), both the Ti powder and hydrogen reductions result in similar behavior; that is, a gradual increase in the specific heat to about 14 K, then a rapid drop to zero by 18 K. The extra specific heat of the vacuum-reduced sample in the high range could not be measured as it is much smaller than the lattice specific heat.

Application of a magnetic field increases the specific heat in all samples measured. In vacuum-reduced material (Fig. 5) this is a rather small increase, while it is much larger in the more highly reduced samples as seen in Figs. 7 and 9. If the increase of the specific heat as a consequence of the magnetic field, hereafter called the magnetic specific heat, is compared to the simple Schottky curve expected from the $\pm\beta H$ splitting of paramagnetic levels in the field, the measured magnetic specific heat is found to be higher in the low range and lower in the midrange for vacuum-reduced rutile. It has just the opposite behavior for highly reduced material.

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[25] J. S. Dugdale, J. A. Morrison, and D. Patterson, Proc. Roy. Soc. (London) A224, 228 (1954).

[26] H. N. Pandey, Phys. Status Solidi 11, 743 (1965).

[27] A. S. Barker, Jr., J. Chem. Phys. 38, 2257 (1963).

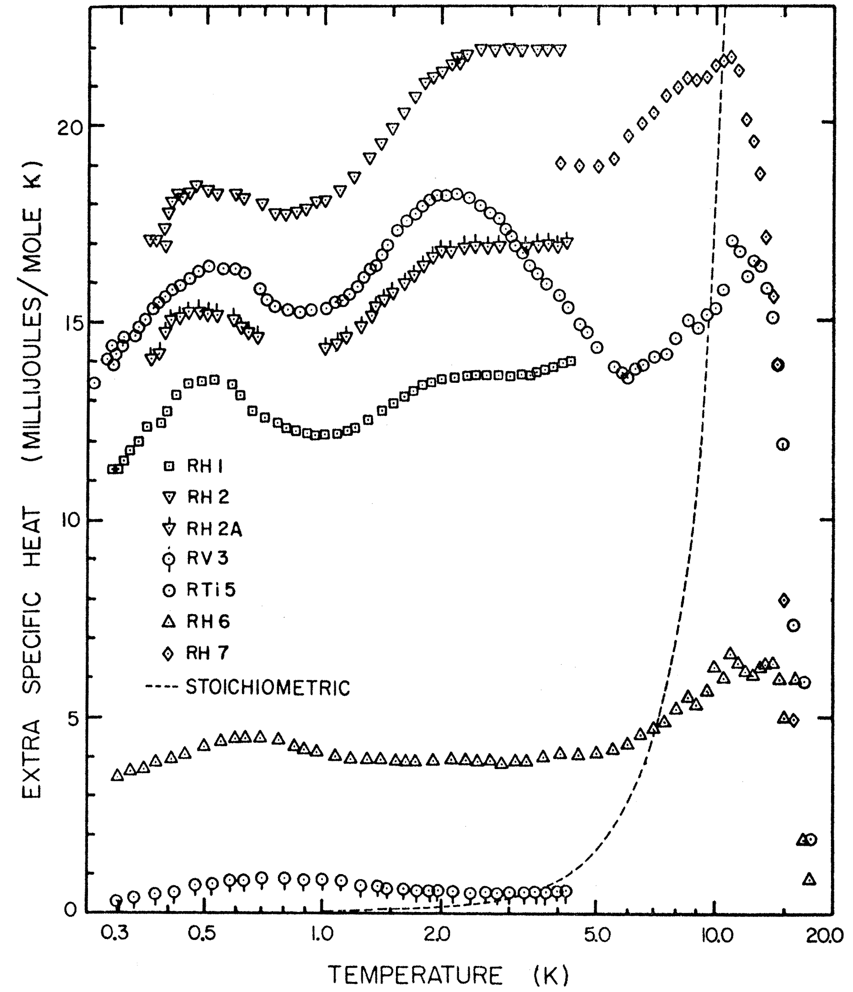

FIG. 4. The extra specific heat due to reduction of rutile in zero field with lattice term assumed unchanged. The temperature scale is logarithmic.

The magnetic susceptibility is plotted versus reciprocal temperature in Fig. 8. Identical values were obtained with measuring frequencies of 17 Hz and 130 Hz. The same values were also obtained for RH2A whether the measuring fields were applied parallel to the c (=[001]) or a (=[100]) axes; for the cerium magnesium nitrate (CMN) the fields were perpendicular to the crystalline axis.

B. Discussion

1. *Vacuum-Reduced Rutile*

The specific heat of the vacuum-reduced sample RV3 was measured between 0.3 and 4.5 K in zero field and below 1.3 K in fields of 3200 and 6400 Oe. Heating rutile in a vacuum is a common method of preparing reduced samples, but the specific heat of vacuum-reduced rutile has not been previously measured. The extra specific heat resulting from the reduction is plotted in Fig. 5. The assumption is made that the lattice specific heat is not changed by the reduction, but this is not critical over much of the temperature range measured. For sample RV3, the lattice specific heat is less than 10% of the extra specific heat up to 1.7 K and equals the extra specific heat by 3.7 K. As the charge states and level separations of the impurity ions present are not known, no correction has been made for impurities. If the impurity correction is the same as for stoichiometric material, its effect will be small.

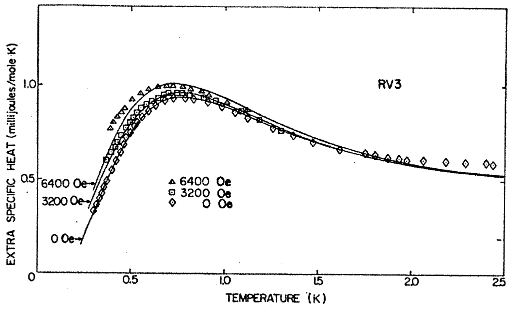

FIG. 5. The extra specific heat of vacuum-reduced rutile sample RV3. The solid lines were calculated by the method described in the text.

