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Comparative study of helimagnets MnSi and Cu_2OSeO_3 at high pressures

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The heat capacity of helical magnets Cu_2OSeO_3 and MnSi has been investigated at high pressures by the ac-calorimetric technique. Despite the differing nature of their magnetic moments, Cu_2OSeO_3 and MnSi demonstrate a surprising similarity in behavior of their magnetic and thermodynamic properties at the phase transition. Two characteristic features of the heat capacity at the phase transitions of both substances (peak and shoulder) behave also in a similar way at high pressures if analyzed as a function of temperature. This probably implies that the longitudinal spin fluctuations typical of weak itinerant magnets like MnSi contribute little to the phase transition. The shoulders of the heat capacity curves shrink with decreasing temperature suggesting that they arise from classical fluctuations. In the case of MnSi the sharp peak and shoulder at the heat capacity disappear simultaneously probably signifying the existence of a tricritical point and confirming the fluctuation nature of the first-order phase transition in MnSi as well as in Cu_2OSeO_3.

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I. INTRODUCTION

Manganese silicide (MnSi), a model itinerant helimagnet, crystallizes in a B20 structure, whose non-centro-symmetric space group $P2_13$ allows a helical (chiral) magnetic structure. The phase transition in MnSi from helical to paramagnetic states at ≈30 K reveals some remarkable features such as sharp peaks and shoulders on the high temperature side of the peaks in the heat capacity, thermal expansion, temperature dependence of resistivity, and sound absorption [1–7]. As is recognized now the sharp peaks in the above properties indicate a first-order nature of the phase transition, whereas the origin of the shoulders is still not quite clear [4–8]. There is some evidence that the shoulders arise from intense helical (chiral) fluctuations in the vicinity of the phase transition in MnSi [8–10]. These fluctuations must be responsible for the first-order phase transition in MnSi, symmetry of which principally allows a second-order one [11,12]. The simultaneous disappearance of the shoulder and first-order features at the phase transition in MnSi on decreasing temperature supports this conclusion [13].

Insulator Cu_2OSeO_3 crystallizes in a complicated structure, which belongs to the same space group $P2_13$ common to MnSi, and hence permits piezoelectricity [14]. On cooling below 60 K Cu_2OSeO_3 becomes magnetically ordered and demonstrates an enhanced magnetodielectric effect. The latter implies existence of the magnetoelectric coupling in the system. Careful structural studies of Cu_2OSeO_3 show no measurable structural distortion occurring down to 10 K. This means that there is no a spontaneous lattice distortion involved in the magnetoelectric coupling mechanism. So a pure electronic coupling should be responsible for the observed magnetodielectric response [14]. These observations predict an incommensurate magnetic structure [15]. Finally, a helical spin structure in Cu_2OSeO_3 was found in a small angle neutron scattering experiment [16]. But despite a similar spin structure, major differences between metallic MnSi and insulating Cu_2OSeO_3 lies in their magnetic moments. The moments are itinerant in MnSi and local in Cu_2OSeO_3. Nevertheless, the behavior of the heat capacity and magnetic susceptibility at the magnetic phase transitions in MnSi and Cu_2OSeO_3 appears to be very similar. Indeed, the heat capacity of Cu_2OSeO_3 shows a peak and shoulder on the high temperature side of the peak at the phase transition [16] like the heat capacity of MnSi.

Actually the difference in nature of the magnetic moments between the two substances noted above reveals itself in a pressure dependence of the phase transition temperature T_c. T_c of MnSi decreases with pressure and tends to zero, whereas T_c of Cu_2OSeO_3 increases with pressure at least up to 2 GPa [17].

It would be of great interest to track an evolution of the features of the phase transitions in both materials in the hope of shedding more light on its nature and the origin of the strongly fluctuating region (shoulder). The evolution of resistivity in the vicinity of the phase transition in MnSi with pressure was analyzed in Ref. [13].

