Possibility of Kauzmann points in the vortex matter phase diagram of single crystal $YBa_2Cu_3O_{7-\delta}$

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Abstract

We highlight interesting thermomagnetic history effects across the transition line between the (quasi) ordered and disordered vortex states in single crystal $YBa_2Cu_3O_{7-\delta}$, and argue that these features are indicative of the first order nature of the transition line. We suggest that the destruction of the ordered vortex state in $YBa_2Cu_3O_{7-\delta}$ leading to vortex liquid (at high temperatures and low fields) and amorphous vortex solid (at low temperatures and high fields), takes place along a unified first-order transition line. The nonmonotonic behavior of this first order transition line gives rise to the possibility of more than one Kauzmann point where the entropies of the ordered and disordered vortex states are equal. In the high temperature region, one may order the vortex lattice by warming it, giving rise to an inverse melting effect.

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In a recent report Avraham et al[1] has shown that the destruction of the quasi-ordered vortex lattice or Bragg glass[2] in single crystal samples of $Bi_2Sr_2CaCu_2O_8$ (BSCCO) takes place along a unified first order transition line. Two different types of energy – thermal energy and pinning energy – actually compete with the elastic energy leading to the destruction of the ordered vortex lattice. At low temperatures and high fields pinning dominates, leading to a field/disorder induced destruction of the ordered vortex lattice. At high temperatures this unified transition line changes its character from disorder induced transition to thermally-induced melting. The apparently unusual finding is the non-monotonic nature of this first-order transition line, leading to the paradoxical situation that in a certain field-temperature (B-T) window the ordered vortex state has larger entropy than the disordered vortex state. This in turn has the interesting implication that a crystal transforms into liquid or amorphous state on decreasing the temperature. Such a situation is quite rare but not unknown, one classic example being the the melting curve of ^{3}He showing a pressure minimum[3]. Similar situation also exists in spin lattice systems[4] where the spin-glass state transforms into a long-range magnetic ordered state with the increase in temperature. However, such a transition is known to be a continuous transition with definite critical response[4].

The same non-monotonic character of the transition line between two kinds of vortex solids has been reported earlier for $YBa_2Cu_3O_{7-\delta}$ (YBCO) single crystals[5,6]. In addition the presence of metastability has also been highlighted across this phase transition[6,7]. We extend this study to argue that the vortex solid-solid transition line in YBCO is also a first order transition line, and there exists a situation of "ordering by heating" in a certain B-T window of YBCO as well. We shall use the minor hysteresis loop (MHL) technique[8] to study the first order transition line. This technique, although less rigorous than an actual equilibrium thermodynamic measurement, has been quite successful recently in studying the first-order nature of the vortex solid-solid transition in low tempearture superconductors like $CeRu_2$[9–11] and $NbSe_2$[12,13], and in high temperature superconductors such as YBCO[6] and LaSrCuO[14].

Local magnetization measurements using an array of $10 \times 10\mu m^2$ Hall sensors (sensitivity better than 0.1 G) were carried out on a $0.5\times0.3\times0.02$ mm^3 untwinned YBaCuO single crystal[15].

A typical field dependence of magnetization showing peak-effect, which we use to track the vortex solid-solid phase transition line, is shown in Fig. 1. We identify four characteristic fields: B^+_{onset}, B^-_{onset}, B^+_{kink} and B^-_{kink}, marked by arrows in Fig.1. We have earlier argued that the solid-solid thermodynamic transition field B_{SS} can actually be identified with the B^-_{kink}[6]. Collating these characteristic field B^-_{kink} at various temperatures from our isothermal magnetization studies we present a B-T phase diagram in Fig.2 showing this B^-_{kink}(T) line. This is similar to the (B-T) phase diagram that has been reported earlier[6], but is reproduced here again to make the present study a self contained one.

It is apparent from Fig. 2 that the non-monotonic nature of the phase transition line is more prominent in comparison to BSCCO[1]. The slope of the transition line changes sign twice as a function of temperature, first at around 50K going from negative to positive, and then at around 75K back to negative again. We shall now concentrate on the 50K-75K regime of this phase transition line where, akin to that in BSCCO[1], exists the interesting suggestion of the transition from the disordered-solid to ordered solid achieved by heating. We present results in the form of MHLs obtained after preparing the vortex state following two distinct experimental protocols:

1. Zero field cool (ZFC) the sample to the temperature of measurement and then increase the field to go to the vortex solid-solid phase transition region denoted by the shaded area in Fig.2. The field is then lowered to zero so that an MHL is obtained.

2. Cross the vortex solid-solid phase transition line by varying temperature in the presence of an external field. To do this in the 50K-75K regime, which had not been explored before, we cool the sample from above T_C to 50K in the presence of external field of 40 kOe. We then lower the field to the target value at 50K, and then increase the temperature to the temperature of measurement. This is the counterpart of the step-

down procedure used in Ref.6, where only the low-temperature region was explored.

