Magnetic field dependence of the electronic specific heat of $TiBe_2$: An estimate from magnetization data

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An estimate of the variation with magnetic field in the electronic specific heat of $TiBe_2$ is given. From the thermodynamic relationship $\partial S/\partial H = \partial M/\partial T$ and from M-vs-T data it follows that C/T (at $T < 2$ K) should remain constant within 0.2% for $0 \leq H \leq 40$ kOe. A further increase in H up to 70 kOe should cause C/T to drop by about 10%. This is in fair agreement with recent experimental results for $C/T(70\text{ kOe}) - C/T(0)$. The origin of the drop in C/T is still uncertain. Paramagnon theory gives no satisfactory fit of the high-field data.

Several experimental studies of the effect of magnetic field on the electronic specific heat of exchange enhanced paramagnetic metals and compounds have been made recently[1–5] in the hope of gaining more information on the much debated subject of spin fluctuations.[6,7]

In that context, Béal-Monod pointed out that a finite variation of the electronic specific heat C will be found if the second derivative of the magnetization M with respect to temperature is nonzero, and conversely.[8] Whatever causes M and C to vary, the relation

$$\frac{\partial^2 M}{\partial T^2} = \frac{\partial (C/T)}{\partial H} \qquad (1)$$

must hold, as it follows directly from thermodynamics. Hence, in principle, measurement of $M(H,T)$ or $C(H,T)$ alone should suffice. However, the experimental difficulties in measuring M or C differ and depend on the values of H and T.

It was noticed by Béal-Monod that the available experimental data for some strongly paramagnetic substances, e.g., Pd and $LuCo_2$, are not consistent with Eq. (1).

$TiBe_2$, seemingly a well-behaved compound,[9] may be viewed as an ideal material for testing spin-fluctuation models.[10] In Ref. 10 we showed that below 3.5 K the increase in the low-field susceptibility with increasing temperature is well described by the formula $\chi(T) = \chi(0)(1+\alpha T^2)$ in agreement with the paramagnon model.[11] For $H \to 0$, $\alpha = 6\times 10^{-4}$ K^{-2}. Considering that figure for α, and using Eq. (1), Béal-Monod predicted a relative *increase* of 5% in $\gamma = C/T(T\to 0)$ between $H=0$ and $H=70$ kOe.[8]

Subsequent specific-heat experiments carried out in Los Alamos[5] confirmed that $TiBe_2$ may be described in the paramagnon model. However, the variation of C with magnetic field did not come up to the expectations. Depending on the sample used, the low-temperature specific heat was observed to *decrease* by 1 to 4% in 70 kOe. This lack of reproducibility, together with the discrepancy between the sign of $\partial^2 M/\partial T^2$ and that of $\partial C/\partial H$ was interpreted in Ref. 5 as evidencing the presence of a magnetic impurity phase (in different amounts in each of the samples). The specimen with the largest susceptibility ("sample 2," $\chi = 9.5\times 10^{-3}$ emu/mole) was thought to be the less pure.

There is a simpler and—as regards the $TiBe_2$ samples— restoring explanation. It is known that M decreases when T increases, provided that a field higher than about 40 kOe is applied.[10] Thus $\partial^2 M/\partial T^2$ and $\partial(C/T)/\partial H$ may have the same sign in high fields. Clearly, M and C, as well as their partial derivatives, are to be viewed as functions of T and H.[12] Hence, at a fixed temperature T_0, we obtain

$$\frac{C(H)}{T_0} = \frac{C(0)}{T_0} + \int_0^H \frac{\partial^2 M(T=T_0,H)}{\partial T^2} dH \ . \qquad (2)$$

By making the assumption that the low-temperature magnetization of $TiBe_2$ varies proportionally to T^2 also in high fields, it may be deduced from earlier $\chi(H,T)$ data[10,13,14] that $\partial^2 M/\partial T^2$ between 40 and 70 kOe has the right order of magnitude to account for the measured negative variation with field of C/T.[5]

One aim of the present experiments was to verify this by measuring directly M vs T in a high field, bearing in mind that beyond a formal check of thermodynamics the physical interpretation of the $M(H,T)$ data is still a challenging problem. Using the moving sample method we measured M(55 kOe) between 1.4 and 25 K. Measurements were made on two samples: the $TiBe_2$ 5-mm-diameter sphere (sample A) used previously[10,14] and an irregularly shaped

7-mm-long piece (sample B) of the ingot from which a fragment (precisely sample 2 of Ref. 5) was taken for the specific-heat experiments.

It is seen in Fig. 1 that the low-temperature magnetization of samples A and B at 55.1 kOe differ by only 0.7%. The zero-field susceptibility obtained from Arrott plots (not shown)[10] is the same for both samples, within 1% [$\chi(4.2\text{ K}) = 9.78 \times 10^{-3}$ emu/mole for sample B]. The sensitivity of the magnetometer shows a weak dependence on the shape and on the size of the specimen. This would correctly explain the small discrepancy.

