Specific heat of the antiferromagnetic garnet Ca$_3$Mn$_2$Ge$_3$O$_{12}$

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The specific heat of the garnet Ca$_3$[Mn$_2^{3+}$]Ge$_3$O$_{12}$ is investigated in the 2–26°K temperature range and in the magnetic fields up to 40 kOe. The Néel point is determined from specific-heat measurements (T_N = 13.85 ± 0.05 °K). Data on the magnetic entropy and spin state of the Mn^{3+} ion are obtained. The exchange interaction parameter is calculated in the molecular-field approximation. It is shown that the best approximation for the garnet under investigation is apparently the model of inequivalent neighbors in a Heisenberg antiferromagnet. It is found from specific-heat measurements in strong magnetic fields ($H > 5$ kOe) that an additional strong maximum appears near T_N in the specific-heat dependence C_H (T). This behavior of the specific heat is ascribed to peculiarities in the phase diagram of the Ca$_3$Mn$_2$Ge$_3$O$_{12}$ garnet and of its magnetic structure.

INTRODUCTION

Several garnets with 3d ions forming a single octahedral sublattice have been synthesized recently.[1] Measurements of the magnetic properties [1,2] and specific heat, [3] and neutron-diffraction investigations [4-6] have demonstrated that at helium temperatures most of these compounds are antiferromagnetic. The garnet Ca$_3$[Mn$_2^{3+}$] Ge$_3$O$_{12}$, whose magnetic structure is shown in Fig. 1, has been found to exhibit unusual magnetization isotherms (at T < T$_N$): [1] beginning from a critical field which depends on the temperature, the magnetization rises sharply and then continues to increase approximately linearly with the applied magnetic field without showing any saturation up to 60 kOe.

It has been suggested that this behavior of the manganese garnet is due to a metamagnetic transition in strong magnetic fields. However, the information on the magnetism of this garnet is very limited because it has not yet been possible to synthesize single crystals of Ca$_3$Mn$_2$Ge$_3$O$_{12}$. The pupose of our investigation was to obtain information on the special features of the paramagnetic-antiferromagnetic phase transition in Ca$_3$Mn$_2$Ge$_3$O$_{12}$ garnet by measuring the specific heat in the absence and in the presence of a magnetic field.

EXPERIMENTAL INVESTIGATION

A sample of Ca$_3$Mn$_2$Ge$_3$O$_{12}$ was prepared at 1170°C in the form of a polycrystalline ceramic, which was compacted into pellets of 12 mm in diameter and h = 3 mm thick. The phase composition was checked by x-ray diffraction. There were no impurity lines in the diffraction patterns of the investigated samples.

The specific heat was measured using a vacuum calorimeter. We took 12-13 garnet pellets and smeared them with a thin layer of vacuum grease. We place them in a cylinder which was sealed hermetically with a small amount of heat-exchange medium (helum) in a copper calorimeter. The weight of the investigated material was about 12.5 g. A Manganin heater (R$_{4.2°K}$ = 410Ω) was
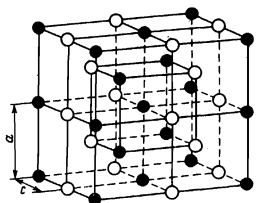

FIG. 1. Magnetic structure of the garnet Ca$_3$Mn$_2$Ge$_3$O$_{12}$ based on the Plumier data. [14] The black and open circles represent oppositely directed magnetic moments of Mn^{3+}.

wound bifilarly on the calorimeter. An Allen-Bradley carbon resistor (1/8 W, R$_{300°K}$ = 50Ω) was attached to the lower end of the calorimeter. The temperature was deduced from the Clement-Quinnell formula: [7]

$$1/T = A / \log R + B + C \log R, \qquad (1)$$

where the numerical constants A, B, and C were found by calibrating the thermometer relative to the vapor pressue of liquid hydrogen (14.3-20.3°K) and liquid helium (2-4.2°K) in magnetic fields 0-40 kOe.

