Specific heat of well-characterized $TiBe_2$ at 0 and 7 T

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The low-temperature specific heat at magnetic fields of 0 and 7 T, dc susceptibility, and resistivity data for two samples of $TiBe_{2.00}$ and one sample of $TiBe_{1.94}O_{0.05}$ are presented. The temperature dependence of the low-temperature specific heats of all three samples of $TiBe_2$ is found to include an important $T^3 \ln T$ term, confirming that spin fluctuations are present in $TiBe_2$, the first metal besides UAl_2 where such a $T^3 \ln T$ term has been found. Evidence for a magnetic impurity present in one of the two pure $TiBe_2$ samples is inferred from the measurements and confirmed by the same measurements on the sample with oxygen intentionally added. The impurity is thought to increase the low-temperature susceptibility, shape the resistivity, and cause a 3% decrease of the low-temperature specific heat in a 7-T field at lower temperatures. At higher temperatures in the impure samples, and at all temperatures in the purer sample of $TiBe_2$, there is no change from the zero-field values in the specific heat to $\pm 1\%$ in a 7-T field, in contradiction to the theoretical prediction of Béal-Monod. These field results are discussed with respect to the recent measurements of the low-temperature specific heats in a field of Pd and $LuCo_2$. Previous low-temperature specific-heat results on $TiBe_{2.06}$ and $TiBe_{1.79}Cu_{0.21}$ are also discussed.

I. INTRODUCTION

Since the claim by Matthias *et al.* that $TiBe_2$ is an itinerant antiferromagnet,[1,2] extensive work has been done on $TiBe_2$. The original interpretation of the magnetic susceptibility as evidence of antiferromagnetism is now believed to be incorrect.[3] Succeeding measurements of $TiBe_2$ have revealed properties like those of Pd, a strongly enhanced paramagnet. The fact that $TiBe_{2-x}Cu_x$ was later discovered[4] to be an itinerant ferromagnet for $x \geq 0.16$ has made this field of research both richer and more complex. Any view of the magnetic behavior of $TiBe_2$ must take into account the similarities to the behavior of $TiBe_{2-x}Cu_x$.

By combining low-temperature specific heat (LTSH), magnetic susceptibility, resistivity, and x-ray measurements on three samples of $TiBe_2$, the present work attempts to reduce the number of conflicting explanations still being proposed to explain the disparate properties of $TiBe_2$: Antiferromagnetism,[5] strongly enhanced paramagnetism (spin fluctuations),[3,6–8] and metamagnetism.[9,10] As will be seen below, the LTSH data in zero field on the three samples of $TiBe_2$ give fairly conclusive evidence for the spin-fluctuation description. By measuring the LTSH in a 7-T field on these samples, not only will a test be made of Béal-Monod's prediction[8] of a 5% increase for γ, the linear term coefficient of the LTSH, of $TiBe_2$ in 7 T, but also an important caution will be raised concerning the recent studies of the LTSH of other materials in magnetic fields and the description of those results by invoking spin fluctuations. Finally, a somewhat radical view of the magnetic behavior in $TiBe_{2-x}Cu_x$ will be put foward based on the present work on $TiBe_2$.

This paper has been divided into six sections. The experimental section discusses the preparation of the three samples, their lattice parameters, and their residual resistivity ratios. In addition, four improvements in the measurement of low-temperature specific heats over the earlier work are described. The results section, Sec. III, discusses the low-temperature susceptibility, resistivity, and specific-heat data with attention given to impurity effects. The low-temperature specific heats of the samples in a 7-T field are compared with a theoretical prediction and with recent measurements of the low-temperature specific heats of Pd and $LuCo_2$ in magnetic fields. Section IV discusses the temperature dependence of the specific-heat data for the three $TiBe_2$ samples using least-squares computer fits in light of spin-fluctuation theory. A spin-fluctuation characteristic temperature is derived. Section V then discusses previous low-temperature specific-heat data for $TiBe_{2.06}$ and $TiBe_{1.79}Cu_{0.21}$ in light of the present work.

II. EXPERIMENTAL

Sample preparation techniques for $TiBe_2$ have improved since the original work.[1,2,4,11] Although arc melting of the pure elemental components is still used, the weight loss originally observed has been much reduced, both by starting with bulk Ti metal instead of Ti powder and by the experience concerning

weight losses gained in previous work. Whereas the arc-melted bead of $TiBe_2$ from which a piece was measured in the first LTSH study actually had a stoichiometry of $TiBe_{2.06}$ (due to an overcorrection for the expected weight loss of Be in arc melting), the two $TiBe_2$ arc-melted beads, from which samples were taken for the present work, had an overall composition of $TiBe_{2.00}$, based upon final weights. The purity of the starting materials for these two samples was quite good—Fe (25 at. ppm) and Al (30 at. ppm) were the predominant metallic impurities. X-ray fluorescence on the actual samples measured confirmed qualitatively (to 100 at. ppm) the absence of any increase in impurities heavier than Si in the arc-melting and annealing processes. A third sample was prepared with oxygen intentionally added via TiO powder to the melt to give $TiBe_{1.94}O_{0.05}$. All samples were wrapped in tantalum foil, sealed under a helium atmosphere in a quartz tube, and annealed for 60–90 hours at 900° C. The residual resitivity ratios (RRR), $\rho(300\ \mathrm{K})/\rho(4\ \mathrm{K})$, and lattice parameters for the three samples are given in Table I. Since $TiBe_2$ forms over a very limited homogeneity range,[12] the range of lattice parameters for the $C15$ structure $TiBe_2$ samples is quite small. Based on metallography, samples 1 and 2 have a few volume percent (2–3) of $TiBe_x$, where $x \geq 3$, as, in fact, do all arc-melted specimens of $TiBe_2$. Based on microprobe and gross optical observation of the distribution of $TiBe_x$ in samples 1 and 2, the piece of sample 1 chosen for LTSH measurements had the composition $TiBe_{2.0\pm0.1}$, whereas the corresponding piece of sample 2 was probably closer to stoichiometry. Since LTSH measures the bulk properties of a material, these several percent of possible impurities (Ti and $TiBe_x$) will affect the LTSH data by less than 5%. Sample 3 has not been examined metallographically, but does have several faint x-ray lines corresponding to less than 5 at.% BeO. Based on these lines and the lattice parameter data it is apparent that less than the added 5% of oxygen is in the $C15$ lattice.

