

# Cooperative Jahn–Teller effect in the garnet $\text{Ca}_3\text{Mn}_2\text{Ge}_3\text{O}_{12}$

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The tetragonal structure distortion ( $c/a_{\text{MAX}} = 1.003$ ) due to the cooperative Jahn–Teller effect was observed for the first time and investigated by neutron diffraction in a compound with garnet structure ( $\text{Ca}_3\text{Mn}_2\text{Ge}_3\text{O}_{12}$ ) in the interval 4.2–300°K.

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The garnet  $\text{Ca}_3\text{Mn}_2\text{Ge}_3\text{O}_{12}$ , which contains the Jahn–Teller  $\text{Mn}^{3+}$  ions in the oxygen octahedra, is an antiferromagnet with  $T_N = 13.85^\circ\text{K}$  and exhibits a metamagnetic behavior. <sup>[1,2]</sup> Its magnetic structure, according to neutron-diffraction data, <sup>[3]</sup> is an antiferromagnetic array of ferromagnetic chains (of third type according to Smart), and is typical of compounds with body-centered tetragonal lattice. <sup>[4]</sup> It is known that the  $\text{Mn}^{3+}$  ion in the ground state has in an octahedral field of cubic symmetry a lower orbital doublet, and the electron degeneracy can be lifted by a tetragonal distortion of its environment. Tetragonal distortion of the octahedra is forbidden in the cubic structure of the garnet (space group  $1a3d-O_h^{10}$ ) (point symmetry 3 of octahedral positions), and if it were to occur the symmetry of the octahedra in the lattice as a whole would be altered. The dynamic Jahn–Teller effect is discussed in <sup>[5]</sup> in yttrium iron garnet with  $\text{Mn}^{3+}$  impurity. In our case, the  $\text{Mn}^{3+}$  concentration is high,

and at sufficiently low temperatures (according to the published data,<sup>[6,11]</sup>  $\text{Ca}_3\text{Mn}_2\text{Ge}_3\text{O}_{12}$  at room temperature is cubic with  $a = 12.315 \text{ \AA}$ ) one must expect a cooperative Jahn-Teller distortion of the structure, and a magnetic ordering of the corresponding type. It is of interest to ascertain whether the proposed structure distortion is independent of the magnetic order or takes place simultaneously with it.

To obtain information on the crystal structure of  $\text{Ca}_3\text{Mn}_2\text{Ge}_3\text{O}_{12}$  at low temperatures, we performed an x-ray diffraction investigation of this garnet in the interval 4.2–300°K. At the same time we investigated the garnet  $\text{Ca}_3\text{Fe}_2\text{Ge}_3\text{O}_{12}$  ( $a = 12.325 \text{ \AA}$ ), which contains in octahedral positions  $\text{Fe}^{3+}$  ions in the  $s$ -state and has below 12.5°K antiferromagnetic order of the second type,<sup>[1,7,8]</sup> which does not require distortion of the crystal lattice.

The low-temperature x-ray diffraction study of polycrystalline samples of garnet was carried out in a CF-108 flow-through cryostat (Oxford Instruments) mounted on a "Geigerflex 30113" (Rigaku-Denki) diffractometer. The temperature was stabilized accurate to  $\pm 0.1^\circ\text{K}$  by means of the helium flow and with a DTS-2 temperature regulator. The sample was kept at the specified temperature for 10 minutes prior to the photography, to establish thermal equilibrium.  $\text{Cu } K_\alpha$  radiation was used for the Mn garnet and  $\text{Co } K_\alpha$  radiation for the Fe garnet. The lattice parameter of  $\text{Ca}_3\text{Fe}_2\text{Ge}_3\text{O}_{12}$  was determined from the reflection 12.6.0; 10.8.6 ( $2\theta = 152^\circ$ ) accurate to  $\pm 0.0005 \text{ \AA}$ . The parameters  $a$  and  $c$  of the tetragonal phase of  $\text{Ca}_3\text{Mn}_2\text{Ge}_3\text{O}_{12}$  observed by us were calculated from the reflections (10.4.2 + 10.2.4) – 2.4.10 ( $2\theta \approx 86^\circ$ ), for which the splitting was most clearly pronounced. Since the reflections 10.4.2 and 10.2.4 are slightly shifted relative to each other (by at most  $0.01^\circ$  in  $\theta$ ), we determined  $a$  and  $c$  by averaging the values obtained for the pairs 20.4.2 – 2.4.10 and 10.2.4 – 2.4.10. The error in the determination of the parameter  $a$  was  $\pm 0.0015 \text{ \AA}$  for the entire investigated interval of the temperatures, and the error in the parameter  $c$  ranged from  $\pm 0.0015 \text{ \AA}$  at  $T < 100^\circ\text{K}$  to  $\pm 0.003 \text{ \AA}$  at  $270^\circ\text{K}$ . At  $290^\circ\text{K}$  it was no longer possible to measure  $c$  reliably.