In Fig. 3 we present MHLs obtained under the protocol 1 at 70K. These MHLs are obtained by terminating the field increasing cycle of the M-B curve at various points in the field regime $B^{-}_{onset} \leq B \leq B^{+}_{kink}$. Within the Bean critical state model (which explains well the irreversible magnetization of a type-II superconductor) such MHLs are expected to meet the enevlope M-B curve after the field is decreased by an amount $2B^*$, where B^* is the field for full penetration[16] at that particular B. In fact the MHLs drawn at various fields $B > B^{+}_{kink}$ show this expected behaviour. However, the behaviour changes markedly at the onset of the peak effect (PE) regime, and the MHLs obtained by procedure 1 (ZFC) saturate without reaching the the upper envelope curve (see Fig. 3). Since the amount of hysteresis ΔM is proportional to the size D of the sample exhibiting pinning, it is clear that the vortex disordered solid (with enhnaced pinning) starts nucleating at $B > B^{+}_{onset}$ and its formation is complete only at B^{+}_{kink} where the MHLs saturate only on reaching the upper envelope curve. This kind of nucleation and growth of the enhanced pinning state are typical characteristics of a first order transition, and have earlier been observed in low temperature superconductors like $CeRu_2$[8–11] and $NbSe_2$[12,13], YBCO[6] and LaSrCuO[14].

In Fig.4 we present MHLs at 70K obtained under the experimental protocol 2. The MHLs obtained both by increasing and decreasing B overshoot the enevelope curve. This in turn implies that flux pinning obtained in this manner is more than that obtained in crossing the vortex solid-solid transition line by isothermal field variation. It has been argued earlier that extent of metastability (i.e. supercooling/superheating) associated with a first order transition is more if the transition line is crossed by the variation of temperature in presence of a constant magnetic field in comparison to the situation where the line is crossed by isothermal variation of the applied field[17]. This is because the variation of the magnetic field produces fluctuation which drives the metastable state in the local minimum of the free energy curve to the stable state across the energy barrier. We argue that the observed overshooting of the MHLs in Fig. 4 is thus another indication of the first order nature of the vortex solid-solid transition line.

It is to be noted here that the metastability across the first order vortex solid-solid transition line has been highlighted recently in BSCCO[1,18,19]. In fact the associated irreversibility in this transition region was removed by using an applied ac field H_{ac} to reveal the step-jump in the magnetization, which in turn was used to establish the first order nature of the transition line[1]. In contrast we use the metastable characteristic across the transition line itself to identify its first order nature. We have earlier used the same technique to study the nature of the vortex solid-solid transition line of YBCO below 50K (Ref. 6).

Combining the present study as well as the earlier ones on YBCO[5,6] we argue that as in BSCCO the extended B_{SS}(T) line coincides with the melting line vortex ordered solid B_M(T) line at high temperatures. Hence the disordering of the vortex ordered solid is apparently always a first order transition. We note that B_{SS}(T) being a phase transition line allows one to assert that the free energies of the two solid phases are equal along this line, and they satisfy the inequality of opposite signs as the B_{SS} (T) line is crossed. Our conclusion that this line corresponds to a first order phase transition implies, in addition, that the entropies of the two solid phases viz. the 'ordered' Bragg glass and the 'disordered' vortex glass, are unequal along this line. The shape of this combined transition line, however, gives rise to many interesting possibilities, including two Kauzmann points[20]. In the present (B-T) phase diagram of YBCO (Fig. 2) we define these Kauzmann points as the points where the slope of B_{SS} changes its sign - once around 50K and then at around 75K. At a Kauzmann point the entropies of the disordered and ordered state are equal. The Kauzmann point is well known in the context of (molecular) liquid-glass transition, where to avoid entropy crisis below $T_{Kauzmann}$ the liquid is frozen into a glassy state at a temperature $T_G > T_{Kauzzman}$. On the other hand, a Kauzmann point can actually be reached in the pressure(P)-temperature(T) phase diagram of ^{3}He. It leads to the apparently anomalous situation where the solid entropy is higher than the liquid entropy[3]. This is of course now understood in terms of the (nuclear) spin contribution to entropy which due to Pauli exclusion principle is less for liquid than for the solid. At very low temperatures the spin contribution dominates over the structural contributions, and thus the entropy per atom of the solid is greater than the liquid. Experiments also indicate that poly(4-methylpentene-1) exhibits a pressure maximum, hence a Kauzmann point along its melting curve (see Ref. 20 and references therein). The interpretation of this observation becomes complicated because of the appearence of an additional phase (Ref.20). In the proposed (B-T) phase diagram of oxide superconductors with reentrant melting of a vortex solid[21], there would be a Kauzmann point at the 'tip of the nose'. This phase diagram, however, still has to be confirmed experimentally. With these information we now attempt to rationalize the entropic relations between various phases in the vortex matter phase diagram of YBCO.