The low-temperature small sample calorimeter has been described elsewhere.[13,14] In the original LTSH work[11] on $TiBe_{2.06}$, several problems were present which have been eliminated in the present work. First, the size of the specific heat of $TiBe_2$ at low temperatures is quite large, leading to excessive time constants (35 sec) for the thermal response of the size sample used (67 mg) in the previous work.[11] Therefore much smaller samples have been used in the present work, ranging from 7.4 mg for the $TiBe_{1.94}O_{0.05}$ sample to 15.7 mg for sample 2. At the lowest temperature of measurement, 1.4 K, the addenda correction to the LTSH of all three samples was less than 1.5%; at the highest temperature, 24.5 K, the addenda correction for the oxygen sample was 54%, and 35% for the other two samples. Since the addenda contribution is known to better than ±4%,

TABLE I. Physical parameters for the $TiBe_2$ samples of the present work. Parameters for fits to the lower-temperature data, $T^2 < 80\ \mathrm{K}^2$, are given in parentheses.

	Lattice parameters (Å)	RRR[a]	$\chi(T=0)$ (emu/mole Oe)	No. of points	γ (mJ/mole K^2)	ϵ (mJ/mole K^4)	δ (mJ/mole K^{4}lnK)	Maximum error of fit[b]	For Θ_D: 400	T_{SF} 500	600
Sample 1 $TiBe_{2.00}$	6.4538 ± 0.0004	39	0.802×10^{-2}	28	51.09	−0.2072	0.06563	2.3%	89	45	33
				(13)	(52.67)	(−0.3692)	(0.1247)	(1.1%)	(38)	(27)	(23)
Sample 2 $TiBe_{2.00}$	6.4510 ± 0.0005	110	0.947×10^{-2}	33	56.33	−0.2207	0.06724	2.6%	97	50	38
				(15)	(56.86)	(−0.2556)	(0.07408)	(1.7%)	(101)	(56)	(42)
Sample 3 $TiBe_{1.94}O_{0.05}$	6.4536 ± 0.0007	15	0.768×10^{-2}	29	37.88	−0.2208	0.0724	2.0%	70	38	29
				(15)	(38.68)	(−0.3348)	(0.1189)	(1.8%)	(34)	(24)	(20)

[a] Due to the presence of second phase in all three samples, the residual resistivity ratios cannot be used as an index to purity, as may be done for single-phase material.
[b] The maximum error of the fit is the largest deviation of fit from the data.

the inaccuracy due to the addenda contribution to the LTSH is no more than ±4% at the highest temperature for the $TiBe_{1.94}O_{0.05}$ sample and is negligible at the lowest temperatures for all samples.

A second, minor problem encountered in the previous work[11] was a slight "τ_2" problem[15] arising from poor thermal conductivity within the sample. This was only a 2% correction to the LTSH at the lowest temperatures and was negligible by 4 K. Due to the smaller size sample used in the present work, this "τ_2" problem was totally absent.

A third, more important problem is the accuracy to which the thermal conductivity, K, of wires supporting the sample platform in the calorimeter is known at temperatures below 2 K, where the total specific heat C_{tot} is given by

$$C_{\text{tot}} = C_{\text{sample}} + C_{\text{platform addenda}} = K\tau \tag{1}$$

and τ is the thermal response time, or time constant, of the sample plus platform. At temperatures below 2 K, it is difficult in the present calorimeter to measure K, since the temperature rise due to a known dc input to the sample platform heater is partially obscured by ac noise heating. This problem lessens as the temperature is raised due to the increase in K and the size of the heat input therefore being increased to obtain a reasonable temperature rise. This increased dc input then makes the ac component of the heating negligible. In the previous work,[11] a linear extrapolation to $K=0$ at $T=0$ was made from $T>2$ K, which could introduce several percent of error at the lowest temperatures. For the sample platform used in the present work (a lower addenda version of the platform used earlier), the LTSH of a 500-mg piece of high-purity Ge has been measured between 1.3 and 12 K. Since the specific heat of Ge is well known and since the addenda contribution is small for such a large piece, especially at the lower temperatures, a thermal conductivity below 2 K can be inferred from Eq. (1) that should be accurate to ±2%.

A fourth improvement in the measurement of LTSH over the previous work is the addition of a dedicated small computer to analyze all of the time constant data from the signal averager rather than a limited subset of these data as done previously.[13,14] This lowers the amount of scatter in the sample specific heat. This will be apparent below when the data in the present work are shown with those of the previous work.

A four-probe ac technique was used to measure the resistance of the three samples with a relative precision of 3×10^{-4}. The susceptibility was measured from 1.4 to 300 K using a vibrating sample magnetometer in fields to 5.5 T.

III. RESULTS

The low-temperature susceptibility data at an applied field of 1.5 T for the three samples are shown in Fig. 1. There is some scatter in such measurements. Sample 1 has $\chi(T=0)$ of approximately 0.80×10^{-2} emu/mole Oe, whereas Acker *et al.* measured[6] a significantly higher value in their specimen of $TiBe_2$, $\chi(T=0)=0.975\times10^{-2}$ emu/mole Oe. Sample 2 of the present work verifies this sample variation with $\chi(T=0)=0.95\times10^{-2}$ emu/mole Oe. Sample 3, with $\chi(T=0)=0.77\times10^{-2}$ emu/mole Oe, agrees well with the earlier work of Matthias *et al.* in that most additions (except Cu) to $TiBe_2$ are found to decrease $\chi(T=0)$.