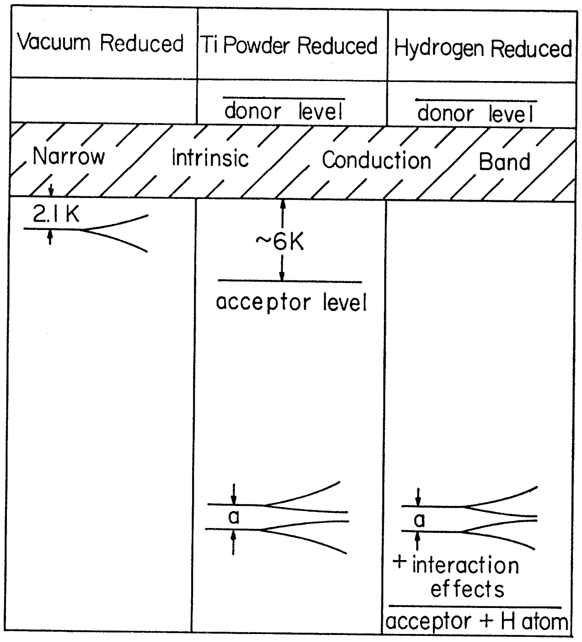

FIG. 6. Representation (not to scale) of the models used for reduced rutile. Within each column, the levels split as the magnetic field increases to the right. The effect of the field on the band is not represented.

In zero field, the extra specific heat has a broad maximum near 0.8 K which tails off to a relatively constant value above 2 K. The application of a magnetic field increases the height and decreases the temperature of the maximum slightly, leaving the values above 1 K nearly unchanged. The magnetic specific heat is relatively and absolutely smaller than that observed for higher reductions. There were too few centers in the vacuum-reduced material for the measurement of paramagnetic susceptibility with the apparatus previously described.

The behavior of the specific heat is inconsistent with that derived for simple models like Schottky transitions between spin degenerate levels in paramagnetic ions, e.g. the Fe^{3+} levels in the stoichiometric material. The specific heat of such a system in a magnetic field would be increased by an amount much greater than that observed, especially above 1 K. The magnetic specific heat is much more suggestive of paramagnetic levels which are empty at high temperatures and which are being filled as the temperature drops. A model which includes this feature and which also agrees with observed narrow band conduction and dielectric measurements is described below.

In this model, represented in the left column of Fig. 6, spin-degenerate localized donors feed a narrow conduction band. The activation from the donor sites into the band yields the maximum in the specific heat, while the nondegenerate electrons in the band yield a constant value of $\frac{3}{2}k_B$ per electron at higher temperatures. The number of electrons in the band equals the number of empty donors or, in zero field,[28]

$$8\sqrt{2}\pi m^{*3/2}h^{-3}\int_0^W \frac{E^{1/2}dE}{1+\exp[(E-\mu)/(k_BT)]} = \frac{n}{1+2\exp[(\mu+\Delta E)/(k_BT)]}. \quad (2)$$

The band is assumed parabolic in the region of interest. Following discussions will indicate that this should be an adequate assumption below 5 K. Here m^* is the density-of-states effective mass, μ is the Fermi energy (chemical potential), n is the electron density, ΔE is the (positive) activation energy for the donors, W is the energy of the top of the band, and other symbols have their usual meanings. All energies are measured relative to the bottom of the band. For the region of interest, k_BT is small compared to W, so that the top of the band may be considered to be effectively at infinity. Equation (2) may then be expressed in terms of the Fermi integral $f_{1/2}(\eta)$,[29] where $\eta=\mu/k_BT$. A magnetic field acts on both the donor levels and the band, giving an additional $\pm\frac{1}{2}g\mu_BH=\pm\beta H$ magnetic energy per electron, where μ_B is the Bohr magneton, g is the g factor, and H is the magnetic field strength. If $x=k_BT/E_0$, $y=\beta H/(k_BT)$, and $z=\Delta E/(k_BT)$, Eq. (2) can then be written as

$$\tfrac{3}{4}x^{3/2}[f_{1/2}(\eta-y)+f_{1/2}(\eta+y)] = [1+\exp(\eta-y+z)+\exp(\eta+y+z)]^{-1}, \quad (3)$$

where $E_0=(h^2/2m^*)(3n/8\pi)^{2/3}$. In the calculations, all energy terms in Eq. (3) are divided by E_0, and then the equation is solved for the reduced temperature k_BT/E_0 as a function of η for a given $\beta H/E_0$ using a computer iteration process. The parameter E_0 may be recognized as the Fermi energy at $T=0$ K for a free electron gas. If does not have that significance in this model, where the Fermi energy always lies below the band (and is the reason that the electrons in the band do not become highly degenerate). Having found the dependence of the Fermi energy on the temperature from Eq. (3), the reduced energy of the system is

$$\begin{aligned} E/(nE_0)=&\tfrac{3}{4}x^{5/2}\{f_{3/2}(\eta-y)+f_{3/2}(\eta+y) \\ &+y[f_{1/2}(\eta-y)-f_{1/2}(\eta+y)]\} \\ &+x\left[\frac{y-z}{1+\exp(-\eta+y-z)+\exp(2y)}\right. \\ &\left.-\frac{y+z}{1+\exp(-\eta-y-z)+\exp(-2y)}\right]. \quad (4)\end{aligned}$$

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[28] H. M. James, Purdue University Semiconductor Research Quarterly Report, 1952, p. 8 (unpublished); and references in R. A. Smith, *Semiconductors* (Cambridge University Press, Cambridge, 1959), p. 88.

[29] J. McDougall and E. C. Stoner, Phil. Trans. Roy. Soc. (London) **237**, 67 (1938).

After the energies are found from Eq. (4) for the various values of k_BT/E_0, the specific heat per electron is calculated by an interpolative differentiation of the reduced energy with respect to k_BT/E_0.

