Reply to "Comment on 'Muon-spin-rotation study of the superconducting properties of Mo_3Sb_7' "

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Khasanov *et al.* [preceding Comment, Phys. Rev. B **82**, 016501 (2010)] have published a Comment aiming to show that our analysis with the assumption of two superconducting energy gaps in Mo_3Sb_7 [Tran *et al.*, Phys. Rev. B **78**, 172505 (2008); Acta Mater. **56**, 5694 (2008)] cannot be justified. Further, they have shown that our heat-capacity data can be accounted for using a single isotropic gap with a small amount of impurity but failed to mention the quantitative amount of the impurity. In this Reply, we address the key issues raised by Khasanov *et al.* in their Comment and show again with our analysis that our μSR data fit better with two energy gaps. Furthermore, our reanalysis of the heat-capacity data based on a single gap with the impurity term reveals that one needs 7.3% of the impurity to account for the low-temperature heat capacity, which is very high and has not been seen in our x-ray diffraction or electron probe micro-analyzer studies. We also discuss the point on the London model raised by Khasanov *et al.* Further, we present some experimental evidence that supports the two-gap model over the one-gap model.

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The Comment by Khasanov *et al.* on our paper "Muon-spin-rotation (μSR) studies of the superconducting properties of Mo_3Sb_7" recently published in Ref. 1 is twofold: first they argue that our μSR results are in contradiction with their μSR study published previously;[2] second they claim that the our heat-capacity result,[3] which was interpreted based on two-gap model can be fitted with a single gap. Both of their arguments are weak to completely rule out the possibility of two gaps as will be showing in the following discussion. By replying to their Comment, we would first like to point out to a confusion with any comparison of the two sets of the experimental data obtained at PSI and ISIS because these two sets of the data are not comparable due to many differences between them as well as in the differences in the samples quality used by both groups, and then we will address the issues raised by the authors. Finally, we will present some arguments of advantages of the two-gap model over the one gap.

In Fig. 1, we compare the relaxation rate σ_{sc}, data obtained by Khasanov *et al.*[2] and by us. It is clear that the relaxation rate obtained by Khasanov *et al.*[2] at 0.02 K should be larger than that of Tran *et al.* at 0.1 K (Ref. 1) but actually is even smaller than that of Tran *et al.* at 1 K. For a comparison at 40 mT between the two data sets at 0.02 K (Ref. 2) and 0.1 K (Ref. 1), the difference is about 30%. The doping effect was studied for numbers of superconductors, for instance, C doping in MgB_2 (Ref. 4) and Zn doping in YbaCuO.[5] In these cases, doping decreases both superconducting transition and also muon-spin relaxation rates. Therefore, in our opinion, there is no consistency between these data and the big difference between them makes the comparison difficult to derive solid conclusions. If there were no errors due to instrumental imperfections at ISIS and PSI, the big difference between two sets of data may be related to the different qualities or compositions of the measured specimens. The quality and composition of our polycrystalline sample were checked carefully using various techniques,[6] such as scanning electron microscopy image, energy dispersive x-ray (EDX) (Mo: 29.2 and Sb: 70.8 at.%), and powder x-ray diffraction. The lattice parameter of $a=0.9551(1)$ nm is in very good agreement with that previously reported by Dashjav *et al.* for a single crystal of Mo_3Sb_7 (0.9559 nm).[7] In contrast, the Mo_3Sb_7 single crystals investigated by Khasanov *et al.*, obtained from surface of Mo crucibles during a Sb-flux synthesis, have a lattice parameter $a=0.9582$ nm, which is more comparable to that of Ni-involved $Ni_{0.04}Mo_3Sb_7$ ($a=0.95734$ nm) reported by Soheilnia *et al.*[8] Moreover, the measurements at PSI were performed on the ensemble of single crystals, which were in fact have not been carefully characterized (at least the EDX analysis was not carried for each, separate crystals). Previously, the problem of quality of Mo_3Sb_7 single crystals was signaled by Dmitriev *et al.*[9] Good quality of the polycrystalline sample was also confirmed by higher superconducting transition 2.25 K,[6] compared to single crystals of 2.08 K.[10]

Let us address the key issues raised by Khasanov *et al.* in their Comment. *The magnetic field dependence of the* μSR depolarization rate σ_{sc}. In our opinion, the fit done by Khasanov *et al.* for our data (Fig. 1 of the Comment) using Eq. (2) in the Comment yielded larger errors compared to our fits using the modified London equation. Note that the muon relaxation rate $\sigma_s(H)$ does not depend only on the magnetic penetration depth $\lambda(H)$ but depends also on the coherence length $\xi(H)$. Therefore, the field dependence of $\sigma_s(H)$ is better modeled using the modified London model.