Between two Kauzmann points (50K,(≈)1.1T and 72K,(≈)2.1T) in the B-T phase diagram of YBCO, the dB_{SS}/dT has a positive slope; and from the Clausius-Clapeyron relation this will indicate a neagative entropy change across this first order transition line. (The implicit assumption here is that the equilibrium magnetization shows a positive jump at the phase transition point as in BSCCO). A negative entropy leads to the paradoxical situation where the ordered vortex solid has larger entropy than the disordered vortex solid. The name ordered vortex solid itself indicates that it is structurally more ordered. Hence, as in the case of solid ^{3}He the extra entropy needs to be attributed to some additional degrees of freedom. In the same vein as in BSCCO (Ref. 1) it can be argued that in the disordered vortex solid the the flux-lines or vortices wander out of their unit cells and become entangled. However, their fluctuations are small on short time scales. In contrast, in the ordered vortex solid there is no large scale wandering of the vortex and entanglement. But the effect of thermal fluctuations within the unit cell is comparatively large, which in turn results in larger entropy.

An important aspect which is not commonly addressed in the studies of vortex matter is the electronic structure of the vortex cores. The existence of bound quasi particle states in the normal vortex cores of a conventional superconductor has been predicted in early sixties by Caroli et al[22] but was not established experimentally until late eighties when Hess et al[23] observed tunneling spectra in the vortex core of $NbSe_2$ consistent with localized quasi particle states. With the arrival of HTSC the questions are now asked regarding the low energy physics associated with a vortex core, nodal structure (associated with the proposed $d_{x^2-y^2}$ wave pairings) and quasiparticle transfer between vortices, which will ultimately govern the physical properties of the vortex states. While localized quasi particle states inside the vortex core has now been observed in YBCO (Ref. 24), an intersting gap like structure at the Fermi level is found at the centre of the cores of BSCCO which scales with the superconducting gap[25]. Then there exists the theoretical prediction that the vortex cores are magnetically ordered[26]. Recent neutron experiments on $La_{2-x}Sr_xCuO_4$ suggest that while at optimal doping individual vortices are associated with enhnaced low frequency antiferromagnetic fluctuations, the vortex state acquire static long-ranged antiferromagnetism in the underdoped sample[27]. In a very recent neutron experiment commensurate antiferromagnetic ordering has also been observed in $YBa_2Cu_3O_{6.5}$ (T_C=55K) (Ref. 28).

With these informations on the quasiparticles in the vortex cores of the HTSC materials, one can probably bring the analogy between the P-T diagram of ^{3}He and vortex matter phase diagram a bit closer. In an ordered vortex solid the quasi particles in the individual vortex core will act independently as the spins associated with individual ^{3}He do in ^{3}He solid. In the entangled disordered vortex state the qusiparticles are likely to be more correlated, and hence their contribution to the entropy is reduced.

We conclude that the vortex ordered solid-disordered solid transition line in YBCO is probably a first order transition line. Combing with the earlier results on high temperature low field melting line we suggest that the destruction of the ordered vortex state in YBCO takes place along a unified first-order transition line. The non-monotonic nature of this transition line suggests the existence of two Kauzmann points at around 75K and 50K. To explain the entropy crisis between this two Kauzmann points, sources for additional degrees of freedom are needed to be identified. Competition between elastic energy and pinning energy in the temperature region of interest and its consequence on the thermal contribution of entropy may be one such source. The other possibility related to the correlation between quasiparticles in the individual vortex cores is also discussed. From the experimental studies on both YBCO and BSSCO there is no indication as yet of the vortex solid-solid transition line ending in to a critical point, and in order to avoid further entropy crisis the slope of this first order transition line below 50K needs to be finite and reaching the zero value at T=0K only. In ^{3}He phase diagram the T=0 point is a Kauzmann point but without any entropy crisis since both the ordered and the disordered vortex phase have zero entropy at T=0 K. This need not necessarily be the case in the vortex matter of YBCO and BSSCO where in contrast with the ^{3}He the disordered phase has higher entropy at low temperatures, and this disordered phase will be relatively more susceptible to zero-point vibration at T=0 K.

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REFERENCES

[1] N. Avraham et al, Nature (in press).

[2] G. Blatter, Physica **C282-287** 19 (1997).

[3] R. Baierlein, Thermal Physics (Cambridge Univ. Press,1999) (and references therein).