Here we report results of a high pressure study of the heat capacity of MnSi and Cu_2OSeO_3 and the ac-magnetic susceptibility of Cu_2OSeO_3. The data obtained show different pressure but similar temperature dependencies of specific features of the phase transition, therefore confirming the classical character of the strongly fluctuating region and the fluctuation nature of the first-order transition in MnSi at ambient and moderate pressures.

II. EXPERIMENT

Single crystals of Cu_2OSeO_3 of size 0.5–1.0 mm were grown by a gas transport technique in a 610–550 °C temperature gradient using a 2:1 CuO/SeO_2 mixture and $CuCl_2{\cdot}2H_2O$ as a transport agent. High pressures were created in a small Teflon capsule filled with liquid and inserted in a miniature toroid-type clamped device [18]. Experiments with MnSi were performed with a cylinder-piston type clamped device. The specific heat $C(T)$ at high pressure was measured by the ac-calorimetry technique as described earlier [19]. For

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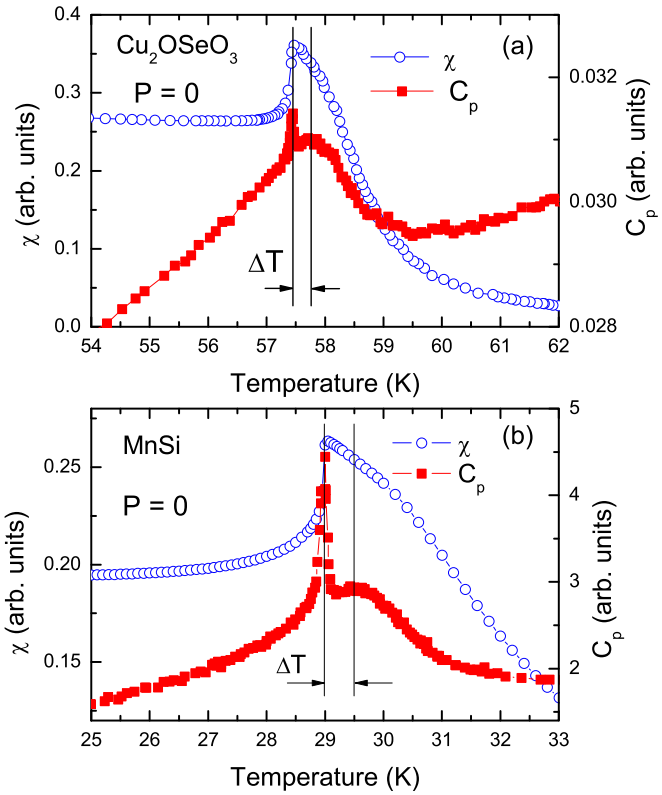

FIG. 1. (Color online) Heat capacity C_p and magnetic susceptibility χ of (a) Cu_2OSeO_3 and (b) MnSi at ambient pressure. ΔT is the temperature difference between the peaks indicated, a first-order phase transition and the maxima of the anomaly, stipulated by the strong helical fluctuations.

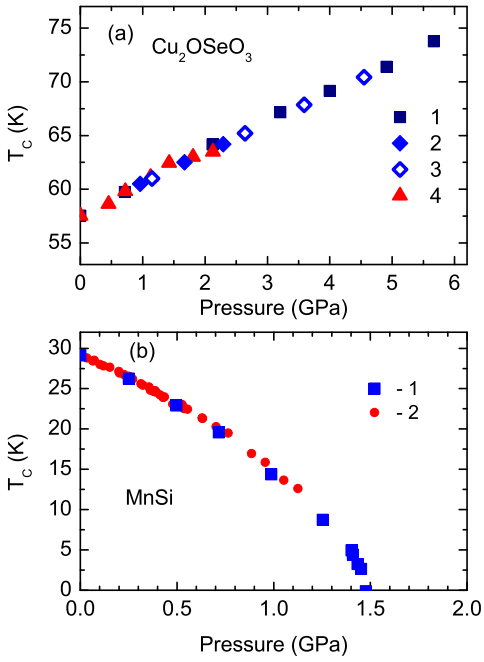

FIG. 2. (Color online) Pressure dependence of the magnetic phase transition temperature in Cu_2OSeO_3 (a) 1 ac susceptibility, 2 ac calorimetry, sample 1, 3 ac calorimetry, sample 2, 4 Ref. [17], and MnSi (b) 1 Ref. [21], 2 Ref. [22].