The calorimeter containing the sample was centered by three quartz beads and suspended by a nylon filament inside a vacuum jacket whose lower part was filled with activated carbon. The calorimter was cooled using a mechanical heat switch, similar to that described by Kostryukova. [8]

When measurements were made in an external magnetic field the whole device was placed inside a superconducting solenoid which generated magnetic fields up to 50 kOe and these fields were axially homogeneous to within 2% along the length of the sample. The instability of the field during an experiment did not exceed 1% of the set value. The demagnetization factor of our sample was N ≈ 0.75. Therefore, the demagnetizing field did not exceed 50 Oe throughout the investigaed temperature range and it was ignored in our results.

The power consumption in the heater was calculated from the current in its circuit and the resistance. The temperature dependence of the resistance was determined in the absence and presence of a magnetic field in a series of preliminary measurements. The heating time was determined with a digital electronic counter which produced a triggering pulse that connected the heater to the power source. The duration of heating was determined to within 0.1% for the usual periods of ~100 sec.

The specific heat was determined in the temperature range 2-26°K from the heating curves, which were recorded employing a potentiometric circuit and an F128/1 photoamplifier. The results obtained were corrected for the specific heat of the sample and the correction amounted to 1.4% at 20°K and to 0.03% at 5°K. The error in the determination of the specific heat was 1.5% at T = 4.0°K at ~4% at T = 20°K.

RESULTS AND DISCUSSION

At low temperatures the investigated garnet was a magnetic insulator so that its specific heat was

$$C = C_{lat} + C_{mag} + C_{nucl}.$$

The last term was mainly due to the dipole-dipole interaction between the electron and nuclear magnetic moments of the Mn^{3+} ions. Our estimates indicated that the contribution of the nuclear component at $T > 2°K$ did not exceed 0.05% of C.

The lattice specific heat C_{lat} was determined from measurements of the temperature dependence of the specific heat of the garnet $NaCa_2Zn_2V_3O_{12}$, whose octahedral sublattice consisted of diamagnetic zinc ions. We found that the specific heat of this garnet varied as BT^3 in the 5-25°K temperature range and the coefficient of proportionality was $B = 3.7 \times 10^{-4}$. Allowing for the experimental error, we deduced that the Debye temperature of this garnet was $\Theta = 500 \pm 20°K$. We assumed, in accordance with [9], that $\Theta \propto M^{-1/2}$, where M is the molecular weight of the garnet and we thus found that the Debye temperature of $Ca_3Mn_2Ge_3O_{12}$ was $\Theta = 480 \pm 20°K$.

According to our measurements, the lattice specific heat at 20°K was ~50% of the magnetic specific heat C_{mag} and at $T < 5°K$ it was about 1%. The temperature dependence of C_{lat} is represented by the continuous curve in Fig. 2a. The circles in Fig. 2a are the results of measurements of the total specific heat of the manganese garnet in the absence of a magnetic field. The λ anomaly at $T = 13.85 \pm 0.05°K$ corresponds to antiferromagnetic ordering. This is in agreement with the results of susceptibility measurements, which give the Néel temperature of $Ca_3Mn_2Ge_3O_{12}$ as $T_N = 13.0°K$. [1]

Figure 2b shows the temperature dependence of the magnetic entropy found by integrating the experimental data for C_{mag}/T in the range 2-26°K. The total change in the magnetic entropy $\Delta S = S_\infty - S_0^0$ was found by extrapolating to 0-2°K on the basis of $C \propto T^3$, predicted for the specific heat of antiferromagnets at $T \ll T_N$ on the basis of the theory of spin waves without allowance for the anisotropy field. The specific heat at $T > 26°K$ was calculated from the law bT^{-2}, [10] which was satisfied to within $\approx 2\%$ by our results in the 21-26°K range. In this way, we found the total change in the magnetic entropy (per one Mn^{3+} ion) which was $\Delta S = S_\infty - S_0 = 1.63R$, in good agreement with the theoretical value $\ln(2s + 1)R = 1.61R$ for the spin $s = 2$ (R is the universal gas constant).