[4] Y. Yeshurun, M. B. Salamon, K. V. Rao and H. S. Chen, Phys. Rev. Lett. **45**, 1366 (1980), Phys. Rev. **B24**, 1536 (1981).

[5] D. Giller et al, Phys. Rev. **B60** 106 (1999).

[6] Y. Radzyner et al, Phys. Rev. **B61** 14362 (2000).

[7] A. A. Zhukov et al, Phys. Rev. Lett. **87** 017006-1 (2001).

[8] S. B. Roy and P. Chaddah, Physica **C209** 70 (1997); J. Phys. :Condens. Matter **9** L625 (1997).

[9] S. B. Roy, P. Chaddah and S. Chaudhary, J. Phys.:Condens. Matter, **10** 4885 (1998), **10** 8327 (1998).

[10] S. B. Roy, P. Chaddah and L. E. DeLong, Physica **C304** 43 (1998) ; Physica **C308** 312 (1998).

[11] S. B. Roy, P. Chaddah and S. Chaudhary, Phys. Rev. **B62** 9191 (2000).

[12] G. Ravikumar et al, Physica **C322** 145 (1999).

[13] G. Ravikumar et al, Phys. Rev. **B61** 12490 (2000).

[14] Y. Radzyner et al, (unpublished).

[15] J. P. Rice and D. M. Ginsberg, J. Crystal Growth **109** 1 (1991).

[16] P. Chaddah et al, Phys. Rev. **B46** 11737 (1992).

[17] P. Chaddah and S. B. Roy, Phys. Rev. **B60** 11926 (1999), Pramana-J. Phys, **54** 857

(2000).

[18] D. Giller et al, Phys. Rev. Lett. **84** 3698 (2000).

[19] C. J. van der Beek et al, Phys. Rev. Lett. 84, 4196 (2000).

[20] P. G. Debenedetti and F. H. Stillinger, Nature **410** 259 (2001).

[21] D. J. Bishop, Nature **365** 394 (1993).

[22] C. Caroli, P. G. de Gennes and J. Matricon, Phys. Lett. **9** 307 (1964).

[23] H. F. Hess et al, Phys. Rev. Lett. **62** 214 (1989).

[24] I. Maggio-Aprile et al, Phys. Rev. Lett. **75** 2754 (1995).

[25] Ch. Renner et al, Phys. Rev. Lett. **80** 3606 (1998).

[26] D. P. Arovas et al, Phys. Rev. Lett. **79** 2871 (1997).

[27] B. Lake et al, Science **291** 832 (2001); cond-mat/0104026.

[28] Y. Sidis et al, Phys. Rev. Lett. **86** 4100 (2001).

FIGURES

FIG. 1. Magnetization loop with peak effect for the $YBa_2Cu_3O_{7-\delta}$ crystal at T=55K. Four characteristic fields B^+_{onset}, B^-_{onset}, B^+_{kink} and B^-_{kink} are identified and marked in the figure.

FIG. 2. Magnetic phase diagram for $YBa_2Cu_3O_{7-\delta}$ crystal showing B^+_{onset}(square), B^-_{onset}(circle), B^+_{kink} (triangle), B^-_{kink}(diamond) lines. As discussed in Ref.6 B^-_{kink}(T) line is the vortex solid-solid phase transition line B_{SS}(T). Also marked are the Kauzmann points (stars). Path marks the second field-cooling experimental protocol (see text for details).

FIG. 3. Magnetization loop (represented by diamonds) and zero field cooled minor hysteresis loops (MHLs) following the experimental protocol 1 (see text for details) at 70K. The MHLs were initiated by reversing the field cycling at 10 kOe (down triangles), 12 kOe (up triangles) and 15 kOe (circles).

FIG. 4. (a) Magnetization loop (represented by the solid line) and field cooled minor hysteresis loops (MHLs) following the experimental protocol 2 (see text for details) at 70 (K). The MHLs are obtained at various target fields both by lowering and raising field. (b) The overshooting of the FC MHLs beyond the complete magnetization loop (solid line) is highlighted while raising field at 8 kOe (open triangle) and 12 kOe(circle), and while lowering the field at 8 kOe (square) and 6 kOe(circle).