ac-calorimetry measurements a flat zigzag heater made of constantan wire of 12 μm in diameter was glued to one side of a platelike crystal ($\sim 0.8 \times 0.8 \times 0.15$ mm^3). This heater was at the same time a sensitive strain gauge and the change of its resistance under pressure allowed us to calculate the change in length and hence compressibility of the Cu_2OSeO_3 sample at room temperature as described earlier [20]. The coil system for magnetic ac-susceptibility measurements $\chi(T)$ was placed inside the Teflon capsule. Pressure was measured by monitoring the superconducting transition temperature of Pb located near the Cu_2OSeO_3 sample.

III. RESULTS

Figures 1(a) and 1(b) display the temperature dependence of the heat capacity and the magnetic susceptibility of Cu_2OSeO_3 and MnSi in the vicinity of the magnetic phase transition at ambient pressure. A striking similarity of physical properties of both substances is obvious.

Figure 2(a) shows the pressure dependence of the temperature of the phase transition T_c of Cu_2OSeO_3, determined from magnetic susceptibility (Fig. 3) and heat capacity (Fig. 4) measurements. As is seen in Fig. 2(a), T_c of Cu_2OSeO_3 increases continuously with pressure in contrast with the case of MnSi [Fig. 2(b)]. Our data on T_c of Cu_2OSeO_3 are in good agreement with that obtained earlier up to 2 GPa by Huang *et al.* [17]. Figures 4–7 show the evolution of the anomalous part of heat capacity of Cu_2OSeO_3 and MnSi with pressure and temperature.

The length of the sample of Cu_2OSeO_3 decreases linearly under pressure up to 4.5 GPa. The bulk modulus calculated from the change of the sample length is equal to 197 ± 2 GPa.

At this point to avoid confusion at the discussion of the experimental data and to be properly understood by potential readers we should shortly describe Figs. 1(a) and 1(b). As is seen at ambient pressure the heat capacity forms of Cu_2OSeO_3 and MnSi at the phase transition could be pictured as shallow maxima with sharp peaks (like a smeared out Δ-function)

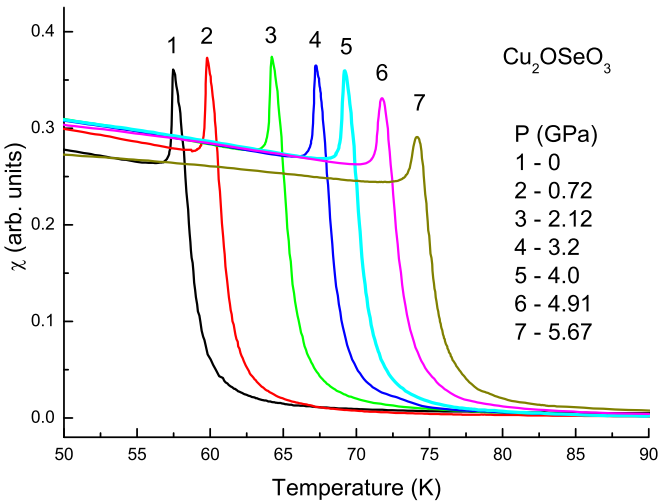

FIG. 3. (Color online) Magnetic susceptibility χ of Cu_2OSeO_3 at different pressures.