The zero-field specific heat predicted by this model shows excellent agreement with the measured data, yielding a donor activation energy of 2.1 K (1.8×10^{-4} eV), electron density of 1.1×10^{18} cm^{-3}, and density-of-states effective mass of 190 times m_e, the mass of a free electron. Application of a magnetic field will split the donor levels and orient the spin-up and spin-down electrons in the band as indicated in Eq. (3). As a result, the magnitude of the specific-heat maximum increases while its temperature decreases. Good qualitative agreement is evident between the predictions of the model and experiment under the application of a field. The quantitative agreement decreases as the field is increased. This may result from an increase in the density of states which is due to the shrinkage of wave functions and the corresponding decrease in the electronic-energy-overlap integral. An increase in the density-of-states effective mass of about 2% in the 3200-Oe field and 10% in the 6400-Oe field improves the quantitative agreement. However, an unknown amount of additional magnetic specific heat from other paramagnetic ions will also be present, so no definite values for the change in density of states with applied field can be calculated.

Above 2 K the measured specific heat diverges somewhat from the calculated curve. Measurements to 4.5 K indicate that this divergence could be due to a higher energy (about 14 K) excitation, but the rapid increase of the lattice term in the high-temperature region makes identification of the excitation impossible. Dielectric[9] and resistivity[7,8] measurements also indicate higher-energy excitations. The divergence of the specific heat is at too low a temperature to be a result of the nonparabolicity of the energy function discussed later. The conduction band in vacuum-reduced rutile is most likely the polaron-narrowed intrinsic band of the crystal described in a following section.

The donor activation energy is slightly lower than that observed for less reduced samples ($>10^{16}$ cm^{-3} donors) in dielectric studies,[9] but a decrease in activation energy with increasing donor concentration is a well-known phenomena in other semiconductors.[30] The dielectric results were interpreted, however, in terms of a polaron-hopping model, not a polaron-band model.

Reducing rutile at 1000 C in a vacuum of 5×10^{-5} Torr resulted in much less reduction of the sample (shown by weight loss, color change, specific heat, etc.), than reduction at the same temperature by the other methods used in this research. This is because the lowest pressure obtained is higher than the oxygen partial pressure obtained with flowing hydrogen or argon gas, or Ti powder with its gettering action. The effect of partial pressure on reduction is apparent from the two-slope behavior of the electric conductivity versus oxygen partial pressure seen elsewhere[10] at the reducing temperature of 1000 C. Both electrochemical[10] and dielectric[9] studies can be interpreted to favor impurity-related defects as resulting from relatively high partial pressures and low reductions. The model which explains the dielectric behavior in the He range is that of a center composed of a trivalent impurity and an oxygen vacancy. This center has a net positive charge and can trap one electron, which then must be thermally activated to hop between adjacent cations in the crystal. In RV3, if one electron is donated by each ion core, then the 1.1×10^{18} cm^{-3} electrons are equivalent to 12 ppm of trivalent impurities connected with oxygen vacancies, well within the range of impurity concentration of the adjacent piece of vacuum-reduced rutile from the same boule. If the impurity is iron, as indicated[9] as a possibility, then the reduction process must convert some Fe^{2+} into Fe^{3+}.

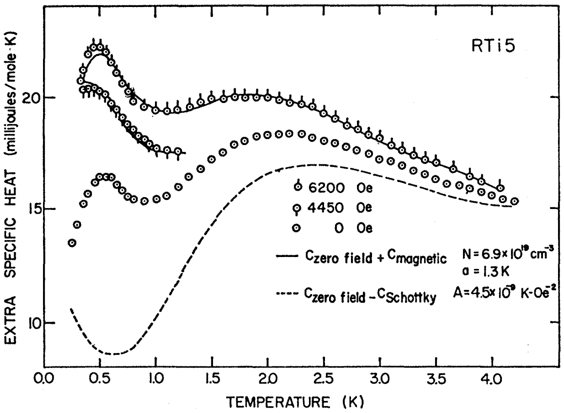

FIG. 7. The extra specific heat of Ti-powder–reduced sample RTi5 below 4.2 K.

2. *Highly Reduced Rutile*

Specific results. For rutile highly reduced in flowing hydrogen or with Ti powder, specific heats were measured between 0.3 and 20 K in zero field and below 4.2 K in various magnetic fields. In addition, paramagnetic susceptibility measurements were made from 0.3 to 4.2 K. The only previous measurements of these properties on hydrogen-reduced material were the specific-heat measurements of KP in the midrange and the magnetic susceptibility measurements of Honig and Keesom[15] down to 1.25 K. No measurements have previously been reported for Ti-powder–reduced rutile, but its specific heat seems to possess the same features as sample XR measured by KP in the mid and high ranges. (Sample XR was reduced twice as heavily as sample RTi5 in an argon atmosphere at 1200 C.)

The extra specific heat above the lattice term is plotted in Figs. 4, 7, and 9, where the assumption is again made that the lattice contribution is unchanged

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[30] H. Fritzsche, J. Phys. Chem. Solids 6, 69 (1958).