The behavior of χ for $T<8$ K in Fig. 1 for the three samples is quite different. Sample 2 has essentially a constant χ for $T<8$ K; sample 1 decreases about 1% below 8 K; and sample 3 is intermediate in behavior. In the work[6] of Acker *et al.*, χ decreases

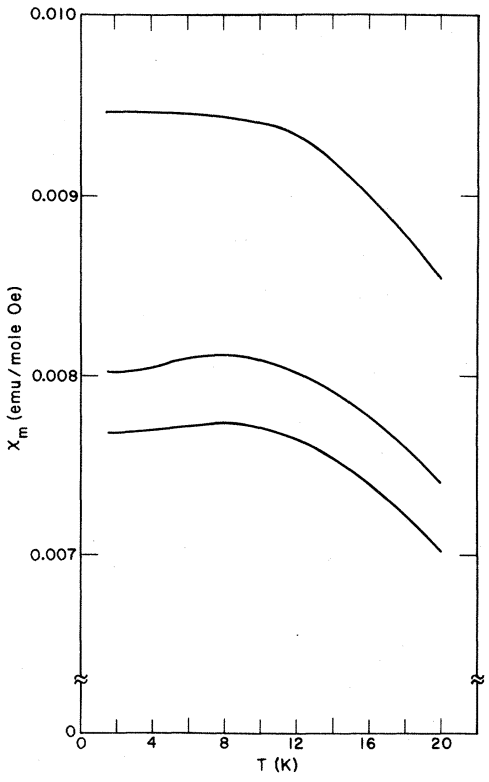

FIG. 1. Low-temperature susceptibility for the three $TiBe_2$ samples. Note that the lowest curve for the $TiBe_{1.94}O_{0.05}$ sample is consistent with the decrease in susceptibility in $TiBe_2$ upon second atom additions, except Cu, in Ref. 1. Also note that the susceptibility shown in the upper curve for sample 2 is constant for $T<5$ K. The middle curve is for sample 1. These data were taken at a field of 1.5 T.

0.9% from 4 down to 1.9 K. Acker *et al.* use their very accurate χ data below 3.3 K to obtain a T^2 temperature dependence in support of their view of $TiBe_2$ as a strongly enhanced paramagnet with paramagnons or spin fluctuations. While our data are not as accurate as that taken by Acker *et al.* using a squid susceptometer, it is clear from Fig. 1 that the result of T^2 temperature dependence at low temperature for χ is likely to be sample dependent.

The low-temperature resistances of samples 1–3 are shown in Fig. 2. The lowest temperature resistance behavior of sample 1 is significantly different from that of the other two. Both samples 2 and 3 have a T^2 temperature dependence over a limited range above a change in slope, or "kink," at about $T^2 = 5\ K^2$, below which one can also fit the data as having T^2 temperature dependence. As is well known, fitting a particular temperature dependence to data over a limited range is nonunique. As seen in Fig. 3, where the resistances for samples 1 and 2 are shown to higher temperatures, the data have an approximate $T \ln T$ behavior above the kink, rather than

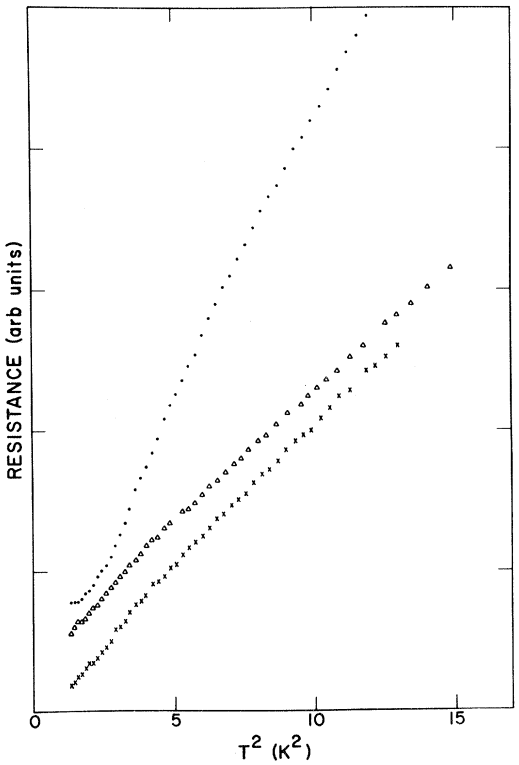

FIG. 2. Resistance at the lowest temperatures on an expanded scale for the three $TiBe_2$ samples plotted vs T^2. Note the kink at about $T^2 = 5\ K^2$ for all of the samples. Note also the non-T^2 behavior for sample 1 (filled circles) at the lowest temperatures. ×'s are for sample 2; triangles are for sample 3. The relative magnitude of the resistance of each sample with respect to that of others is arbitrary.

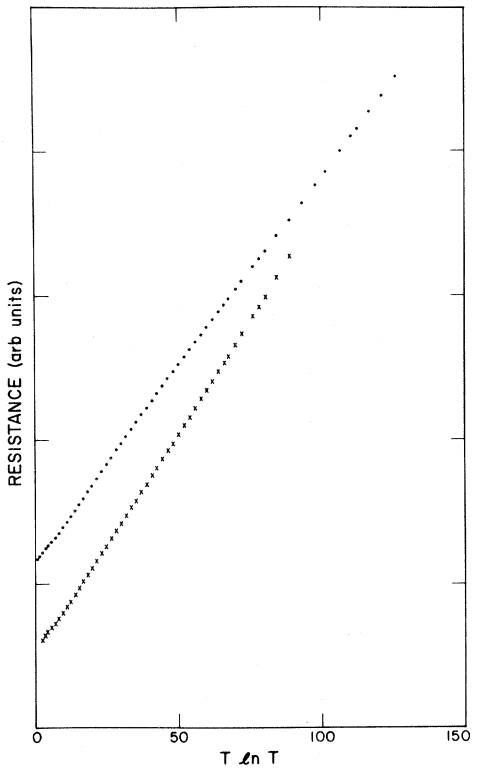

FIG. 3. Resistance at low temperatures for samples 1 (filled circles) and 2 (×'s) plotted vs $T \ln T$.

T^2. Thus these data show that the assignment of T^2 temperature dependence between 2 and 3 K by Acker *et al.* for their resistance data on $TiBe_2$ is a bit problematical. In addition, Fig. 2 of the present work shows significant sample variation in the lowest-temperature resistance behavior, with samples 2 and 3 being different than sample 1.