The contributions to the entropy at temperatures above and below T_N were

$$\frac{S_\infty - S_N}{R} = 0.51, \quad \frac{S_N - S_0}{R} = 1.12.$$

A theoretical calculation based on the Heisenberg model of equivalent neighbors in a body-centered lattice (s = 1/2) gave $(S_\infty - S_N)/R = 0.235$. [11] Since, according to Fisher, [12] this value should vary linearly with $1/s(s + 1)$, the interpolation for $s = 2$ gave $(S_\infty - S_N)/R \approx 0.33$.

The difference between the experimental and theoretical values of $(S_\infty - S_N)/R$ decreased considerably if we assumed that the number of interacting neighbors in $Ca_3Mn_2Ge_3O_{12}$ was q = 6. The justification for this assumption was the magnetic structure of the investigated garnet. It is clear from Fig. 1 that the magnetic configuration of the garnet consists of ferromagnetic chains along one of the cubic axes ([001]) and the directions of the spins are reversed on translation along [100] and [010]. According to Smart, [13] such antiferromagnetic ordering (of the third kind) can arise only as a result of a tetragonal distortion of a body-centered lattice. Clearly,
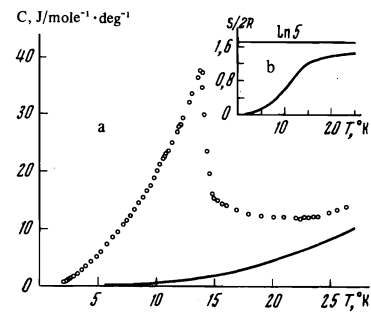

FIG. 2. a) Temperature dependence of the specific heat of $Ca_3Mn_2Ge_3O_{12}$ in $H = 0$: the points represent the experimental values and the continuous curve is the lattice specific heat calculated from the data for the garnet $NaCa_2Zn_2V_3O_{12}$. b) Temperature dependence of the entropy of $Ca_3Mn_2Ge_3O_{12}$.

in the case of $Ca_3Mn_2Ge_3O_{12}$ this distortion is due to the Jahn-Teller effect, which is predicted by the theory of the crystal field for octahedral complexes with Mn^{3+} ions. [14] The first manifestation of this effect for Mn^{3+} in garnets was established experimentally by Gyorgy et al. [15] on the basis of large changes in the acoustic and magnetostrictive properties of yttrium iron garnet on introduction of the Mn^{3+} ions.

We shall now consider exchange interactions in a body-centered tetragonal lattice and assume that c > a (Fig. 1). Each atom then has eight neighbors at the corners of a rectangular parallelepiped (the corresponding exchange interaction parameter is J_1), four neighbors along the [100] and [010] axes (J_2), and two neighbors along the [001] axis (J_3). A molecular field analysis shows [13] that in the case of an antiferromagnetic structure formed by ferromagnetic chains along the c axis the temperature of the antiferromagnetic transition is described by the following combination of the exchange interaction parameters:

$$T_N = \frac{2s(s+1)}{3k}(-4J_2 + 2J_3), \qquad (2)$$

where s is the spin and k the Boltzmann constant.

A special feature of the structure considered here is that J_1 (the interaction of the nearest neighbors in a body-centered lattice) makes no contribution to T_N and the main contribution comes from six second-nearest neighbors; moreover, $J_2 < 0$ and $J_3 > 0$. Therefore, we may assume that the garnet $Ca_3Mn_2Ge_3O_{12}$ is best described by the model of inequivalent nearest neighbors proposed by Wood and Dalton [16] for a Heisenberg antiferromagnet. A calculation of the value of $(S_\infty - S_N)/R$, in accordance with this model, improves the agreement with the experimental values.