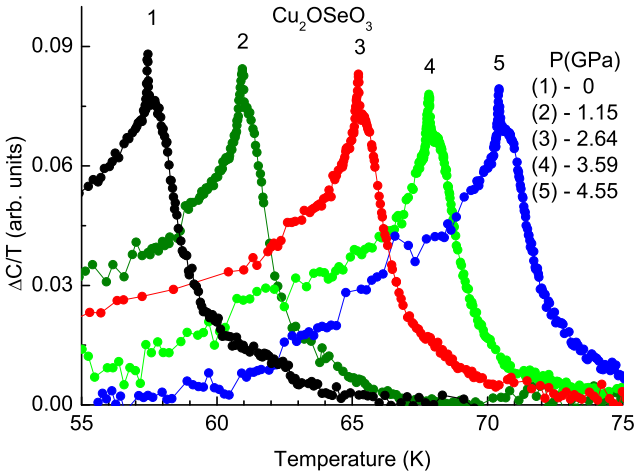

FIG. 4. (Color online) Anomalous part of the heat capacity of Cu_2OSeO_3 at different pressures.

on top of it. The sharp peaks shifted from the vertexes of the maxima, therefore forming shoulders at high temperature sides of the peaks.

The sharp peak corresponds to a weak first-order transition, which, as we will see in the case of MnSi, obviously disappears at high pressure and the sharp peak and the shoulder are replaced by a simple maximum. The latter is typical of a second-order transition. So the sharp peak and maximum should not be confused. Unfortunately a resolution of the heat capacity measurements at high pressure is not great, which probably could support the confusion. To prevent this, we included in the paper Fig. 8 showing behavior of the temperature derivative of resistivity of MnSi at the phase transition [13]. As is known the temperature derivative of resistivity at the phase transition and heat capacity can be perfectly scaled [4,5] (see Fig. 9). So the heat capacity data should be analyzed together with the resistivity behavior to get a clear picture of the situation.

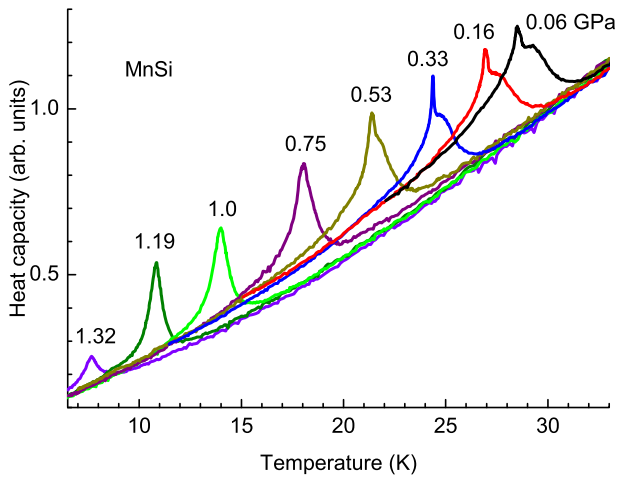

FIG. 5. (Color online) Heat capacity of MnSi at different pressures.

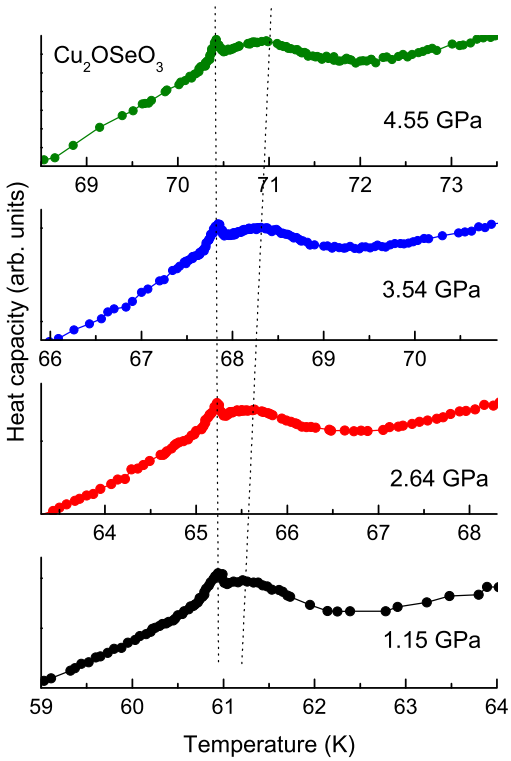

FIG. 6. (Color online) Illustration to determination of the temperature interval ΔT between the peak and the maximum of the shoulder for Cu_2OSeO_3. It is clearly seen that ΔT increases with temperature.