The low-temperature specific-heat data for the three samples is shown in Fig. 4. The data for all three samples have the same shape. Sample 3, with oxygen added, has a significantly lower specific heat due to a decreased density of states, which is consistent with its lower susceptibility (see Fig. 1). The LTSH of samples 1 and 2 are essentially identical at higher temperatures; at lower temperature, sample 2 has a larger specific heat. This, coupled with the susceptibility data, is consistent with there being a magnetic impurity, perhaps an oxide of Ti, present in sample 2 which is ordered at lower temperatures and, therefore, has increased specific heat. This supposition also explains the constant $\chi(T)$ for sample 2 below 8 K (see Fig. 1), as well as the significantly larger χ of sample 2 versus that of sample 1, 18% larger at the lowest temperature. This is not to say that sample 1 does not have a magnetic impurity present, only that it has less. Since Ti has such an affinity for oxygen, if the magnetic impurity is an ox-

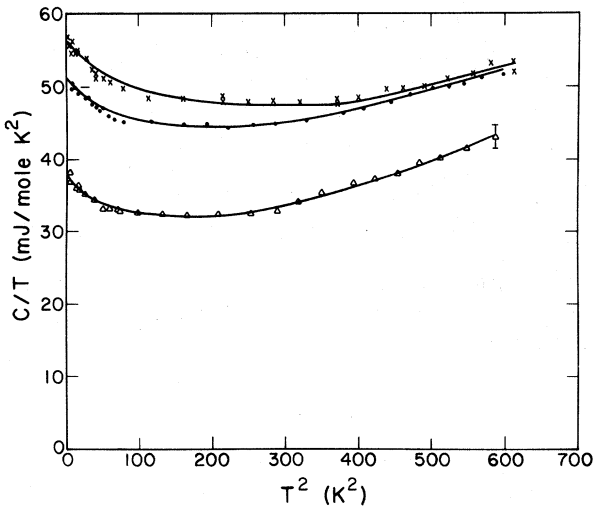

FIG. 4. Low-temperature specific heat for the three $TiBe_2$ samples. Note the almost equal data for sample 1 (filled circles) and sample 2 (×'s) at higher temperatures. Note also the significantly smaller specific heat for the $TiBe_{1.94}O_{0.05}$ sample (triangles).

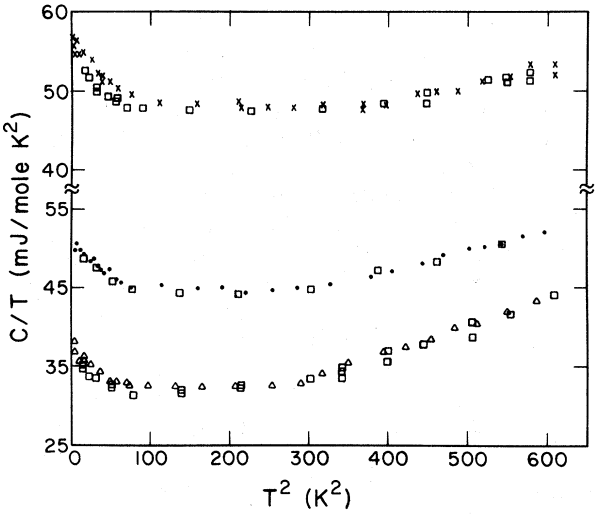

FIG. 5. Low-temperature specific heat for the three samples in 0 field (sample 1—filled circles; sample 2— ×'s, sample 3—triangles) and in 7 T (squares for all three samples). Note that although the data show a slight decrease in 7 T at lower temperatures for samples 2 and 3, the data for both 0 and 7 T *is identical* for all samples at higher temperatures, implying that the decrease in 7 T at lower temperatures could be an impurity effect.

ide of Ti, then it is likely that it is present in sample 1 also. The intentional addition of oxygen to sample 3 was meant to resolve this question. However, the decrease in the specific heat due to the decreased density of states has obscured the effect in the zero-field specific-heat data. It is certainly true that the oxygen in sample 3 has had a drastic effect on its susceptibility, since, if the density of states for sample 3 is 30% less than that of sample 1 (as may be inferred from Fig. 4), then so should the susceptibility of sample 3 be 30% less than that of sample 1, at least to first approximation. Thus it is plausible that: there is a magnetic impurity in sample 2 (or at least more than in sample 1), the impurity contains oxygen, and the susceptibility and specific heat of sample 2 are larger than those of sample 1 due to this impurity.

If there is such a magnetic impurity, the resistance as a function of temperature should differ qualitatively between the samples thought to have the impurity (samples 2 and 3) and the sample (sample 1) thought to have less or none of the impurity—as is the case. In order to confirm the impurity as being magnetic, as suggested by the low-temperature susceptibility magnitude and shape, another measurement in a field should be done. Since, additionally, Béal-Monod has a prediction for the change of specific heat in 7 T of $TiBe_2$ (+5%), such a measurement was done.

The LTSH data for all three samples in 0 and 7 T are shown in Fig. 5 and expanded at the lower temperatures in Fig. 6. We see that the supposition that sample 2 has an increased specific heat over that of sample 1 due to a magnetic impurity, is consistent

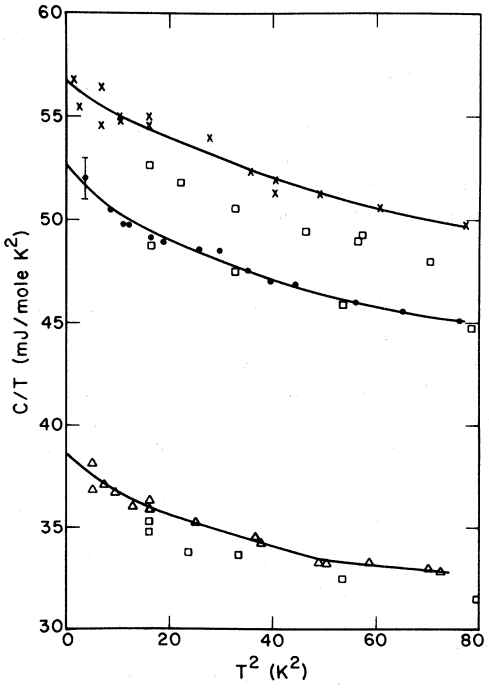

FIG. 6. The low-temperature specific-heat data in 0 and 7 T from Fig. 5 is shown expanded for $T^2 < 80$ K^2. The decrease of the data in 7 T (shown as squares for all three samples) at the lower temperatures is evident for samples 2 (upper curve) and 3 (lowest curve).

with the LTSH field data. At lower temperatures (Fig. 6), the LTSH of sample 2 decreases approximately 3 to 4% in 7 T, while at higher temperatures the 0- and 7-T LTSH data (Fig. 5) are the same. Also, to within 0.75%, there is no decrease in the LTSH data in 7 T of sample 1 at all temperatures. It should be noted that the precision, as distinct from the absolute accuracy, of the present calorimeter is approximately $\pm 1\%$. Thus the reader is cautioned not to presume that the LTSH of sample 1 of $TiBe_2$ decreases 0.75%, when in fact such a decrease is, within the limits of the precision of the data, equivalent to zero.