The modified London model. We should mention that London equation used by us in Ref. 1 is general case of Eq. (2) of Khasanov *et al.* given in the Comment. Moreover, the use of the Eq. (2) will require that the flux-line lattice is well ordered and it is triangular. There is no direct evidence of the triangular vortex lattice in Mo_3Sb_7 so the application of Eq. (2) by Khasanov for analysis equally needs justification as the use of the modified London equation by us.

Dependence of the inverse squared magnetic penetration

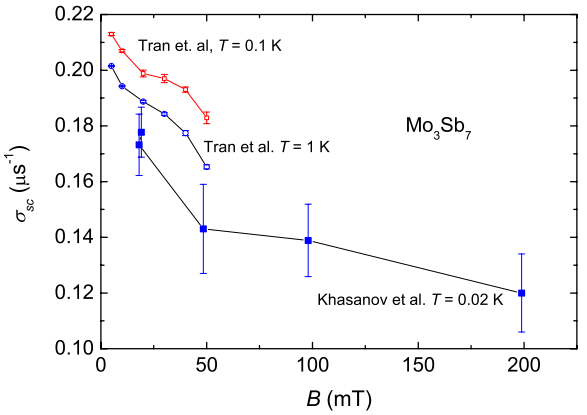

FIG. 1. (Color online) σ_{sc} vs applied magnetic fields. There is a big difference between data of Refs. 1 and 2.

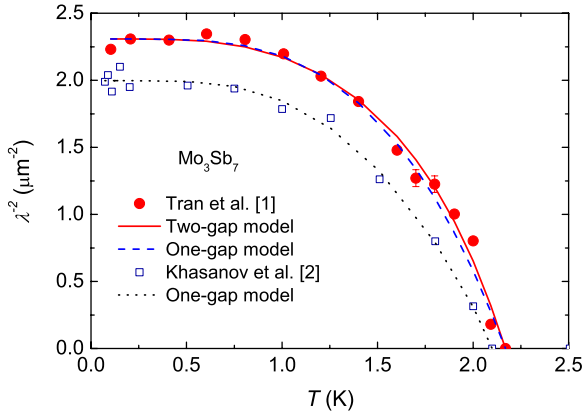

FIG. 2. (Color online) Magnetic penetration depth deduced from Ref. 1 (closed circles) and is compared to the data of Ref. 2 (open squares). The lines are fits based on the theoretical models. Due to the lack of H_{c2} data for $T<0.4$ K, the evaluated λ^{-2} should be taken with caution.

depth λ^{-2} on temperature. From the temperature dependence of the upper critical field H_{c2} (Fig. 7a of Ref. 3) and our muon data (Fig. 3 of Ref. 1), and using Eq. 2 of the Comment, one deduces λ^{-2} for our Mo_3Sb_7 sample denoted as closed circles. With a naked eye, the difference in the data deduced by us (closed circles) and the data obtained by Khasanov *et al.* (open squares) is pronounced (Fig. 2). While the data obtained by Khasanov *et al.* were perfectly followed by one-gap model, our data rather favored two-gap (solid line) models with error $\Sigma(\lambda^{-2}_{theo}-\lambda^{-2}_{exp})^2=0.015$, compared to one-gap model (dashed line) with an error of 0.02. In the fitting, values of the superconducting gaps were the free parameters.