IV. DISCUSSION

The two substances under study belong to different classes of solids. Cu_2OSeO_3 is a covalent insulator with local magnetic moments, whereas metallic MnSi is an itinerant magnet. Normally the exchange interaction, giving rise to magnetic order in a system with local magnet moments, depends on interparticle distances in such a way that increases a phase transition temperature with pressure. This is what happens with T_c of Cu_2OSeO_3 with applied pressure [see Fig. 2(a)]. In the case of itinerant magnetics an energy gain occurring at magnetic ordering arises as a result of competition between the exchange interaction and electron kinetic energy. Their changes on compression lead to a decrease of the transition temperature in itinerant magnets with pressure [see Fig. 2(b)]. Despite the mentioned difference both substances demonstrate a surprising similarity in behavior of magnetic and thermodynamic properties at the phase transition [Figs. 1(a) and 1(b)]. Probably this implies that the longitudinal spin fluctuations typical of the weak itinerant magnets do not contribute much to the discussed properties.

Remarkably the similarity between Cu_2OSeO_3 and MnSi found at ambient pressure can be seen at high pressures as well, if one uses temperature as a variable. Indeed, analyzing Figs. 4 and 5, which depict the behavior of the anomalous part of heat capacity of Cu_2OSeO_3 and the heat capacity of MnSi at different pressures and temperatures, one can see that the heat capacity peaks and shoulders clearly change at decreasing temperature. The shoulder becomes less and less

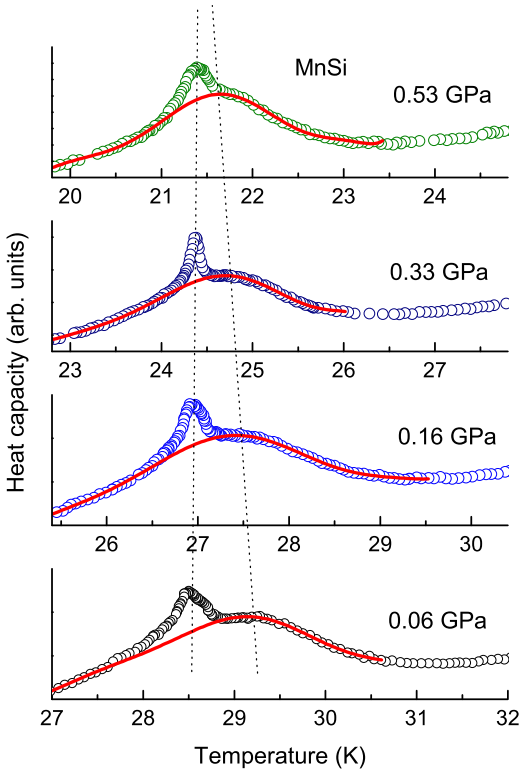

FIG. 7. (Color online) Illustration to determination of the temperature interval ΔT between the peak and the maximum of the shoulder for MnSi. Again ΔT increase with temperature, like in the case of Cu_2OSeO_3.

prominent and completely disappeared in the case of MnSi (see also Figs. 6 and 7). This conclusion is obviously supported by resistivity measurements [13] (Fig. 8). A variation of the temperature interval ΔT between the peak and the maximum of the shoulder may serve as some sort of semiquantitative measure of this process as illustrated in Figs. 1 and 10. Taking into account these data, tentative phase diagrams of Cu_2OSeO_3 and MnSi were constructed in Fig. 11. As can be seen, the splitting of the two characteristic features of the heat capacity curve (peak and shoulder) decreases along the phase transition line towards lower temperatures, irrespective of the different