Two interpreations of this zero LTSH decrease in 7 T for sample 1 can be made. If there is no magnetic impurity in sample 1, then this result is characteristic of pure $TiBe_2$ and the prediction[8] of Béal-Monod of a 5% increase is incorrect. However, it should be remembered that the low-temperature resistance of *all three* samples has a kink, which may be associated with an impurity. Such a kink has been seen[16] in the low-temperature resistance of TiRuP. The use of oxygen-free Ti eliminates[16] the resistance kink. Thus the second interpretation of the zero decrease of the LTSH in 7 T for sample 1 is that there is indeed impurity present and that there are two competing effects—the predicted[8] increase due to spin fluctuations and the known decrease observed in samples 2 and 3 due to the supposed impurity.

It is impossible to distinguish between these two interpretations. Perhaps higher-field LTSH measurements, recently achieved[17] for the first time at 18 T, in fields high enough to saturate the impurity effect, would show an increase, predicted[8] to go as H^2.

A brief comment should be made on the recent LTSH measurements in fields of 10 to 11 T on Pd and $LuCo_2$. Béal-Monod has predicted[8] from the low-temperature susceptibility data, on very fundamental thermodynamic grounds, an increase in the LTSH in field for both materials, whereas experimentally, the LTSH in a field decreases substantially—11% in 10 T for $LuCo_2$ (Ref. 18) and 7.8% in 11 T for Pd (Ref. 19) at the lowest temperatures. The work on Pd did not go over 11.5 K, while the discussion of the work[18] on $LuCo_2$ states that the observed decrease in the LTSH decreases above 12 K, but shows no data above 6 K. This lessening of the decrease above 12 K in $LuCo_2$ progresses to the point where, at 20 K, the high-field data are only about 1.5% less than the zero-field data.[18] The estimate[18] of the characteristic spin-fluctuation temperature from magnetic measurements for $LuCo_2$ is two orders of magnitude too high to explain this decrease in the field effect in $LuCo_2$ at 20 K as being due to a dampening of the spin fluctuations due to increased temperature. Based on the present work, this disagreement between prediction and experiment could be analogous to the suggested impurity effect between samples 1 and 2 of $TiBe_2$. Not only could a magnetic impurity affect the LTSH data for $LuCo_2$ and Pd, which would then respond to field differently, but also the susceptibility data from which the predictions were made could be changed both in magnitude and shape by impurities. As suggested by Béal-Monod,[8] measurements of χ and LTSH on the same samples, as done in the present work, are needed to investigate this discrepancy.

The accuracy of the χ data in Fig. 1 ($\pm 1\%$) is not sufficient to investigate the thermodynamic relationship

$$\left.\frac{H\partial^2\chi}{\partial T^2}\right|_{H=0} = \left.\frac{\partial\gamma}{\partial H}\right|_{T=0}$$

used by Béal-Monod[8] for her prediction of a 5% increase in γ, the linear term coefficient in the LTSH, in a 7-T field for $TiBe_2$. Acker *et al.*[6] observed less than a 1% change in their very accurate χ data on a $TiBe_2$ sample between 2 and 4 K. However, as shown in the present work on $TiBe_2$ by the obvious sample-to-sample variation in both the magnitude and shape of χ at low T (Fig. 1), coupled with the range of observed responses of the LTSH to 7 T (0 to -4%), more accurate χ data for these, or any similarly prepared, samples of $TiBe_2$ would be pointless, since the general response of the LTSH to magnetic field reported here is not an intrinsic property of pure $TiBe_2$, but is instead impurity dominated. Thus the investigation of spin-fluctuation theories by the measurement of the LTSH of $TiBe_2$ in magnetic fields must wait upon purer samples.

The correct explanation for $LuCo_2$ and Pd may in fact not be an impurity effect. Certainly in the case of the Pd work[19] the purity was stated to be quite good, with a residual resistivity ratio over 10 000. Measurements of the LTSH on this sample in 11 T to higher temperatures to look for a decrease in the field effect should certainly be done before any purity-dependent study is made. In the case of $LuCo_2$, perhaps the spin-fluctuation temperature implied from magnetic susceptibility is incorrect. The commentary here concerning this other work is not intended, by any means, to do other than suggest a possible alternative for discussion.

IV. TEMPERATURE DEPENDENCE OF THE SPECIFIC HEAT; DERIVATION OF THE SPIN FLUCTUATION TEMPERATURE

The LTSH data shown in Fig. 4, with the upturn at low temperatures, look startingly like that of UAl_2. UAl_2 has been identified[20] as the only metal to have a $T^3 \ln T$ temperature dependence in the LTSH. Brodsky[21] has stated that the presence of a $T^3 \ln T$ term in the LTSH is the only "hard proof" of spin fluctuations. While it is true that the electron-phonon in-

teraction has theoretically been predicted[22] to give a $T^3 \ln T$ term in the LTSH, the overwhelming likelihood, based on the work of Acker *et al.*,[3,6] the analysis of Béal-Monod,[7,8] and numerous other works, is that if there is a $T^3 \ln T$ term in the LTSH of $TiBe_2$, it is due to spin fluctuations ($\leftrightarrow$ paramagnons).