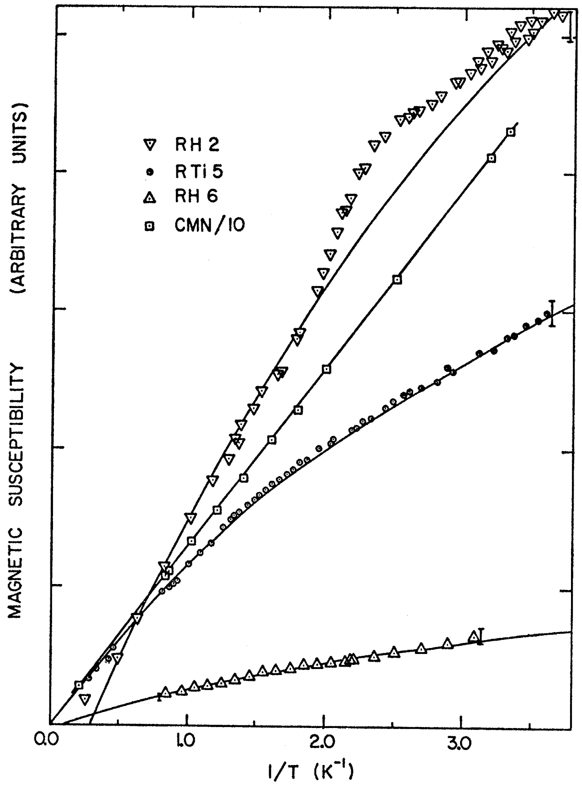

FIG. 8. The magnetic susceptibility of three reduced samples. The ordinate units are arbitrary with each sample having a different zero. The theoretical curves were calculated using the parameters in Table I which were determined from the specific-heat data. The paramagnetic susceptibility of CMN was divided by 10.

by the reduction. If it were changed, the effect would be small in the low and mid ranges where the lattice specific heat is relatively small. The common features of the specific heat of all hydrogen-reduced samples below 4 K are a maximum in the low range and a constant value through much of the midrange. Both features show an important dependence on the degree of reduction. The low-range maximum is at 0.62 K for the lowest reduction and decreases to 0.47 K for the highest reduction. The lowest temperature at which the specific heat appears to become constant, on the other hand, is 2.5 K for the most highly reduced sample and decreases with decreasing reduction. For the least-reduced sample, this lowest temperature is so low as to be obscured by the tail of the low-range process.

The slope of the paramagnetic susceptibility versus reciprocal temperature for the Ti-powder–reduced sample decreases steadily as $1/T$ increases. For the hydrogen-reduced sample RH2A, the slope does not decrease monotonically with $1/T$; in some ranges the change in slope increases and in others it decreases, with the greatest change in slope occurring near the temperature of the specific-heat maximum.

Low range. The model which best agrees with the data for Ti-powder–reduced rutile in this range is that of a paramagnetic center which has two spin-degenerate levels separated by energy a. The thermal excitation of the ion from the ground state to the higher state will then result in a Schottky anomaly in the specific heat with a maximum of $0.44k_B$/ion at a temperature of $0.42a/k_B$. The dependence of the slope of the susceptibility upon reciprocal temperature for the noninteracting ions in RTi5 is due to the behavior of the ion energy levels in a magnetic field. When the field is applied, two effects occur, and are represented in the center column of Fig. 6. The spin-degenerate levels split about their centers of gravity by an amount $\pm\beta H$, while the centers of gravity of the two levels move apart, each by an amount AH^2. The constant A has an order of magnitude of β^2/a.[31] If the levels did not move apart, the magnetic specific heat would be a simple Schottky anomaly for two levels with a separation $2\beta H$, and the paramagnetic susceptibility would be strictly proportional to the reciprocal temperature. However, the effect of the H^2 term is to make the magnetic specific heat the sum and difference of three Schottky terms for two levels; that corresponding to a separation of $2\beta H$ plus that for a separation of $a+2AH^2$ minus that for a separation of a. This results in a magnetic specific heat which is lower in the low range and higher in the midrange than the simple Schottky anomaly for $2\beta H$, and is in at least qualitative agreement with the magnetic specific heat of all highly reduced specimens. This dependence is exactly the opposite of that observed in the vacuum-reduced material, and is one of the main reasons for assuming the centers to be different in lightly and highly reduced rutile.

When the H^2 term is included in the energy of the levels, the paramagnetic susceptibility can then be derived from general expressions[32] to be

$$\chi = N[\beta^2/k_BT + 2A \tanh(a/2k_BT)]. \qquad (5)$$

Since $\tanh(x)\approx x$ for small x and approaches 1 for large x, it is seen that the tanh term is responsible for the steady decrease in slope with increasing reciprocal temperature seen in Fig. 8. The magnetic specific heat of RTi5 in two different fields was obtained from Fig. 7 and analyzed using a nonlinear least-squares computer program, and the values obtained, $a=1.3$ K, $A=4.5\times10^{-9}$ K/Oe^2, and $N=6.9\times10^{19}$ cm^{-3}, were then used in Eq. (5) to calculate the paramagnetic susceptibility. The calculated susceptibility seen in Fig. 8 agrees with the measured data within the limits of error of the measurements, indicating the validity of the model for the Ti-powder–reduced material.

The paramagnetic susceptibility of the hydrogen-reduced sample RH2 deviates from the temperature dependence of Eq. (5). As the temperature decreases below 1.2 K the slope in Fig. 8 is seen to increase, sug-

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[31] M. Kotani, J. Phys. Soc. Japan 4, 293 (1949).

[32] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, Oxford, 1932), pp. 181, 182, and 226.

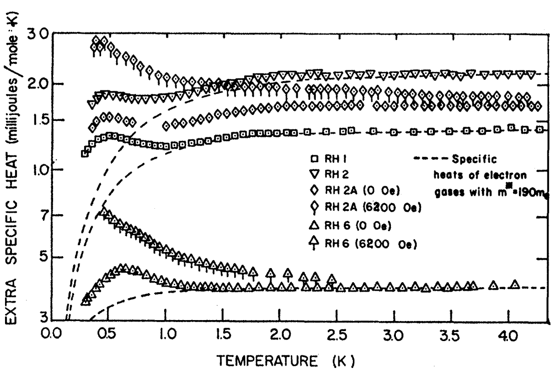

FIG. 9. The extra specific heat of hydrogen-reduced rutile. The specific heat scale is logarithmic.

gesting that the susceptibility may depend on $1/(T-\theta)$ instead of $1/T$. This leads to the speculation that there may be a ferromagnetic type of interaction between the paramagnetic ions, possibly aided by the hydrogen. Near 1.2 K many of the ions are in their excited state, but near the position of the specific-heat maximum, i.e., in the range in which the ions drop down to the ground state at the greatest rate, the susceptibility begins to return to the temperature dependence of Eq. (5). This would then indicate that the interaction between ions is smaller in the ground state than in the excited state.