We assumed the Heisenberg exchange interaction for $Ca_3Mn_2Ge_3O_{12}$ and used the specific heat results to estimate the exchange interaction parameter $\bar{J}_2$ representing the average interaction of the second-nearest neighbors in a fictitious bcc lattice, i.e., $\bar{J}_2 = (1/6)(-4J_2 + 2J_3)$. We could then ignore the contribution of the dipole-dipole interactions. In fact, an order-of-magnitude estimate gives $C_{dip}T^2/R \approx 10^{-2}$. This is much smaller than the measured specific heat C_{mag} in the temperature range were $C_{mag}T^2 = $ const. Our value is $C_{mag}T^2/R = 180.4$ and, therefore, we may assume that at $T \gg T_N$ the main contribution to the magnetic specific heat is made by the exchange interaction so that, following Van Vleck, [10] we find that

$$\frac{C_{mag}T^2}{R} = \frac{C_{exch}T^2}{R} = \frac{2}{3}qs^2(s+1)^2\left(\frac{J_2}{k}\right)^2. \qquad (3)$$

In the molecular field approximation the magnetic energy of an antiferromagnet is given by: [17]

$$\frac{E}{R} = qs^2\left(1+\frac{\gamma}{qS}\right)\left|\frac{J_2}{k}\right|, \qquad (4)$$

where the factor γ depends on the crystal structure and is 0.6 for a bcc lattice. [17] We calculated the magnetic energy from the experimental data.

$$\Delta E = \int_{T_1}^{T_2} C_{mag}\, dT,$$

using extrapolation in accordance with the same laws as in the case of entropy.

The relationship between the exchange interaction parameter and the value of T_N was given by the empirical formula of Rushbrooke and Wood: [18]

$$kT_N = \frac{5}{96}(q-1)[11s(s+1)-1]\left[1+\frac{2}{3qs(s+1)}\right]|J_2|. \qquad (5)$$

The quantities $\mathcal{J} = |J_2/k|$ were calculated by three methods for q = 6 and it was found that
according to Eq. (3): $C_{mag}T^2/R = 180.4$, $\mathcal{J} = 1.1°K$;
according to Eq. (4): $E/R = 23.42$, $\mathcal{J} = 0.89°K$;
according to Eq. (5): $T_N = 13.85°K$, $\mathcal{J} = 0.82°K$.

The greatest error was obviously made in the calculations of $C_{mag}T^2$ because in the range of temperatures under investigation (up to 26°K) the condition $T \gg T_N$ was not satisfied very well and this was the condition for which $C_{mag}T^2$ = const; the values of $\mathcal{J}$ determined from E/R and T_N were in agreement to within 10%.

Figure 3 gives the results of measurements of the specific heat of $Ca_3Mn_2Ge_3O_{12}$ in the absence of a magnetic field and in fields of 5-40 kOe. Some of the experi-

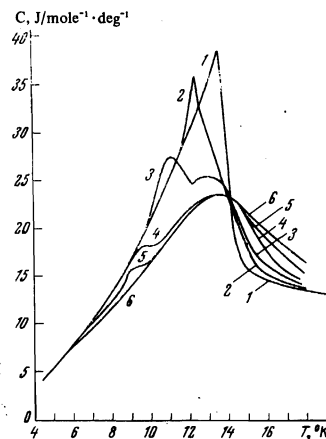FIG. 3. Specific heat of the garnet $Ca_3Mn_2Ge_3O_{12}$ in magnetic fields: 1) H = 0; 2) H = 5 kOe; 3) H = 10 kOe; 4) H = 20 kOe; 5) H = 30 kOe; 6) H = 40 kOe.
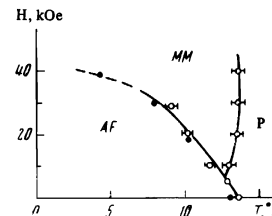
FIG' 4. Phase diagram of $Ca_3Mn_2Ge_3O_{12}$: ●) results of magnetic measurements reported in [1]; O) our results.