Thus the zero-field data in Fig. 4 have been fitted by a least-squares computer program to

$$C/T = \gamma + \epsilon T^2 + \delta T^2 \ln T \tag{2}$$

where, from the theories of Doniach and Engelsberg[23] and Berk and Schrieffer[24]

$$C/T = \gamma m^*/m + T^2[\beta - (\alpha\gamma/\bar{T}_F^2)(\ln \bar{T}_F - B_0)] + T^2 \ln T(\alpha\gamma/\bar{T}_F^2) \ . \tag{3}$$

The parameter $\bar{T}_F$ is $4T_{SF}/\pi\bar{I}$, where T_{SF} is the characteristic spin-fluctuation temperature and $\bar{I} = 1 - 1/S$, where S is the Stoner factor. $\bar{I}$ is, for $TiBe_2$, very close[8] to 1 (0.9846 for $S = 65$). The parameter β is due to the lattice specific heat and may be related to the Debye temperature, Θ_D, via $\Theta_D = (1944 \times 3/\beta)^{1/3} \times 10$. The coefficient γ is proportional to the electronic density of states, $N(0)(1+\lambda) = 0.1415\gamma$, where λ is the electron-phonon coupling constant and m^*/m in Eq. (3) above may be viewed as the renormalization of $N(0)$ by a λ due to electron-electron interactions:

$$m^*/m = m(1+\lambda_{e-e})/m = 1 + \lambda_{e-e}.$$

The constant B_0 has been, in the UAl_2, alternatively ignored,[20] or bypassed[25] by approximating γ by higher-temperature data and using an expression for α from theory which involves low-temperature susceptibility data. Due to the possibility of a contribution to $\chi(T=0)$ from a magnetic impurity in the present work, this bypass route is not open. Therefore B_0 is approximated in the present work by that derived[23] by Doniach and Engelsberg for Pd, $B_0 = 0.18$.

Trainor, Brodsky, and Culbert[20] give a description of their UAl_2 LTSH data based on the above formalism, although they ignore B_0. In their description, they were unable to achieve a good fit of their data to Eq. (2) over an extended temperature range and chose to fit their data to Eq. (2) between approximately 1 and 6 K. The lines shown in Fig. 4 are fits of the data to Eq. (2) over the entire temperature range by a least-squares computer program. The resultant γ, ϵ, and δ (defined above) are given in Table I.

As may be seen in Fig. 4, the deviation of the fit from the data is a maximum around 8 K. In general, the fit to Eq. (2) of the data is quite good, especially for the oxygen-doped sample 3. In another work[25] on UAl_2, Trainor, Brodsky, and Knapp speculate that higher-order terms in Eq. (3) are important at $T > 4$ K for UAl_2. This may explain the discrepancy between the fitted curves and the data in Fig. 4. In order to be consistent with the earlier work on UAl_2, fits of just the lower-temperature LTSH data, $T < 9$ K, have also been made and are shown in Fig. 6. The values derived from these fits are given in Table I in parentheses. As may be seen in Fig. 6, except for a few scattered points at the lowest temperatures, the fit of the low-temperature data by Eq. (2) is excellent. The sensitivity of the fitted parameters ϵ and δ to whether all or just the low-temperature part of the data is used in the fit is significant for samples 1 and 3, while the fitted γ is mostly independent of the fraction of the data used for all three samples.

By using Eq. (3) and making an assumption for Θ_D, T_{SF} can be derived.

$$\alpha\gamma/\bar{T}_F^2 = \delta \ , \tag{4}$$

$$\bar{T}_F = (4/\pi\bar{I})\,T_{SF} \cong 1.27\,T_{SF} \ ,$$

$$\beta - \alpha\gamma/\bar{T}_F^2(\ln \bar{T}_F - B_0) = \epsilon \ ,$$

$$\ln \bar{T}_F = (\epsilon - \beta)/(-\delta) + B_0 \ ,$$

$$\ln T_{SF} = (\epsilon - \beta)/(-\delta) + B_0 - \ln(4/\pi\bar{I}) \cong (\epsilon - \beta)/(-\delta) + B_0 - 0.24 \ .$$

Using $\Theta_D = 400$, 500, 600 K gives $\beta = 0.0911$, 0.0467, 0.0270 mJ/mole K^4. This assumption, that $B_0 = 0.18$, and the above equations give the values for the characteristic spin-fluctuation temperature, T_{SF}, given in Table I.

Because of assumptions both for β and B_0, the values must be taken as extremely approximate. Additionally, the question of whether to use the low-temperature fitted values for $T < 9$ K in parentheses or the values based on all the data is not easily resolved. A value of $T_{SF} = 50 \pm 25$ K is probably the most precise that can be quoted at present.

Another question that can be raised is the uniqueness of the fit of the LTSH data to the temperature dependence given in Eq. (2). Figure 7 shows the data for sample 1 fitted to Eq. (2) (middle curve) and also to

$$C/T = \gamma + \beta T^2 + \delta/T^2 \tag{5}$$

and

$$C/T = \gamma + \beta T^2 + \delta/T^3 \ , \tag{6}$$

where δ/T^3 (lower curve) corresponds to the temperature dependence above a Schottky anomaly and δ/T^2 (upper curve) corresponds to a spin-glass anomaly. Obviously, the fits are very poor. It is true that the curvature of the LTSH data requires a temperature dependence higher than T^3. Thus four-parameter fits were tried by adding a T^4 term to Eqs. (5) and (6). The fits achieved were much closer to the data, qualitatively similar to the fit of the data to the three-parameter Eq. (2). However, both four-

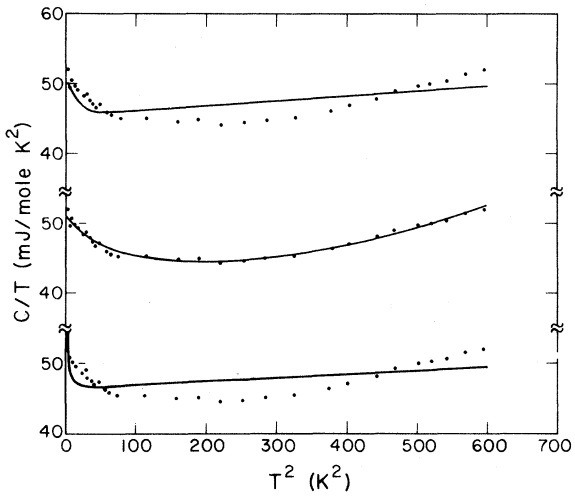

FIG. 7. Fits of the low-temperature specific-heat data for sample 1 to Eq. (2), middle curve; Eq. (5), upper curve; and Eq. (6), lower curve. Clearly, for a three-parameter fit, $T^3 \ln T$ is a better third term than either $1/T^2$ or $1/T$. As discussed in the text, four-parameter fits using these latter temperature dependences give negative lattice specific heats.