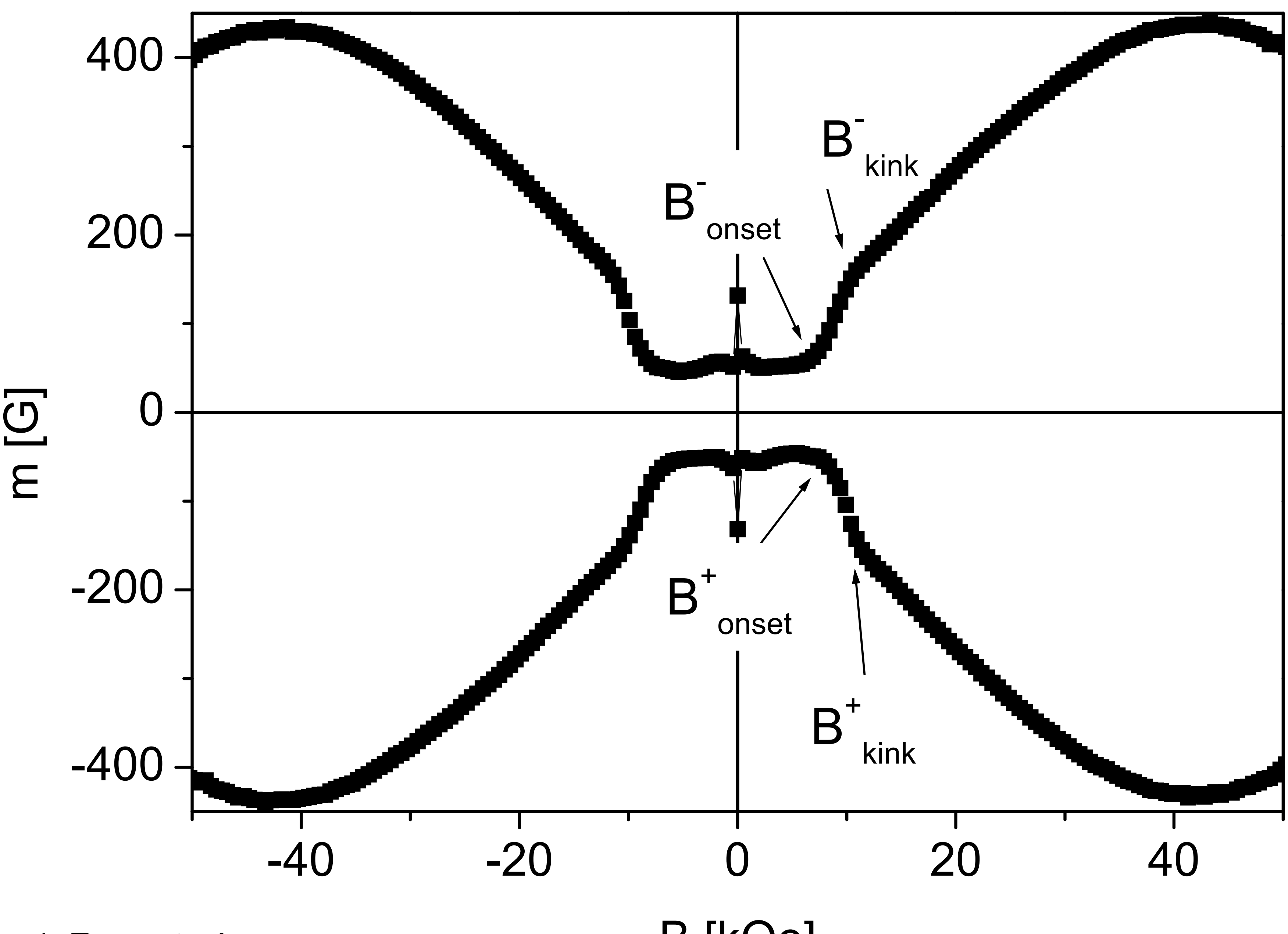
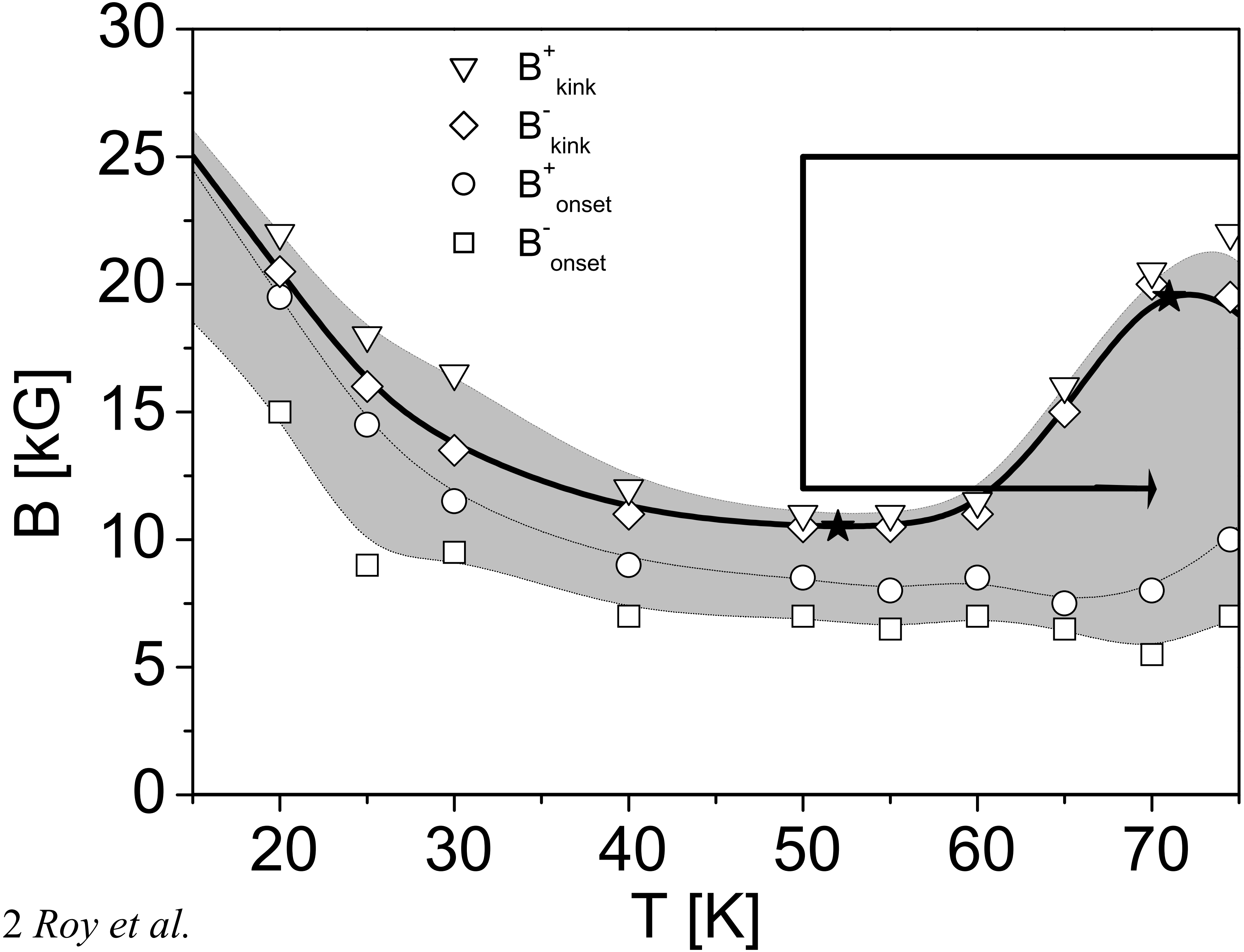