Dependence of σ_{sc} on temperature. We agree that "the temperature dependence of σ_{sc} is not the same as the one of λ^{-2}." However, for a precise treatment of $\lambda^{-2}(T)$, one needs information on the field dependence of the upper critical field, $H_{c2}(T)$. Unfortunately, this information for Mo_3Sb_7 is lacking for $T<0.4$ K, thus evaluated λ^{-2} values are questionable. We note that the same author of the Comment has assumed the proportionality $\sigma_{sc}(T)\propto\lambda^{-2}(T)$ and has performed the muon analysis for $RbOs_2O_6$.[11] For two-gap superconductors, many authors have previously fitted the temperature dependence of $\sigma_{sc}(T)$, for instance, MgB_2,[12] and La_2C_3 and Y_2C_3,[13] $LaFeAs(O_{1-x}F_x)$.[14] In the same method as in the mentioned references, we have carried out analysis of our muon data of Mo_3Sb_7. In the fitting of one-gap model, we fixed the standard BCS-gap value for Mo_3Sb_7. As we have shown in our paper,[1] such a fitting gives a worse agreement between the theoretical and experimental data for comparison with that of the two-gap model.

The absolute value of λ. Our determination of the magnetic penetration depth from the muon data (665 nm) does agree remarkably with heat-capacity data (660 nm), which lead to an important observation that our data do not agree with that determined by Khasanov *et al.*[2] At present, the "accurate information" with the absolute value $\lambda=720$ nm given by Khasanov *et al.* in Ref. 2 has no support from other techniques yet. Please bear in mind that the error (±1) given by us, as indicated in our paper, was obtained from the fit so the total errors for the true λ value must be bigger. However, taking into account smaller errors of our experimental data compared to those of Ref. 2, the total error for the absolute λ value will not reach as high as value as 100 given by Khasanov *et al.*

Temperature dependence of the electronic specific heat. In order to explain our specific-heat data, the Khasanov *et al.* assumed the presence of a second nonsuperconducting band or small inclusions of metallic impurities with a "residual" electronic specific heat. The assumption of a second nonsuperconducting band for Mo_3Sb_7 should be supported by other measurements. In the case of metallic impurities, one considers some amount of free Mo metal since in the Mo-Sb phase diagram, except for Mo_3Sb_7 there are no more binary phases exist. For Mo_3Sb_7 at 0.37 K, the measured electronic specific heat is 4.65×10^{-4} J/mol K while the expected BCS value at this temperature is 1.1×10^{-4} J/mol K. Thus, expected contribution of some impurities at 0.37 K is $C_{el}=4.65\times10^{-4}-1.1\times10^{-4}=3.55\times10^{-4}$ J/mol K. Taking the coefficient of the electronic specific heat of Mo $\gamma_{Mo}=1.1\times10^{-3}$ J/mol_{Mo} K^2,[15] one estimates the amount of possible Mo impurity in the sample to be $3.55\times10^{-4}/(1.1\times10^{-3}\times0.37)=0.872$ mol/mol Mo_3Sb_7 or equals to 7.3% mass of the investigated sample. Such a big quantity of the impurity should have been already detected by our x-ray diffraction and EDX analysis possessing the detection limit better than 3% mass. Furthermore, the presence of any metallic impurity with >5% mass in the sample should have also bee seen in the measurements of the specific heat at high temperatures, electrical resistivity, magnetic susceptibility, inelastic neutron scattering, etc. We should add that our specific-heat data and that obtained by Candolfi *et al.*[16] are very similar and have shown the same deviation from the expected BCS theory for ordinary superconductors (Fig. 3).

Advantages of the two-gap model over the one-gap one. Advantages of using two-gap model for muon-spin rotation over one gap are not only by a better fit of the experimental muon data but are more as follows: (a) consistent with specific-heat data, where there are unusual temperature dependence of electronic specific heat and nonlinear field dependence of C_p/T.[3] (b) Consistent with the electronic band calculations for density state and Fermi surface, where there are two different bands originating from *d* and *sp* states, and

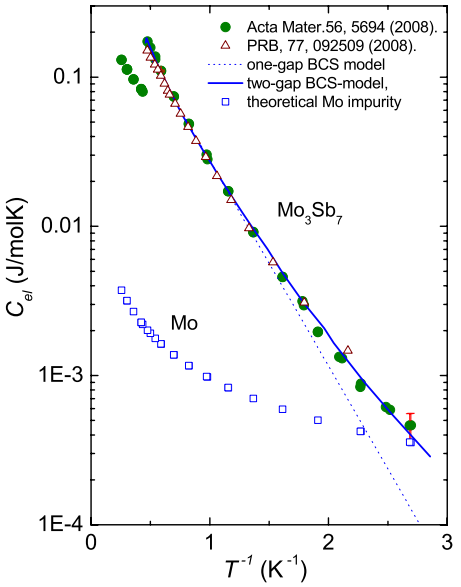

FIG. 3. (Color online) Electronic specific heat of Mo_3Sb_7, contribution of metallic Mo as proposed by Khasanov *et al.* (open squares). Open triangles are data from Ref. 16, showing the same deviation from BCS behavior.