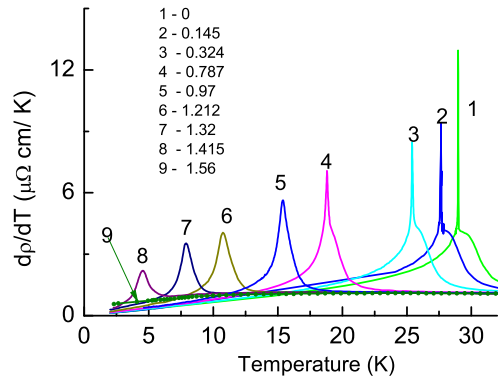

FIG. 8. (Color online) Temperature derivatives of the resistivity $d\rho/dT$ at the phase transition in MnSi at different pressures after Ref. [13].

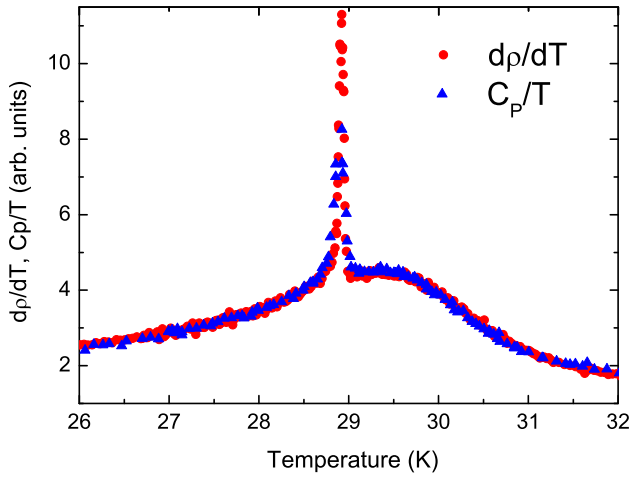

FIG. 9. (Color online) Reduced temperature dependence of the heat capacity and the temperature derivative of resistivity for MnSi [5].

pressure dependence. Narrowing the splitting is a consequence of shrinking the heat capacity anomaly (shoulder) along with the transition temperature reduction. All this helps to identify the shoulder as a product of classical fluctuations. At the same time, in the case of MnSi, the sharp peaks, which classify the transition as first order, cease to exist at low temperatures

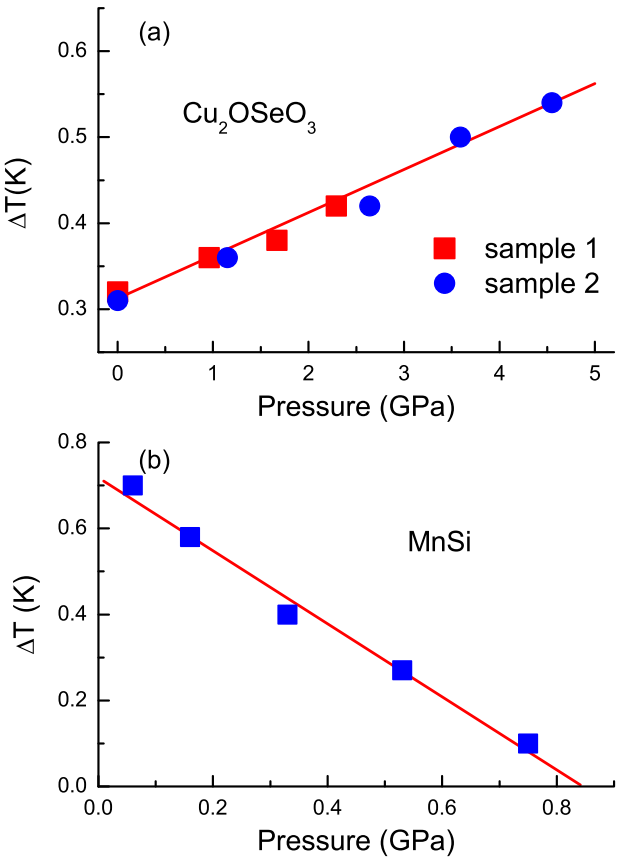

FIG. 10. (Color online) Temperature difference ΔT between the peaks and the shoulder maxima as a function of pressure.