Fig. 1 *Roy et al.*



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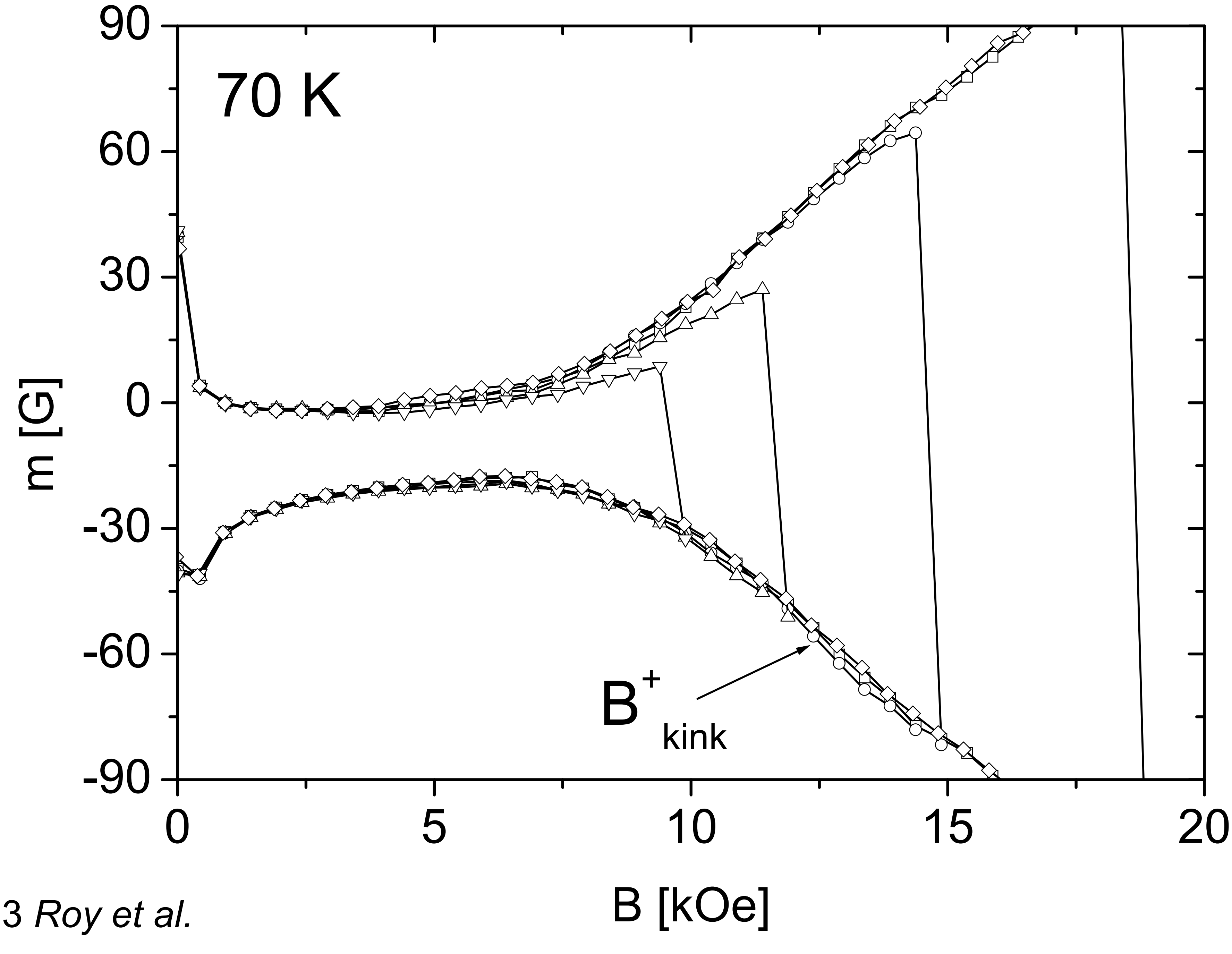