A ferromagnetic interaction between two ions in the excited state should decrease the energy of the state, thereby decreasing the level separation a. As the total number of ions increases, the interaction may be expected to increase, and a to decrease. Indeed, the temperature at which the maximum occurs, and therefore the level separation, does decrease with increasing ion concentration.

The change in level separation is greater than is apparent from the movement of the maximum, because the low-range peaks in the most highly reduced samples are added to steeper portions of the midrange curve than the least highly reduced sample. Adding a rounded peak to a steep curve of positive slope results in an apparent shift of the peak to a higher temperature. Therefore, the level separations should be especially smaller for the most highly reduced samples than they appear from the position of the maxima.

To obtain the precise values of the level separations, it is then necessary to describe quantitatively both the low and midrange processes. However, this cannot be done exactly, as the interaction between the ions will change the low-range specific heat from the simple Schottky curve attained for the noninteracting ions to some unknown temperature dependence. If Schottky curves are used merely as an attempt to obtain some idea of the values for a, the level separations for the most highly reduced samples (see Table I) are found to be about 20% lower than those derived from the position of the maximum only. Also, for RH6, the hydrogen-reduced sample which has the fewest ions and which is therefore assumed to have the smallest interaction between ions, a is then approximately 1.3 K, the same as the level separation for the noninteracting ions in RTi5.

Neither specific-heat nor paramagnetic susceptibility measurements can identify the ions. Electron spin resonance results have been interpreted in terms of Ti^{3+} ions at interstitial positions in hydrogen-reduced rutile.[11] These positions are surrounded by oxygen octahedra. From simple crystalline field theory it follows that the ground state of the Ti^{3+} ion in an octahedral field, including spin-orbit coupling, is fourfold degenerate with $g=0$.[31] This degeneracy will not remain in the crystal, but will be lifted by a small internal field.[33] This might give the level separation a seen in the highly reduced material, but the theory does not explain the $g\approx 2$ values. Simple crystalline field theory has also been found inadequate for Ti^{3+} in other environments.[34–36]

Midrange. The specific heat of hydrogen-reduced rutile is constant over much of the midrange as seen in Fig. 9. The constant value is probably due to nondegenerate electrons in a narrow band as suggested by KP. No maximum in the specific heat is observed in this range and the electrons are seen to become degenerate as the temperature lowers rather than dropping into donor levels as in the vacuum-reduced material. Therefore, the donor levels from the hydrogen-related centers must be in or above the band.

In hydrogen-reduced rutile, then, the electrons are nondegenerate somewhat above the degeneracy temperature

$$T_F=(h^2/2m^*k_B)(3n/8\pi)^{2/3}. \qquad (6)$$

The nondegenerate electrons have a constant specific heat per electron of $\frac{3}{2}k_B$ in the range where the energy of the electrons E is proportional to the square of the wave vector, k. The number of electrons per mole is then simply the value of the specific heat divided by $\frac{3}{2}k_B$. As the temperature is lowered, the electrons begin to become degenerate and the specific heat begins to decrease in the typical manner of an electron gas.[37] From Eq. (6), the degeneracy temperature is seen to be proportional to the $\frac{2}{3}$ power of the electron concentration. It is this dependence then that causes the degeneracy temperature to decrease with decreasing reduction until, for RH6, it is so low as to be obscured by the low-range process.

The lack of knowledge of the exact specific heat due to the low-range process, together with the possibilities that some impurity-related centers are present in the

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[33] W. Low, *Paramagnetic Resonance in Solids* (Academic Press Inc., New York, 1960), pp. 78–80.

[34] B. Bleaney, G. S. Bogle, A. H. Cooke, R. J. Druffus, M. C. M. O'Brien, and K. W. H. Stevens, Proc. Phys. Soc. (London) **A68**, 57 (1955).

[35] D. K. Rei, Fiz. Tverd. Tela **3**, 2525 (1961) [English transl.: Soviet Phys.—Solid State **3**, 1838 (1962)].

[36] I. B. Bersuker and B. G. Vekhter, Fiz. Tverd. Tela **5**, 2432 (1963) [English transl.: Soviet Phys.—Solid State **5**, 1772 (1964)].

[37] E. C. Stoner, Phil. Mag. **25**, 899 (1938).

sample and that the density of states and interaction between the paramagnetic ions may change in a magnetic field, all make it impossible to reproduce the complete low and midrange specific heats in hydrogen-reduced rutile. However, the midrange zero-field specific heat can be well represented if the effective mass is taken to equal $190\,m_e$ for all samples as shown in Fig. 9. Higher values of m^* would not take into account the tailing off of the specific heat from the low-range process, while lower values of m^* make the degeneracy temperature too high to properly reproduce the constant term. This value of $m^* = 190\,m_e$ is the same density-of-states effective mass as seen in vacuum-reduced rutile.

Other measurements on hydrogen-reduced rutile below 20 K include electron spin resonance,[11] thermoelectric power,[12] resistivity,[38] and Hall effect.[13] All can be interpreted in terms of a narrow-band-conduction process. It is often assumed that this is "impurity" band conduction, where the impurities are the defects introduced by reduction. However, this type of conduction in rutile seems somewhat unlikely, as the large effective mass does not suggest a sufficiently extensive wave function for the formation of impurity bands at the concentrations studied. In addition, the apparent independence of the density-of-states effective mass upon method of reduction (and therefore type of defect) and amount of reduction (and therefore density of defects, wave-function overlap, etc.) seems to rule out an impurity band, and to argue that the band is a very narrow intrinsic band of the crystal.