At 4.2°K, splitting of the reflections is observed on the x-ray diffraction pattern of the garnet  $\text{Ca}_3\text{Mn}_2\text{Ge}_3\text{O}_{12}$ , thus attesting to the tetragonal distortion of the structure, with  $c/a > 1$ . A thorough study of the x-ray pattern obtained at room temperature also reveals a small deviation from cubic symmetry. Figure 1 shows the temperature dependences of the parameters  $a$  and  $c$  and of their ratio. Below  $\sim 30^\circ\text{K}$  the ratio  $c/a$  remains constant at 1.003, decreasing smoothly with rising temperature to  $\sim 1.001$  at  $270^\circ\text{K}$ . Extrapolation to  $c/a = 1$  makes it possible to estimate the temperature of the transition to the cubic phase at approximately 350–400°K. The parameter  $c$  is practically constant in the investigated temperature region, i. e., the thermal-expansion coefficient is close to zero over the  $c$  axis, and is maximal in the basal plane.

$\text{Ca}_3\text{Fe}_2\text{Ge}_3\text{O}_{12}$  remains cubic down to 4.2°K (Fig. 2), so that it can be stated with assurance that the structure of  $\text{Ca}_3\text{Mn}_2\text{Ge}_3\text{O}_{12}$  is connected with the onset of the cooperative Jahn-Teller effect. The type of magnetic order in the Mn garnet is obviously governed by the crystal-lattice symmetry.

Attenuation is called to the small value of the deviation from the cubic phase. For example, in spinels that contain  $\text{Mn}^{3+}$ , the ratio  $c/a$  reaches 1.15.<sup>[9]</sup> There is a known mineral anrtermierite  $\text{Ca}_3\text{Mn}_{1.5}\text{Al}_{0.5}(\text{SiO}_4)_2(\text{OH})_4$  with a tetra-

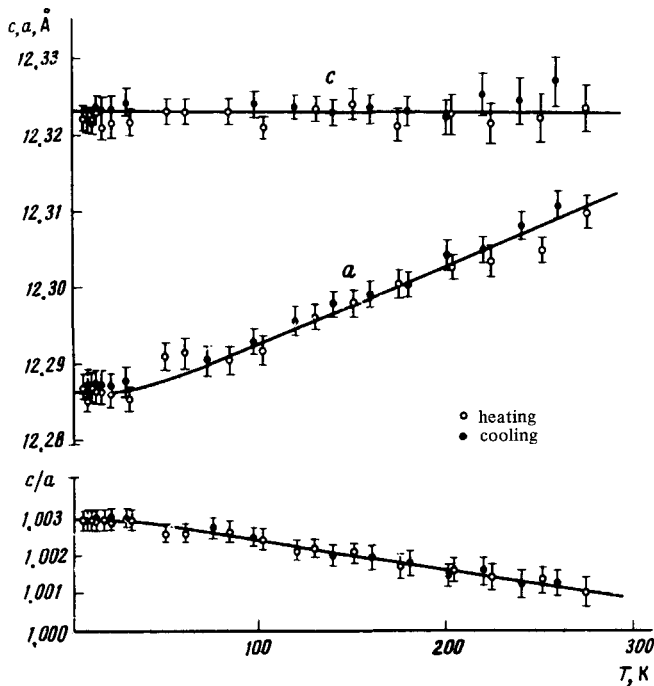


FIG. 1. Temperature dependences of the lattice parameters  $a$  and  $c$  and of the degree of tetragonality  $c/a$  of the garnet  $\text{Ca}_3\text{Mn}_2\text{Ge}_3\text{O}_{12}$ .