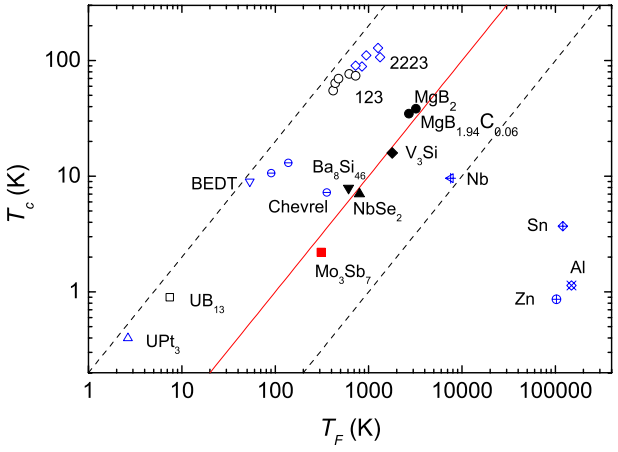

FIG. 4. (Color online) Uemura plot, T_c vs Fermi temperature T_F, for some selected superconductors including unconventional, isotropic *s*-wave (Ref. 21) and considered here Mo_3Sb_7. The dashed lines $T_c/T_F=0.2$ and 0.001 distinguish positions of unconventional superconductors from isotropic BCS superconductors with $T_c/T_F<0.001$. The solid line $T_c/T_F=0.01$ shows the possible positions of two-gap superconductors MgB_2, $MgB_{1.94}C_{0.06}$ (Ref. 4), $NbSe_2$ (Ref. 22), V_3Si (Ref. 23), Ba_8Si_{46} (Ref. 24), and Mo_3Sb_7.

anisotropic Fermi surface.[3,17] (c) The presence of superconducting band associated with the *d* electrons, that causes presumably enhanced effective masses of carriers $\sim 16m_e - 18m_e$. (d) The recent experiments of INS, muon-spin relaxation,[18] electron-tunneling spectroscopy,[19] and resistivity under pressure,[20] indicate the presence of spin-density wave ordering below 7 K, which interplays with the superconducting state. (e) Within the Uemura scheme,[21] the Fermi temperature is defined as $T_F=730\sigma^{3/4}\gamma^{-1/4}$, where T_F in K, σ in μs^{-1}, and γ in mJ K^{-2} cm^{-3}. The obtained ratio in this way $T_c/T_F=0.007$ for Mo_3Sb_7 indicates that the superconducting condensation mechanism in this system is different from that in *s*-wave superconductors (Al, Sn, Zn, Nb,…), for which $T_c/T_F<0.001$. Instead, the electron pairing mechanism in Mo_3Sb_7 would be closely related to those of two-gap superconductors MgB_2, $MgB_{1.94}C_{0.06}$,[4] $NbSe_2$,[22] V_3Si,[23] and Ba_8Si_{46},[24] with respect to the condensation energy since all of them lie on the same line $T_c/T_F=0.01$.

In conclusions, our point of view is that our μSR, specific-heat data, and Uemura plot analysis (Fig. 4), all *suggested possible two superconducting gaps* in Mo_3Sb_7. At this stage, the use of two-gap model has physical justification since it better describes our muon and specific-heat results and other data. Bearing in mind that the muon-spin-rotation technique is an indirect method for determining superconducting gaps, we would be more than happy to accept one-gap model than two-gap model if as soon as we will have new direct evidence for one-gap formation in Mo_3Sb_7, for instance, from angle-resolved photoemission spectroscopy measurements. The different muon data of our and of Khasanov *et al.*, in our opinion, could be due to different qualities and compositions of the studied samples.

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