In the Ti-powder– or argon-reduced samples, a maximum is seen in the midrange extra specific heat somewhat above 2 K instead of the constant term of the other reduced samples. If the Schottky specific heat due to the low-range process is subtracted from the extra specific heat, the curve shown in Fig. 7 is obtained. This curve has the same general features in zero magnetic field as the curve of the vacuum-reduced material, i.e., the specific heat shows a maximum and then drops off at higher temperatures to a term consistent with the behavior of electrons in the band. This similarity leads to the conclusion that highly reduced rutile which contains no hydrogen also has a center below the band. The temperature at which the maximum occurs indicates the activation energy of the center to be approximately 5×10^{-4} eV or 6 K. This center is evidently nonmagnetic, as it does not effect the low-range paramagnetic susceptibility or the magnetic specific heat. Since no maximum in the midrange specific heat is noticed in the hydrogen-reduced material, this center must combine in some manner with the hydrogen, leaving an electron in the band. Complexes containing hydrogen in reduced rutile have been identified in infrared[39,40] and spin-resonance work.[40] A possible scheme for the action of hydrogen in rutile, based on that of Li in GaSb,[41] is represented in Fig. 6. In highly reduced rutile with no hydrogen, there is in this scheme a donor level above (or in) the band and an acceptor level below. At 0 K, the electron is trapped in the acceptor level and is excited into the band as the temperature rises. In the hydrogen-reduced material, the hydrogen combines with the acceptor and neutralizes it; therefore the donor electron goes immediately into the band.

The extra specific heat of RTi5 after the subtraction of the Schottky term has an increase below 0.5 K. The increase may be exaggerated by measurement errors which are especially large in this lowest temperature range, but these errors are not so large as to be the reason for the increase. If there is more than a single energy level in the center, the increase could be due to transitions between the levels. Measurements at still lower temperatures will be necessary to identify the source of the increase.

High range. In the high range, two samples of hydrogen-reduced rutile were studied along with the one Ti-powder–reduced sample. The extra specific heat of the samples shows a gradual increase above the constant term for the hydrogen-reduced material and a similar gradual increase for the Ti-powder–reduced sample for temperatures above 5 K and then a rapid drop at higher temperatures. The argon-reduced sample XR of KP also shows this behavior. The temperature at which the rapid drop begins tends to decrease as the reduction increases. For the two most highly reduced samples, RH7 and XR, the drop continues until the extra specific heat becomes negative near 20 K.

The extra specific heat is defined as the difference between the measured specific heat and the specific heat of the stoichiometric sample. If the lattice specific heat of rutile is changed by the reduction process, then the extra specific heat so defined will contain a term equal to the change in the lattice specific heat as well as a term due to the electrons. Since the extra specific heat below 10 K is greater than the lattice specific heat for all samples measured in this range with the exception of RH6, a change in the lattice specific heat with reduction would not greatly effect the extra specific heat of any of the samples except RH6. The extra specific heat of RH6, however, is similar to the specific heat of the other samples measured, indicating that the change in lattice specific heat, if any, is also small for RH6. Therefore the extra specific heat below 10 K shown in Fig. 4 accurately represents the effects of reduction upon rutile exclusive of any effect on the lattice.

Preliminary band-structure calculations indicate that a narrow conduction band composed mainly of Ti $3d$ orbitals may lie slightly below a wider conduction band

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[38] R. R. Hasiguti, K. Minami, and H. Yonemitsu, J. Phys. Soc. Japan **16**, 2223 (1961).

[39] A. Von Hippel, J. Kalnajs, and W. P. Westphal, J. Phys. Chem. Solids **23**, 779 (1962).

[40] A. Okaya, in *Proceedings of the First International Conference on Paramagnetic Resonance, Jerusalem* (Academic Press Inc., New York, 1963), Vol. II, p. 687.

[41] T. O. Yep and W. M. Becker, J. Appl. Phys. **37**, 456 (1966).

composed mainly of Ti-O antibonding π orbitals.[42] To arrive at some idea of the properties of this narrow band, the approximation can be made that the rutile structure be replaced by a body-centered cubic lattice of Ti atoms with a volume b^3 and an energy variation in the Brillouin zone given by the tight-binding (TB) expression[43]

$$E(k)=\tfrac{1}{2}W(1-\cos\tfrac{1}{2}bk_x\cos\tfrac{1}{2}bk_y\cos\tfrac{1}{2}bk_z)\,, \tag{7}$$

where W is the width of the TB band and $E(k)$ is the energy function in k space. For small k

$$E(k)=\hbar^2k^2/2m^*=\tfrac{1}{2}W\tfrac{1}{8}b^2k^2\,. \tag{8}$$

The bandwidth is then

$$W=8\hbar^2/b^2m^*\,. \tag{9}$$

The volume b^3 of the rutile primitive cell[44] is 62.4 Å^3. With $m^*=190\,m_e$, this results in $W=20\times10^{-3}$ eV, which is equivalent to 240 K. It would be surprising if the TB approximation held all the way to the band edge in the real crystal.[45]

To explain the gradual rise in the specific heat above 5 K, it is necessary to examine the accuracy of the approximation used in going from Eq. (7) to Eq. (8). Tabulation shows Eq. (8) to be good to within 2% up to an energy of 0.03 W, or 6×10^{-4} eV, or 7.2 K. The energy per classical electron equals $\frac{3}{2}k_BT$, so $E(k)$ is proportional to k^2 up to approximately $\frac{2}{3}\times7.2$ K or 4.8 K. Above this temperature the energy function begins to bend over, becoming horizontal at the zone boundary. For a classical gas, the specific heat per particle is equal to $\frac{3}{2}k_B$ only as long as $E(k)\propto k^2$. If, in general, $E(k)\propto k^r$, then the specific heat per particle is equal to $(3/r)k_B$. Near 4.8 K $E(k)$ begins to flatten, which is the equivalent of decreasing r below 2. According to this picture, the specific heat of all the samples should then begin to rise above $\frac{3}{2}k_B$ per particle near this temperature. Figure 4 shows that this indeed is the case. The specific heat of RTi5 can then be extrapolated back to 5 K to obtain the electron concentration given in Table I.