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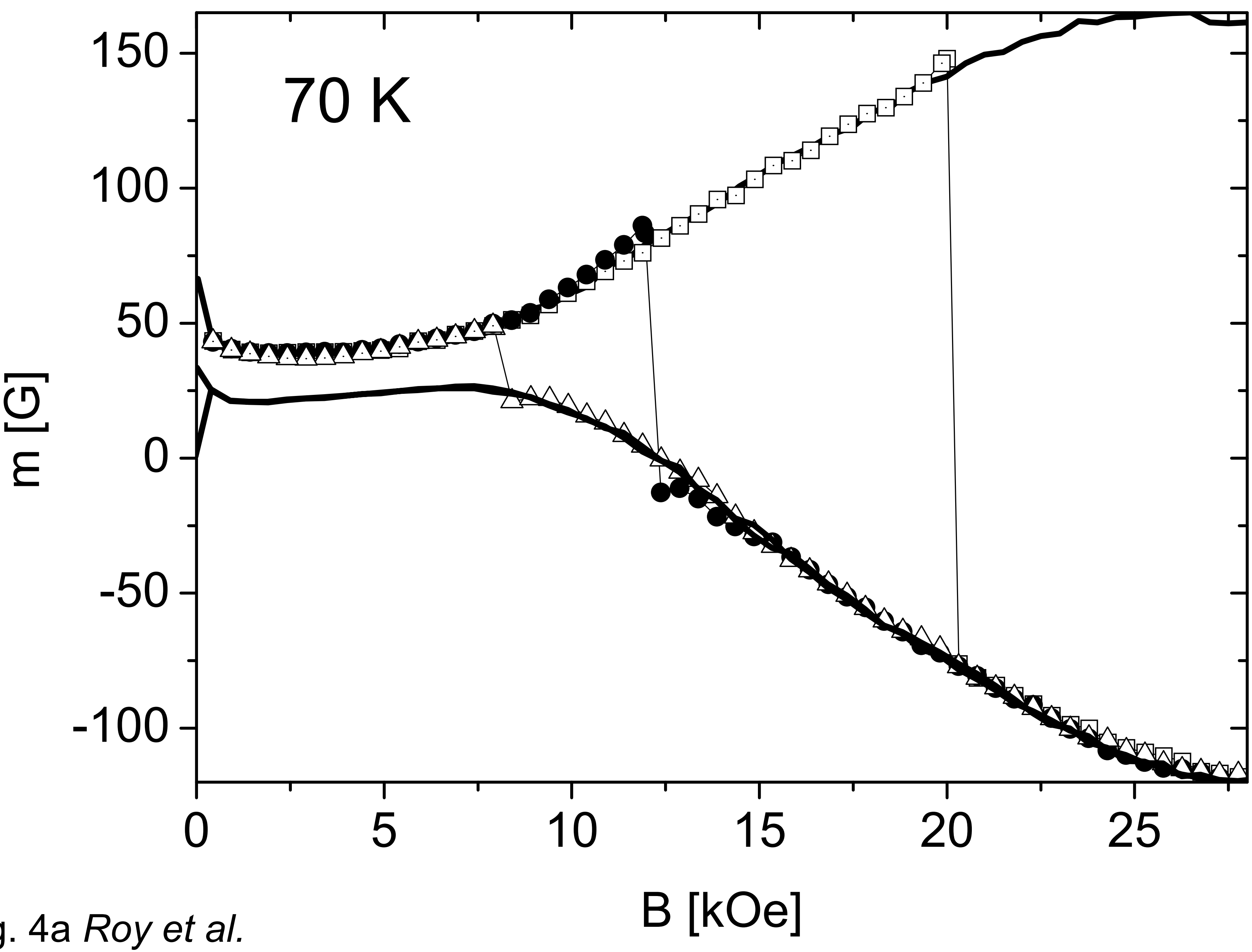