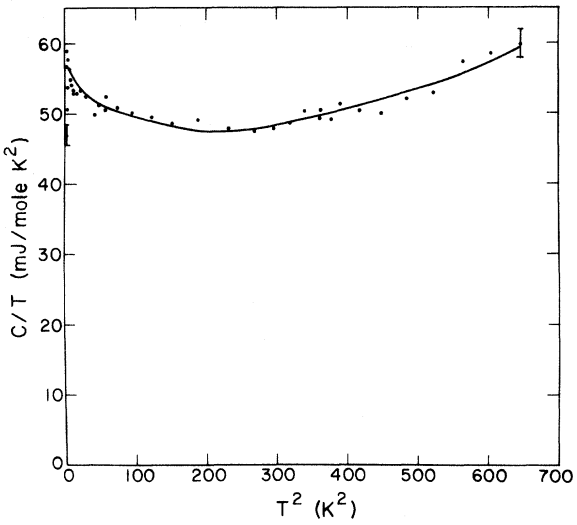

FIG. 8. Previously published low-temperature specific-heat data for $TiBe_{2.06}$. The solid line is a fit of the data to Eq. (2), with the two lowest-temperature points excluded from the fit. Barring the somewhat greater scatter in these data, Eq. (2) gives as good a fit to these data as for the data in Fig. 4.

parameter fits gave negative numbers for $C_{\text{Lattice}} = \beta T^3 + \Delta T^5$ until $T \simeq 19$ K. This unphysical negative lattice specific heat was independent of the number of points included in the fit.

Thus while the $T^3 \ln T$ temperature dependence of the LTSH data may not be unique, no better alternative temperature dependence presents itself to us which is not unphysical.

V. DISCUSSION OF PREVIOUS LTSH DATA ON $TiBe_{2.06}$ AND $TiBe_{1.79}Cu_{0.21}$

The original specific-heat work[11] on $TiBe_{2.06}$ showed a cusp in the lowest-temperature data, based on four data points for $T < 2$ K (see Fig. 8). As discussed in Sec. II, the lowest temperature thermal conductivity used in calculating the specific heat, [see Eq. (1)], was not known in the earlier work to the same accuracy as in the present work. This inaccuracy, coupled with possible effects due to the poorer stoichimetry or increased impurities in the sample measured in the earlier work, indicates that this earlier observation of a cusp, not seen in this work, may have been an artifact. The LTSH data for $TiBe_{2.06}$ from the earlier work (Fig. 8) have been fitted to Eq. (2) with the two lowest-temperature points $T < 1.5$ K, excluded. Although these earlier LTSH data have more scatter than in the present work, due to the lack of a small computer to reduce the τ data, they fit Eq. (2) qualitatively just as well as the data measured in the present work. The fitted parameters are $\gamma = 56.69$ mJ/mole K^2, $\epsilon = -0.2636$ mJ/mole K^4, and $\delta = 0.082\,86$ mJ/mole K^4 lnK, in good agreement with those in Table I for sample 2. Thus the existence of a $T^3 \ln T$ temperature dependence at low temperatures in the LTSH of $TiBe_2$, and therefore proof of spin fluctuations in this compound, was obscured in the earlier work[11] by two data points and, frankly, the early claim[1,2] of itinerant antiferromagnetism. The intervening work by Acker *et al.*[3,6] and by Béal-Monod,[7,8] which proposes that $TiBe_2$ is a spin-fluctuation compound, certainly was a driving force for fitting the LTSH data in the present work to Eq. (2).

It has always been apparent that the LTSH data[4] for $TiBe_{2-x}Cu_x$ were very similar to those of $TiBe_2$. Shown in Fig. 9 are the LTSH data[4] for $TiBe_{1.79}Cu_{0.21}$ and the data for sample 2 from the present work. The data are indistinguishable below about 17.5 K. The line drawn in Fig. 9 is a fit of the $TiBe_{1.79}Cu_{0.21}$ LTSH data to Eq. (2), with the resulting parameters ($\gamma = 56.54$ mJ/mole K^2, $\epsilon = -0.2210$ mJ/mole K^4, and $\delta = 0.06613$ mJ/mole K^4 lnK) within 2% of those shown in Table I for sample 2. Thus, it seems clear that $TiBe_{1.79}Cu_{0.21}$ also has spin fluctuations at low temperatures.

The accepted interpretation[4,26,27] of the behavior of $TiBe_{2-x}Cu_x$ is that it is an itinerant ferromagnet for x greater than about 0.16. There exist two other compounds thought to be itinerant electron ferromagnets: Sc_3In and $ZrZn_2$. The LTSH of both materials[28,29] shows an anomaly at the Curie temperature as deter-

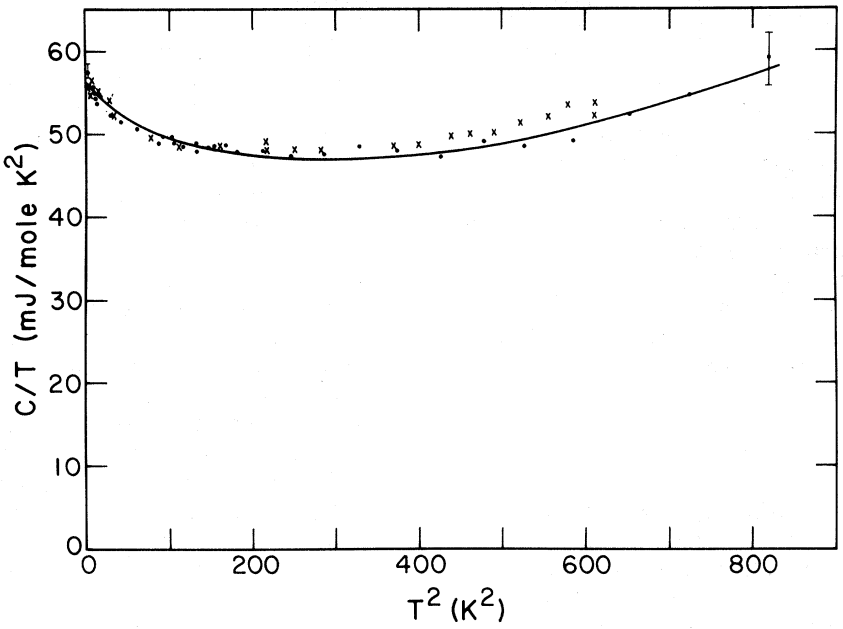

FIG. 9. Previously published low-temperature specific-heat data for $TiBe_{1.79}Cu_{0.21}$ (filled circles) and for sample 2 in the present work (×'s). Clearly, the data are very similar. The solid line is a fit of the data for $TiBe_{1.79}Cu_{0.21}$ to Eq. (2). The data agree with the fit quite well except in the region of 7 to 8 K, just as for the samples measured in the present work. Note the lack of any anomaly at the Curie temperature (determined by magnetic measurements for this sample of $TiBe_{1.79}Cu_{0.21}$ to be $T_C^2 = 169\ K^2$). This supports the conclusion in the text that $TiBe_{2-x}Cu_x$ should be viewed as a spin-fluctuation material.