The rise in the specific heat continues as the energy function continues to flatten, but then above 10 K the extra specific heat drops. This occurs in the range where the lattice term is increasing very rapidly. By 20 K the specific heat of the stoichiometric material has become at least an order of magnitude greater than the maximum value of the extra specific heat of any of the samples measured. It should be understood that the rapid drop in the extra specific heat is not merely a consequence of the subtraction of two large numbers. While the accuracy of the specific-heat measurements is estimated at 1 to 2%, this is a consequence of several factors such as temperature scale and addenda correction. However, the relative measurements reported here were more reliable among themselves as they were performed with the same addenda and with a thermometer whose calibration did not change from one set of measurements to the next. Moreover, similar results were obtained for XR with different addenda, thermometers, and calibration. Therefore, the sudden drop in the extra specific heat and the negative value near 20 K appear to be experimentally established.

Since the rapid drop of the extra specific heat occurs in the range where the lattice term becomes large, a small change in the lattice specific heat due to the reduction can result in a proportionally greater change in the extra specific heat. For instance, for sample RH7 the extra specific heat drops from a maximum value of +22 mJ/mole K at 11 K to −25 mJ/mole K at 20 K. If the specific heat due to the electrons in the band is to be considered to continue its gradual rise to 20 K, then a decrease in the lattice specific heat of about 11% is needed for RH7 to explain the rapid drop and the negative value. An even larger decrease (almost 20%) for XR and smaller decreases for the other samples would be necessary. However, it is hard to understand how the introduction of electrons and defects by reduction could stiffen the lattice and yield these large decreases in the lattice specific heat. As examples, the reduction of $SrTiO_3$ results in a softening of the lattice,[46] as does the increase in carriers in Ge.[47]

Previously, KP suggested that the rapid drop is connected with the electrons approaching the top of the band. When the occupation probabilities of the individual levels of the band become equal, further increases in temperature will not increase the energy of the electrons, causing the electronic specific heat to drop to zero. This will occur when k_BT becomes comparable to the bandwidth. The bandwidth in this model must then be an order of magnitude smaller than that estimated by the TB approximation, but, as stated previously, it would be surprising if the TB approximation with all its assumptions were true far away from the minimum of the energy function in rutile.

If the rapid drop is due to the electrons approaching the top of the band, the dependence upon reduction of the temperature at which the rapid drop begins is another indication that the band is intrinsic, and not an impurity band. The width of an impurity band and therefore the temperature of the rapid drop should increase with increasing reduction. This is not observed, instead the position of the rapid drop decreases slightly with increasing reduction, a process expected when an

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[42] J. M. Honig (private communication).

[43] N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Dover Publications, Inc., New York, 1958), p. 68.

[44] R. A. Parker, Phys. Rev. **124**, 1713 (1961).

[45] A. H. Kahn and A. J. Leyendecker, Phys. Rev. **135**, A1321 (1964).

[46] C. K. Jones and J. K. Hulm, Phys. Letters **26A**, 182 (1968).

[47] C. A. Bryant and P. H. Keesom, Phys. Rev. **124**, 698 (1961).

increasing number of electrons occupy a fixed number of states in an intrinsic band.

The band is much narrower than that ordinarily seen, but very narrow bands can result when small polaron effects are taken into account. Since many of the parameters found in different types of experiments above 30 K can be consistently explained if small polaron effects on the higher conduction band are included, it is reasonable to assume these same effects could also occur in the lower conduction band. In theories of the small polaron,[48,49] the bandwidth is given by $W=W_e \exp(-S)$. The quantity W_e is the electronic bandwidth in the TB approximation without polaron effects, and is related to the TB electronic overlap integrals, while S is related to the relative vibrational mode displacements in the crystal. A typical value of S near five results in a very narrow polaron bandwidth W and correspondingly high effective mass. For example, in $SrTiO_3$, which has a band structure expected to be similar to TiO_2 as well as similar dielectric constants, primitive cell volumes, etc., Eagles[49] calculates an effective mass of $170 m_e$. As this result is based on an assumed value of the electronic bandwidth, the agreement with the $190 m_e$ found for rutile is merely fortuitous, but it indicates that polaron effects can yield the order of magnitude of the effective mass for rutile. This argument is weakened by the disagreement for $SrTiO_3$ between the experimental value of the effective mass of $5 m_e$, and the theoretical value of $170 m_e$.

The approach of the electrons to the top of the band can evidently account for the drop in the specific heat, but a narrow band by itself cannot explain the negative specific heat. If the narrow-band explanation is correct, it could be combined with the decrease in the lattice specific heat with reduction previously discussed to provide the negative value. The lattice specific-heat decrease would then not have to be as large as previously estimated, as it would be needed to explain just the negative value and not the rapid drop.

Another possibility that should be mentioned is that the negative specific heat may be a consequence of the predicted decrease in the polaron bandwidth with increasing temperature. The bandwidth narrows and the electrons near the top of the band lose energy as the temperature increases, resulting in a negative specific heat. The decrease in bandwidth is due to an increase in the quantity S as the number of phonons increases. There are not many phonons present below 20 K, but the specific heat is related to the temperature rate of change of S, and therefore the rate at which new phonons are being created. Referring back to the stoichiometric results, the number of phonons, especially in the 83-cm^{-1} optical mode, is seen to be increasing rapidly in just the range where the extra specific heat becomes negative. Difficulties with this model include the possibility that the 83-cm^{-1} mode may not couple strongly with the electrons[50] and the fact that small polaron theories are derived for cases where the energy function follows the TB expression all the way to the zone boundary.