Fig. 4a *Roy et al.*

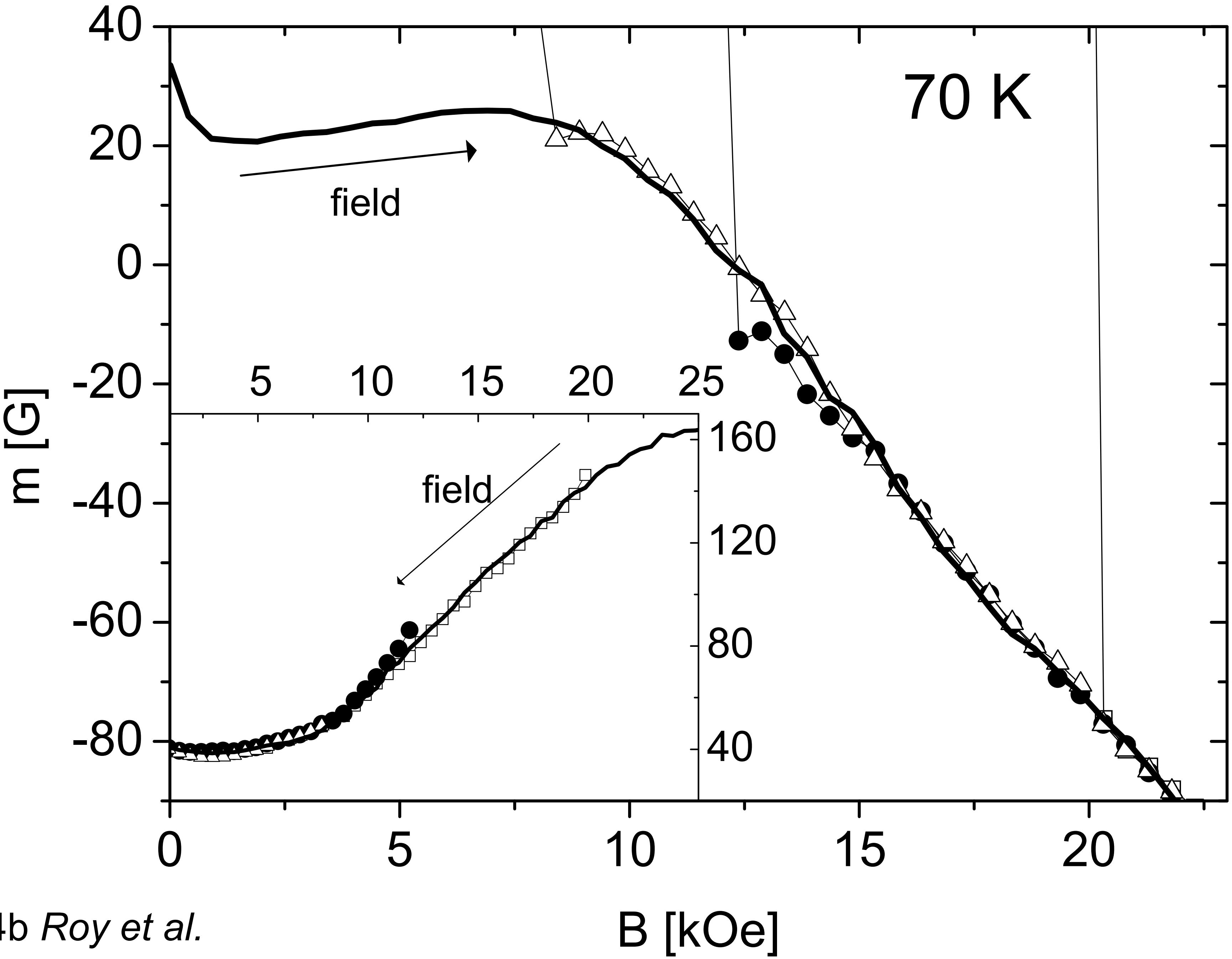

Fig. 4b *Roy et al.*