gonally distorted garnet structure (space group  $14_1/acd-D_4^{2d}$ ), for which  $c/a = 1.040$ , although the  $\text{Mn}^{3+}$  occupies only a fraction of the octahedral voids.<sup>[10]</sup> The large difference in the degree of tetragonality of these two garnets can be

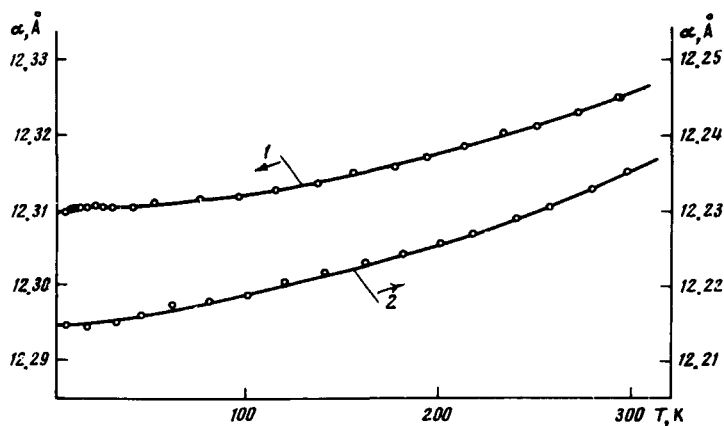


FIG. 2. Temperature dependences of the lattice parameters of the garnets  $\text{Ca}_3\text{Fe}_2\text{Ge}_3\text{O}_{12}$  [1] and  $\text{Cd}_3\text{Mn}_2\text{Ge}_3\text{O}_{12}$  [2].

explained from the structural point of view. In the anrtermierite the  $Mn^{3+}$  surrounding is non-equivalent, since four atoms of the oxygen octahedron are common with the "rigid"  $SiO_4$  tetrahedra (the Si—O bonds are strong), and the remaining two oxygen atoms are common with the  $(OH)_4$  tetrahedra, which are connected by weak O—H hydrogen bonds. The onset of an appreciable tetragonal distortion is aided by the ordering of the tetrahedra—the four  $SiO_4$  groups are located in corners of the square of the octahedraon, and two  $(OH)_4$  groups are located in corners of the square of the octahedron, and two  $(OH)_4$  axis that is approximately normal to the plane of the square. Of the two possible orbitals  $d_{x^2-y^2}$  and  $d_{z^2}$ , the  $e_g$  electron of the  $Mn^{3+}$  ion knocks out  $d_{z^2}$ , i. e., the degeneracy is lifted by moving apart the less strongly bound oxygen ions belonging to the  $(OH_4)$  tetrahedra. At this type of distortion we have  $c/a > 1$ . In the garnet  $Ca_3Mn_2Ge_3O_{12}$ , the tetragonal and dodecahedral voids are occupied by ions of the same sort ( $Ge^{4+}$  and  $Ca^{2+}$ , respectively), all the Mn—O bonds are equivalent, and the structure has no weak bonds; this is indeed the reason why the deformation of the cubic lattice is small. A confirmation of the proposed explanation is the fact that in the other  $Mn^{3+}$  garnet  $Cd_3Mn_2Ge_3O_{12}$  we did not observe, down to 4.2 °K, any distortion (the limit of the resolution corresponds to  $1.0005 < c/a < 1.001$ ) (Fig. 2).<sup>1)</sup> Substitution of  $Ca^{2+}$  by the smaller  $Cd^{2+}$  in the dodecahedra (the effective ion radii are 1.12 and 1.07 Å<sup>[11]</sup> respectively) leads to stronger Cd—O bonds, the structure becomes more rigid and less inclined to be deformed. It can be assumed that in the garnets  $Ca_3Mn_2Si_3O_{12}$  and  $Cd_3Mn_2Si_3O_{12}$  synthesized at high pressures<sup>[12]</sup> no distortion of the structure will be observed down to the lowest temperatures, since the Si—O bonds are stronger than Ge—O.

We have also observed a low-temperature Jahn-Teller distortion of the  $a$  structure with  $c/a < 1$  in the garnet  $NaCa_2Cu_2V_3O_{12}$ , which contains octahedral  $Cu^{2+}$  ions; the results will be published separately.

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<sup>1)</sup>  $Cu K_\alpha$  radiation, the parameter was determined from the reflection with accuracy  $\pm 0.00005$  Å.

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