V. CONCLUSIONS

The specific heat of the stoichiometric rutile boule in the low and midranges is reproduced by a cubic term corresponding to a Debye Θ at $T=0$ K of 778 K plus a Schottky contribution due to 1.08 ppm of Fe^{3+} impurity ions. Spectroscopic analysis indicates more iron in the lattice, but most of this iron is probably in the Fe^{2+} state. In the high range the specific heat can be represented very well by the sum of a cubic term in T and an Einstein contribution from an optical mode at 83 cm^{-1} plus small contributions from two higher frequency modes found in Raman and infrared spectra.

The most unusual feature of the specific heat of reduced rutile below 20 K is the constant term seen in the midrange for the vacuum- and hydrogen-reduced samples. The analysis of Sec. IV B1 and the results summarized in Fig. 9 indicate that this constant value is likely due to nondegenerate electrons of effective mass $190 m_e$ and that these electrons are in a narrow intrinsic conduction band rather than an impurity band. In the hydrogen-reduced material, as the temperature drops, the specific heat starts to decrease due to the increasing degeneracy of the electrons. However, in the vacuum-reduced sample, the electrons drop out of the band into donor sites instead of becoming highly degenerate, thereby causing the specific heat to go through a maximum in the low range. Rutile which is highly reduced without the aid of hydrogen has electrons in the same intrinsic band as judged by the similarity between the high-range specific heats of all highly reduced samples. However, the electrons must be thermally excited into the band and, as a consequence, a maximum is observed in the midrange for the Ti-powder- and argon-reduced samples.

If a body-centered cubic tight-binding model is used for rutile, an effective mass of $190 m_e$ results in a narrow band whose width may be a consequence of small polaron effects. As $E(k)$ is proportional to k^2 only to about 5 K for a band of this type and width, this model predicts that the electronic specific heat should rise as the temperature increases above 5 K, in agreement with the measured results. The simplest explanation of the rapid drop and negative values of the extra specific heat is that they result from an unexpected large decrease in the lattice specific heat. The rapid drop also can be explained by the electrons approaching the top of the band, and the negative value may then be accounted for by a decrease in the lattice specific heat or by the temperature-dependent narrowing of the band predicted by polaron theory.

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[48] T. Holstein, Ann. Phys. (N. Y.) **8**, 343 (1959).

[49] D. M. Eagles, Phys. Rev. **145**, 645 (1966).

[50] D. M. Eagles, J. Phys. Chem. Solids **25**, 1243 (1964).

In the low range, all the highly reduced samples show a maximum in the extra specific heat and a large magnetic specific heat. For the Ti-powder–reduced sample, the magnetic specific heats in fields of 6200 and 4450 Oe, and the paramagnetic susceptibility all agree with a model of a two-level paramagnetic system which has a level separation increasing with the square of the field strength and a spin splitting of the individual levels proportional to the field strength. The hydrogen-reduced samples show indications of interactions between the paramagnetic ions which change the paramagnetic susceptibility and specific-heat behaviors. It was speculated that the interaction is ferromagnetic, but it was not possible to derive a model which completely describes the low-range specific heat and magnetic susceptibility of hydrogen-reduced rutile. This type of paramagnetic ion is not present to any large extent in the vacuum-reduced sample; however, the donor level does split in a magnetic field to yield a magnetic specific heat.

The various centers present, then, are a function of the amount and method of reduction. The vacuum reduction, with its relatively high oxygen partial pressure, results mainly in an impurity-related center, while the main centers introduced by the reductions at low oxygen partial pressure are too numerous to be impurity related. If hydrogen is used in the reduction process, the center responsible for electrons in the band is modified so that there is no activation energy into the band. The hydrogen in the lattice may also contribute to the interactions between the paramagnetic ions.

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Low-Temperature Heat Capacities of Solid Argon and Krypton*

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The specific heats of high-purity argon and krypton have been measured between 0.4 and 12°K, permitting a reliable extrapolation to 0°K. The higher-temperature results are in agreement with those of Morrison *et al.*, but for argon the extrapolation to 0°K is not. At the lowest temperatures the heat capacities are represented by $C=(12/5)\pi^4R(T/\Theta_0)^3$, with $\Theta_0=92.0°\mathrm{K}$ for argon and $71.9°\mathrm{K}$ for krypton. The apparatus and techniques are described, and the results are compared with theoretical estimates.

INTRODUCTION

THE noble-gas solids, with their relatively simple van der Waals attractive forces, are one of the best experimental systems for testing theories of lattice dynamics. A measure of current interest in the field is the number of recent review articles: Since Dobbs and Jones's review[1] of a decade ago, Pollack,[2] Boato,[3] Horton,[4] and Simmons[5] have also reviewed the field. Although these reviews treat mainly the perfect crystalline state, there is also now an interest, both theoretical and experimental, in various defect states of the noble-gas solids (see, e.g., Hartmann and Elliott[6] and Maradudin[7]). In general, the theories are at their best with the heavier noble gases (argon, krypton, and xenon) where one does not have the large zero-point energy effects of helium and neon, and where at the lowest temperatures thermal vibrations are of small amplitude. The Debye characteristic temperature Θ and Grüneisen "constant,"[8] and their values Θ_0 and γ_0 at 0°K, are convenient parameters for describing experimental or theoretical results.

The comparison between theories and experimental results of the lowest-temperature properties of the heavier noble solidified gases has been much improved during recent years due to the following advances: The

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[1] E. R. Dobbs and G. O. Jones, Repts. Progr. Phys. 20, 516 (1957).

[2] G. L. Pollack, Rev. Mod. Phys. 36, 748 (1964).

[3] G. Boato, Cryogenics 4, 65 (1964).

[4] G. K. Horton, Am. J. Phys. 36, 93 (1968).

[5] R. O. Simmons, Solid State Phys. (to be published).

[6] W. M. Hartmann and R. J. Elliott, Proc. Phys. Soc. (London) 91 187 (1967).

[7] A. A. Maradudin, Solid State Phys. 18, 273 (1966); 19, 1 (1966).

[8] See, e.g., C. Kittel, *Introduction to Solid State Physics* (John Wiley and Sons, Inc., New York, 1966), Chap. 6.