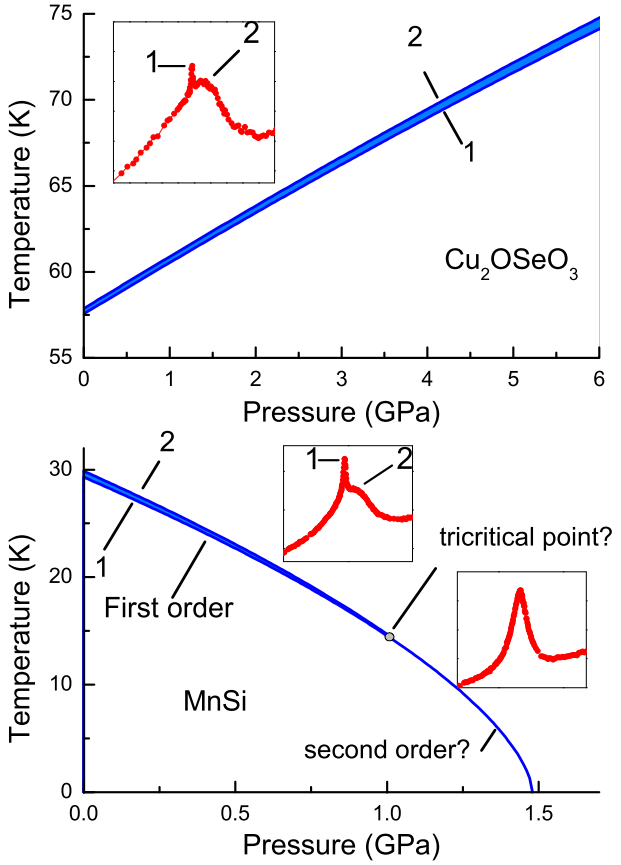

FIG. 11. (Color online) Tentative phase diagrams of Cu_2OSeO_3 and MnSi. Note that as one may expect the transition line of Cu_2OSeO_3 would approach zero temperature under negative pressure, which could be created by a suitable doping. Then the phase diagram of Cu_2OSeO_3 would look as a mirror reflection of the corresponding one of MnSi.

almost simultaneously with the disappearance of the shoulder. Then with further decrease of temperature the heat capacity maxima are progressively reduced in size and width (Fig. 5). This behavior leads us to claim the existence of a tricritical point in the phase diagram of MnSi, as is shown in Fig. 11, in agreement with conclusions of Ref. [13].

V. CONCLUSION

The heat capacity of helical magnets Cu_2OSeO_3 and MnSi has been studied at high pressures by the ac-calorimetric technique. The magnetic ac susceptibility was measured in the vicinity of the magnetic phase transition in Cu_2OSeO_3. The helical phase transition temperature T_c increases with pressure in the case of Cu_2OSeO_3, which is typical of systems with local magnetic moments, whereas T_c of MnSi drops on compression in accordance with standard behavior observed in itinerant magnets. The variation of two characteristic features of the heat capacity at the phase transitions of both substances (peak and shoulder) were investigated at high pressures. Despite the different nature of the magnetic moments in Cu_2OSeO_3 and MnSi these features behave in a similar way when studied as a function of temperature. So probably the longitudinal spin fluctuations can be ignored in an analysis of the phase transition in MnSi.

The shoulders shrink with decreasing temperature, which suggests that they arise from classical fluctuations. In the case of MnSi the peak and shoulder of the heat capacity disappear simultaneously probably signifying the existence of a tricritical point and confirming the fluctuation nature of the first-order phase transition in Cu_2OSeO_3 and MnSi.

ACKNOWLEDGMENTS

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