Reviewers' comments :(if comments are not present please click on reviewer attachment link in EM):

Reviewer #1:

Interesting working shining new light on details of the structure of the tennantite and its low thermal conductivity. I recommend publication after minor revision:

1) More details in the discussion would help. For example provide numbers for the so-called low thermal conductivity and present a few comparisons.

2) Relate your calculation results (fitting and DFT) to experiments where possible, e.g. Debye/Einstein temperatures and phase transitions of tennantites.

3) What is meant with "inconsistent electronic densities"? That expression only shows up in the Abstract and Conclusions, not in the Results/Discussion part.

4) The manuscript needs a consistent clean up:

- polyhedra, not polyhedrons

- tetrahedrite, not tetrahedride

- Figure 1: lines too thin and numbers too small

- Ueq sometimes capitalized, sometimes not, sometimes in italics, sometimes not; Cu2 sometimes with subscript 2, sometimes with regular 2 etc.

Reviewer #2:

The manuscript (JSSC-20-1958) reports the structural distortions in Cu12As4S13 by analyzing anisotropic parameters from single crystal XRD and anharmonic vibration modes from Raman spectroscopy. The tennatite/tetrahedride groups have been extensively studied for local structures. Similar studies have thus ben published for the compounds with As and Sb as a coordination center. The disordered Cu atoms, their dynamics and their influence on physical properties of this family also have been well studied. In this work, the authors analyzed anisotropic displacement parameters from XRD data.

Dear Reviewer,

Thank you for your attention to the manuscript.

The tennatite/tetrahedride groups have much attention now and there are many studies have been published last five years. For example in work of … disscused nature of thermoelectric properties only for tetrahedrite and not for tennantite.

However, such discussion should be given when one solves and reports crystal structures of materials.

We report structural study early

Thus, discussions on it in this manuscript looks too shallow and do not provide useful new information to readers.

The tennantite structure was solved first time by Pauling in 1934 and since then no new information has been proposed. But new technologies and techniques make it possible to more accurately describe the structure and explain the emergence of new properties that have been not understood early.

Those on HAADF image and Raman spectroscopy data are similarly uninteresting.

HAADF был необходим, чтобы создать план для моделирования DFT и подтвердить или опровергнуть результаты маковицкого о заселенности. По его данным заселенность меди Cu2 и Cu21 должны быть более 1. Raman показывает, что имеют место быть низкоэнергетичкие моды, которые обычно возникают из-за решеточных мод. Сам факт наличия таких мод требует отдельного исследования, но в данной работе мы отмечаем, что наши структурные результаты(DFT и X-ray) действительно имеют место быть в структуре.

This manuscript needs more in depth discussions and new findings for the publication.

I belive a short overview above, additional прояснения сделанные в статье по просьбе других авторов gives a change to re-examinate the manuscript again.

Reviewer #3:

The paper of Yaroslavzev et al. deals with the synthetic analog of mineral tennantite, which is an interesting object because substituted compounds of the tennantite-tetrahedrite family have been widely investigated as thermoelectric materials and high thermoelectric figures-of-merit have been recorded. At the same time, the physical backgrounds underlying such promising properties are scarcely understood. This paper provides insights into the origin of appreciably low thermal conductivity on the basis of the temperature-dependent structural study, Raman spectroscopy, and DFT calculations. The paper fits well the scope and scientific level of JSSC and could be accepted; however, certain revision is necessary. My comments are given below.

Dear Reviewer,

Thank you that you find enough time to deal with others papers. Structural study происходило уже два раза в 30ых и 2000ых и в этих исследованиях устоялись понятия, которые используются сейчас, но которые несут другой смысл. Этот факт вызывает большую сложность для восприятия и я согласен с тем, что работу очень сложно воспринимать без контекста.

Our answers on your comments are given below.

1.The paper is very difficult to comprehend without careful examination of the previous paper of the same authors and/or older papers of Takabatake, Makovicky, and others on the crystal structure of the tennantite/tetrahedrite family.

Particularly,

(i) what are the Cu2 and Cu21 atoms?

>Если я правильно понимаю, то в DFT позиции Cu2(идеальная позиция) и Cu21(центр сдвинутой позиции из-за локального окружения) статические и в расчетах не подразумевается, что эти позиции могут быть >динамическими.  
Все верно. В DFT Сu21 как таковой нет, это сдвиг из Cu2.  
Добавить описание к текст

(ii) What are their positions and coordination?

Указать позиции при разных температурах и дать ссылку на suplemmentary

(iii) Is the full list of interatomic distances listed in Supplemental Materials?

Не понял вопрос

(iv) Is the sum of the Cu2 and Cu21 occupancy factors equal to unity?

(v) Were any atomic displacement parameters constrained upon the structure refinement?

Да. Детально о структуре мы обсуждали ранее. Текст из предыдущей статьи

This information is missing.

Brief of answers above added to the manuscript.

2.The same story is with the Laves polyhedron. Without reading other papers on this topic, it's not possible to imagine this polyhedron. Moreover, in Introduction it reads that copper is in the center of the Laves polyhedron, whereas in Results and Discussion, including Figure 6, sulfur centers those polyhedra. Please reconcile!

Thank your for careful reading. Text … was changed to …

3. The authors mix two different objects - polygons and polyhedra. There are "Laves polygons" in Highlights and "Laves polyhedra" in the main text. It looks like the term "polygon" is incorrect in this case.

Definitions were changed …

4. From Figure 3 it looks like the experimental data for Cu21 should be fitted using two Einstein temperatures. A kink near 150 K should appear then on the fitting curve. This might characterize anisotropic/anharmonic localized vibrations. Probably, the same is true for Cu2. Moreover, five experimental points for each atom may be not enough to make correct fits, especially when the systematic error is high as for Cu21.

That is good point to discussion. A short answer is We are working on detailed study of ADP. The main problem here that refinement не позволяет разделить две вещи:

* Electron phase transition
* тепловые колебания атома и разупорядоченность

As a solution of that структурный температурный эксперемент на краю полшщения меди может дать результат и нужно сказать о том, что ячейка не центросимметричная.   
Но стоит отметить, что цель данной работы было показать причины возникновения теплопроводности и особенности изменения ADP представляют дальнейший интерес для исследований.

Becoude of it we did HAADF to be sure

5. The following sentence is unclear (page 16): "The resulting complex charge distribution, and variances in the copper atom states, may, in turn, be the reason for complex exchange interactions and the reported antiferromagnetic ordering[9] in tennantite." Which copper atom states are meant? Atomic charges? Or oxidation states? Or atomic positions that alternate because of splitting? Please rephrase for better understanding!

6.The final statement of Conclusions tells that the authors "… have demonstrated a new method of the experimental study of a crystal structure and its Brillouin zone". However, I could not find any description of a single Brillouin zone in the text. Nor could I find a figure depicting the variation of bands with a k-vector (spaghetti diagrams).

Подправить заключение

7.The entire manuscript needs proofreading. At places, the English is awful. Here are just two short sentences as examples: "Neither XRD, nor TEM data shown defects." "A results of calculations are presented in Figure 5." Moreover, it looks like the text is a compilation of fragments written by different authors. In particular, the description of the DFT calculations results is written in a much better language.