mined by magnetic measurements. One measure of such anomalies is their entropy. For Sc_3In the anomaly has an entropy of about $0.02R$ ln2; for $ZrZn_2$ the entropy is about 0.005 R ln2; where for a local-moment, spin-$\frac{1}{2}$ system, the entropy would be R ln2. The point should be made that LTSH is a very sensitive tool for detecting such small amounts of ordering—even for $ZrZn_2$, where the LTSH anomaly is broadened and corresponds to only 1/200 of an ordered moment, the anomaly is over 10% of the specific heat at the Curie temperature.[29] For Sc_3In, the anomaly is over 30% of the specific heat at the Curie temperature.

As seen in Fig. 9, the LTSH data for $TiBe_{1.79}Cu_{0.21}$ show no anomaly at the magnetically determined Curie temperature $T = 13$ K, or $T^2 = 169\ K^2$. The data shown in Fig. 9 for $TiBe_{1.79}Cu_{0.21}$ have relatively little scatter; the maximum size of any anomaly at $T^2 = 169\ K^2$ is about 2% of the specific heat—roughly corresponding to $0.001R$ ln2. Again, when the LTSH of $TiBe_{1.79}Cu_{0.21}$ was published, the entire upturn in the data below $T = 20$ K was incorrectly assigned to the entropy of ordering due to the obvious analogy to the LTSH data of $TiBe_2$, which was incorrectly thought to show the entropy of antiferromagnetic ordering. Arguments were made[4] that the entropy of magnetic ordering at $T = 13$ K was somehow spread out between 1 and 20 K, whereas it is now clear that this upturn in the LTSH data is due to a $T^3 \ln T$ temperature dependence due to spin fluctuations.

Thus the question arises: Is $TiBe_{2-x}Cu_x$, for $x > 0.16$, an itinerant ferromagnet? From the lack of an anomaly in the LTSH data in Fig. 9, and from the $T^3 \ln T$ dependence of these data, it is clear that the majority of the electrons at the Fermi energy should be viewed as undergoing spin fluctuations and not ferromagnetic ordering. This contradicts the results[26] of Felcher, Cable, and Smith, who found 0.112 ± 0.004 Bohr magnetons per Ti atom in $TiBe_{1.8}Cu_{0.2}$ via polarized-neutron diffraction. While it is certainly likely that some small fraction of the electrons at the Fermi surface are ferromagnetic in $TiBe_{1.8}Cu_{0.2}$, the LTSH data suggest that $0.112\mu_B$ per Ti atom is a factor of 100 too high. The entropy due to such a moment ordering at 13 K would be over 600 mJ/mole K. This would correspond to a specific-heat anomaly, even allowing for a broader transition then seen in Sc_3In or $ZrZn_2$, which would more than double the specific heat actually observed.

It is possible that the polarized-neutron result[26] for the moment in $TiBe_{2-x}Cu_x$ was influenced by the dis-

cussion of the susceptibility of $TiBe_{2-x}Cu_x$ in the original work,[4] which talks of a Curie-Weiss amount of $1.54\mu_B$ and an induced moment of $0.20\mu_B$. If $TiBe_{2-x}Cu_x$ is correctly viewed as predominantly a spin-fluctuation material, then the original work's discussion[4] is misleading in view of Moriya and Takahashi's observation[30] that the Curie constant, determined from the magnetic susceptibility of such a spin-fluctuation material, is not related to the saturation moment in the ground state. Instead, the Curie constant is merely related to the band structure around the Fermi level,[30] and the scaling of the spin densities in Ref. 26 is improper.

VI. CONCLUSIONS

Both $TiBe_2$ and $TiBe_{1.79}Cu_{0.21}$ have been seen to show a $T^3 \ln T$ temperature dependence in the low-temperature specific heat that is characteristic of spin fluctuations. This result is consistent with the experiments of Acker *et al.*[3,6] and the theories of Béal-Monod.[7,8] The LTSH in a 7-T field of the three samples of $TiBe_2$ has also been measured. This, coupled with susceptibility and resistance data on the same samples, indicates an impurity effect in the field dependence of the LTSH of $TiBe_2$ and the magnitude and temperature dependence of the low-temperature susceptibility. More measurements on purer, well-characterized samples are needed. The size of the field effect on the LTSH of the sample of $TiBe_2$ thought to be most representative of ideal $TiBe_2$ is less than 1%, in disagreement with Beal-Monod's prediction[8] (based on χ data of Acker *et al.*[3] for another sample of $TiBe_2$) of a 5% increase in the γ [Eq. (2)] of $TiBe_2$ in 7 T, since γ is essentially equivalent to C/T at low temperatures for $TiBe_2$, accounting for over 90% of the C/T at 4 K. It is interesting to point out that Béal-Monod bases this prediction[8] on low-temperature susceptibility data on $TiBe_2$ of Acker *et al.*[3] which gives $\chi(T) = \chi(0)(1 + 0.06 \times 10^{-2} T^2)$, from which $\partial^2\chi/\partial T^2$ and thus $\partial\gamma/\partial H$ are derived. However, earlier data of Acker *et al.*[6] gave 0.10×10^{-2} for the coefficient of T^2 instead of 0.06×10^{-2}. As purer samples and similarly accurate χ measurements become available, this number may decrease even further, perhaps even to the point of being consistent with the less than 1% decrease (which, it should be stressed, is equivalent to no change or even a slight positive increase within the precision of the data) observed here for sample 1.

Finally, an analysis of previous LTSH data for $TiBe_{1.79}Cu_{0.21}$ and the lack of an anomaly in those data at the Curie temperature determined by ac susceptibility measurements, suggests that any description of $TiBe_{2-x}Cu_x$ for $x > 0.16$ as having an ordered moment in the range of $0.1-0.3\mu_B$ is two orders of magnitude too high.

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