The moderately precise data shown in Fig. 1 were fitted to the expression $M(T) = M(0) + AT^n$. The best correlation was found for $n = 1.85$ (sample A) and $n = 2.25$ (sample B). It is likely that more precise data would follow a T^2 law at low temperatures for both samples. Taking $n = 2$, we find $\partial^2 M/\partial T^2 = -2.86$ emu/mole K^2 for sample A and -2.79 emu/mole K^2 for sample B, at 55.1 kOe.

Shown in the insert of Fig. 1 is the variation with temperature of the susceptibility (M/H) at 0.5 kOe (Ref. 10) (curve a) and 55.1 kOe (curve b, from two sets of data). Strong deviation from a T^2 law (dashed curves) is observed for $T > 4$ K, at both fields. At 55.1 kOe, $\partial^2 M/\partial T^2$ goes to zero near 10 K.

The measurements shown define only two points of the $\partial^2 M/\partial T^2$ vs H curve. More points were determined by using two previously measured magnetic isotherms (M vs H) for sample A at 1.45 K (Ref. 10) and 4.17 K ($25 < H < 69$ kOe). Assuming a T^2 law (which is not quite correct in that temperature interval), $\partial^2 M/\partial T^2$ was calculated from $M(1.45\text{ K}) - M(4.17\text{ K})$ at several values of H. This is shown in Fig. 2.

At 55 kOe the uncertainty in M is about 0.2%, corresponding to a relative error of about 12% in $M(1.45\text{ K}) - M(4.17\text{ K})$, whereas the uncertainty in $T(\pm 10\text{ mK})$ is reflected in a mere $\pm 1\%$ error in $\partial^2 M/\partial T^2$. Thus the values of $\partial^2 M/\partial T^2$ at 55 kOe obtained from $M(1.45\text{ K}) - M(4.17\text{ K})$ and from the data shown in Fig. 1 agree, within experimental error, for sample A. Since, in addition, there is no significant difference between the data for samples A and B in Fig. 1, all the points in Fig. 2 were taken together to define a $\partial^2 M/\partial T^2$ vs H curve, irrespective of the sample or of the method used.

Even at low field (5 kOe), the data in Fig. 2 clearly deviate from the straight line defined by $H\partial^2\chi/\partial T^2$ $(H \rightarrow 0)$, which is Béal-Monod's approximation.[8] (See also Fig. 3 of Ref. 10 from which the point at 5 kOe was taken.) From Eq. (2) the area under the

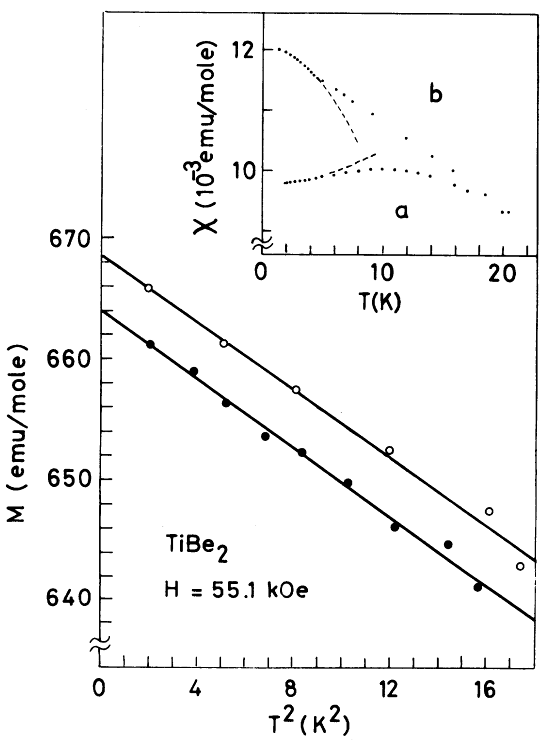

FIG. 1. Magnetization as a function of T^2 for $TiBe_2$ in a field of 55.1 kOe. ●, sample A; ○, sample B. Insert, variation with temperature of the susceptibility of sample A at 0.5 kOe (Ref. 10) (curve a) and at 55.1 kOe (curve b). At 55.1 kOe the data above and below 4.2 K were not taken with the same apparatus.