mental values of the specific heat used in plotting the curves in Fig. 3 are also listed in Table I. It is evident from Fig. 3 that in a field H = 5 kOe the sharp peak corresponding to the antiferromagnetic ordering shifted, as predicted by the theory of antiferromagnetism, in the direction of lower temperatures and its amplitude decreased compared with that in H = 0. In a field of 10 kOe we observed not only the antiferromagnetic maximum, which shifted over to the left and became broader, but also (on the right of this maximum) a wide hump which was evidently due to the appearance of a new magnetic-field-induced structure in $Ca_3Mn_2Ge_3O_{12}$. Bearing in mind the nature of the isotherms of the magnetization of

TABLE I. Specific heat of garnet $Ca_3 Mn_2 Ge_3 O_{12}$

T, °K	C, J/mole·deg	T, °K	C, J/mole·deg	T, °K	C, J/mole·deg	T, °K	C, J/mole·deg	T, °K	C, J/mole·deg	T, °K	C, J/mole·deg	T, °K	C, J/mole·deg
H = 0													
2.115	0.695	5.845	7.37	9.302	17.1	13.08	33.6	14.81	16.0	23.16	12.2		
2.452	1.10	6.412	8.89	9.698	18.8	13.70	36.5	15.27	15.1	23.85	12.2		
2.927	1.72	6.951	10.1	10.111	20.2	13.75	37.6	16.08	14.3	24.88	12.9		
3.650	2.75	7.396	11.4	10.688	22.3	13.92	37.4	16.91	13.5	25.49	13.5		
3.960	3.40	7.732	12.1	11.344	25.0	13.94	34.6	17.54	12.7	26.36	13.9		
4.409	4.13	8.166	13.4	11.944	27.9	14.12	32.00	20.04	12.2				
4.857	5.04	8.531	14.3	12.300	29.3	14.37	23.7	20.93	12.2				
5.438	6.37	8.810	15.5	12.855	32.3	14.55	19.6	22.04	12·0				
H = 5 kOe													
4.506	4.30	7.237	10.7	10.22	20.2	12.42	32.5	13.80	26.3	16.40	14.4		
4.911	5.15	7.859	12.2	10.77	22.6	12.62	35.0	14.04	25.5	17.41	13.4		
5.278	6.01	8.563	14.5	11.36	25.0	12.87	32.6	14.26	23.2	17.97	12.7		
5.768	7.27	8.942	15.5	11.81	27.0	13.01	31.2	14.96	19.8				
6.299	8.59	9.566	17.4	12.05	28.1	13.38	28.8	15.44	16.1				
6.761	9.46	9.894	19.0	12.25	31.7	13.61	27.6	15.94	14.8				
H = 10 kOe													
4.511	4.35	6.472	8.87	9.762	18.4	11.40	27 2	12.91	25.1	16.00	16.25		
4.824	4.96	7.170	10.4	10.03	20.2	11.63	27 1	13.42	25.1	16.52	15.0		
5.147	5.65	7.523	11.4	10.30	21.6	11.90	25 9	13.87	24.6	17.74	13.5		
5.533	6.61	8.161	12.3	10.54	23.6	12.17	25 6	14.54	22.3				
5.855	7.32	8.746	14.9	10.76	24.7	12.48	24 3	15.06	19.6				
6.111	7.64	9.260	16.9	11.10	26.5	12.70	24 9	15.48	17.3				
H = 20 kOe													
5.735	7.75	8.404	14.65	9.642	17.8	11.20	19.2	13.22	22.6	15.37	20.2		
6.158	8.82	8.692	15.4	9.899	17.9	11.69	20.2	13.48	23.1	15.86	19.0		
6.528	9.40	8.927	16.0	10.37	18.2	12.22	21.8	13.89	22.7	16.84	15.8		
7.395	11.9	9.370	17.5	10.96	19.1	12.44	22.1	14.89	21.7	17.40	14.4		
H - 30 kOe													
6.047	7.90	7.760	11.5	9.549	15.5	10.83	18.05	12.90	22.1	16.12	18.6		
6.370	8.65	8.283	12.9	9.833	15.9	11.15	18.6	13.44	22.6	16.59	17.0		
6.707	9.26	8.521	13.15	10.09	16.3	11.65	19.8	14.07	22.7	17.57	15.7		
7.034	10.2	8.960	14.2	10.34	17.15	12.25	20.9	15.08	21.3	18.11	14.4		
7.409	11.0	9.283	15.65	10.60	17.3	12.64	21.9	15.67	19.85	19.0			
H = 40 kOe													
5.301	6.42	8.360	12.2	9.498	19.1	11.08	18.2	13.04	22.4	16.64	18.7		
6.317	8.395	8.666	13.5	9.826	15.7	11.55	19.65	13.52	22.8	17.62	16.6		
7.226	9.90	8.933	13.9	10.10	16.1	12.05	20.1	14.44	22.9	18.15	15.5		
7.928	11.3	9.210	14.2	10.53	17.4	12.56	21.1	15.07	21.5	19.20			