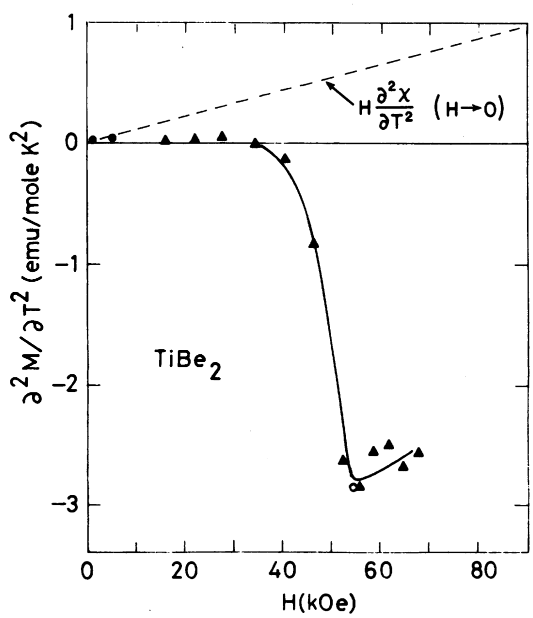

FIG. 2. Second derivative of the magnetization with respect to temperature as a function of field for $TiBe_2$ at low temperature, obtained under the assumption that $M(T,H) = M(0,H) - A(H)T^2$. ● from Ref. 10; ▲ from $M(1.24\text{ K}) - M(4.17\text{ K})$ data; ○ from Fig. 1. The area under the curve yields the estimate of the variation of C/T with field.

curve $\partial^2 M/\partial T^2$ vs H yields directly the variation of C/T with H. We thus find by graphical integration up to 70 kOe, $\Delta\gamma/\gamma \simeq [C/T(70\text{ kOe}) - C/T(0)]/[C/T(0)] = -0.10 \pm 0.02$ at low temperature. It comes out that, within 0.2%, $C/T(40\text{ kOe}) = C/T(0)$. The uncertainty in $\Delta\gamma/\gamma$ at 70 kOe would be significantly larger if we would not assume that M vs T follows a T^2 law up to 4 K at high field. Taking, for, example an empirical $T^{1.5}$ law would result in a decrease by about 40% in the value of $|\partial^2 M/\partial T^2|$ at 2 K. the calculated M vs T curve would still fit in well with the data for $1.4 \leq T \leq 4$ K. This might partly explain the discrepancy between the above result $|\Delta\gamma/\gamma|(70\text{ kOe}) = 10\%$ and the experimental value (3–4%).

In Ref. 5, $\Delta C/T(H)$ was found to be sample dependent. This may be tentatively explained by noticing that a $TiBe_2$ specimen with a lower susceptibility showed only a small increase in χ with increasing H.[13] A corresponding reduction in $\partial^2 M/\partial T^2$ is expected. In other words, curve b in the insert of Fig. 1 would flatten out.

An indication about the variation of $C/T(H)$ in higher fields is given by Fig. 2. It is seen that $\partial^2 M/\partial T^2$ starts decreasing above 55 kOe. This is confirmed by earlier $M(4.2\text{ K}) - M(1.24\text{ K})$ data extending up to 213 kOe (not shown).[14] Hence $C/T(H)$ should tend to saturate slowly. A similar tendency was observed for $LuCo_2$.[2]

At this point the following conclusions can be drawn: (i) There is formal agreement between the $M(H,T)$ and $C(H,T)$ measurements for $TiBe_2$. Obviously, the same must be true for Pd (Ref. 15) or $LuCo_2$, as further experiments should show. (ii) The compound $TiBe_2$ can be prepared in a reproducible way and there is no evidence of a magnetic impurity phase. This is confirmed by recent magnetization measurements of a series of dilute $TiBe_{2-x}Cu_x$ compounds.[14] The zero-field susceptibility data for $x < 0.03$ (four samples) show very little dispersion and confirm that the susceptibility of $TiBe_2$ is $\chi(H=0,\ T=0) = (9.7+0.1)\times 10^{-3}$ emu/mole (Ref. 10)]. This value is close to the susceptibility reported in Ref. 5 for sample 2 which had the highest susceptibility, the best resistivity ratio $[R(300\text{ K})/R(4.2\text{ K}) = 110]$, and the largest low-temperature specific heat. The latter varied most strongly with magnetic field. Hence it would seem that sample 2 is the more characteristic of pure $TiBe_2$.

We wish to stress that no satisfactory physical explanation for the awkward shape of $\partial^2 M/\partial T^2$ vs H (Fig. 2) and for the corresponding $C(H)$ data[5,16] is available. In a recent extension of the paramagnon model to finite fields, Béal-Monod and Daniel[17] obtained for $\partial^2 M/\partial T^2$ an expression of the form

$$\frac{\partial^2 M}{\partial T^2} = aH + bH^3 + \cdots \quad . \tag{3}$$

This is unfortunately not observed here, for $H > 10$ kOe, as seen in Fig. 2. Obviously, the step in $\partial^2 M/\partial T^2$ at $H \simeq 50$ kOe cannot be fitted to Eq. (3). At the same field, $\partial M/\partial H$ shows a pronounced peak.[10]

To summarize, we find agreement between $C(H,T)$ and $M(H,T)$ data for $TiBe_2$. There is no evidence of the presence of magnetic impurity phases in the samples, which can be prepared in a reproducible way. As to the interpretation of the high-field data, spin-fluctuation models[7,17] seem inadequate. It appears safe to conclude with Enz[18] that the $TiBe_2$ problem is not completely solved.

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$$\frac{\partial^2 M}{\partial T^2}(T,H) = \frac{\partial (C/T)}{\partial H}(T,H) \quad .$$

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