our samples (see Fig. 3 in [1]), we concluded that this was a metamagnetic transition stimulated by the presence of ferromagnetic chains in the magnetic structure of $Ca_3Mn_2Ge_3O_{12}$.

In stronger magnetic fields the wide hump increased somewhat in amplitude and broadened without shifting along the temperature axis. In a field H = 20 kOe the antiferromagnetic maximum changed to a step which practically disappeared in a field of 40 kOe. The slight difference between the dependences $C_H(T)$ obtained at high temperatures (T > 15°K) was due to the fact that strong magnetic fields induced "magnetic order" in the paramagnetic region.

This behavior of the investigated garnet can be explained if the results obtained are plotted as an H–T phase diagram (Fig. 4). We can see that the external magnetic field governs two phase boundaries: one is denoted by AF and below this boundary the garnet is in the antiferromagnetic state; the other is denoted by P and to the right of this boundary the sample is paramagnetic. The existence of the antiferromagnetic phase is limited to magnetic fields of ~40 kOe and the direct transition from the antiferromagnetic to the paramagnetic state is possible only in weak magnetic fields (0-7 kOe). In stronger fields an intermediate metamagnetic (MM) phase appears in $Ca_3Mn_2Ge_3O_{12}$ and this phase is destroyed at T ~ T_N (phase transition of the first kind).

A similar phase diagram has recently been given in [19] for $Dy_3Al_5O_{12}$, which is an Ising antiferromagnet with T_N = 2.49°K. However, in contrast to $Ca_3Mn_2Ge_3O_{12}$, there is a wide range of fields in which the AF–P transition is possible in dysprosium aluminate and beginning from fields of ~10 kOe only the paramagnetic phase can exist. In our case, the intermediate phase is more "stable" so that the wide maximum in the dependence $C_H(T)$ hardly shifts along the temperature axis when the external magnetic field is reduced. The shape and magnitude of the broad maximum is governed primarily by the polycrystalline structure of the sample and, as shown in [19], by the dipole-dipole effects associated with the demagnetizing field. Thus, an investigation of the low-temperature specific heat of $Ca_3Mn_2Ge_3O_{12}$ has confirmed the earlier conclusion that the Mn^{3+} ions become ordered in an octahedral sublattice at 13.85 ± 0.05°K. An analysis of the magnetic symmetry and exchange interactions of the Mn^{3+} ions in the octahedral sublattice suggests that the best approximation for the investigated garnet is the model of q = 6 inequivalent neighbors in a Heisenberg antiferromagnet and the behavior of the specific heat near T_N in strong magnetic fields (H > 5 kOe) can be explained by special features of the phase diagram of $Ca_3Mn_2Ge_3O_{12}$ which has a triple point at T ≈ 12.5°K and H ≈ 6 kOe.

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