

Magnetic properties of a layered and anisotropic rhombohedral compound: $\text{Bi}_{2(1-x)}\text{Gd}_{2x}\text{Te}_3$

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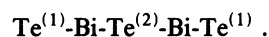
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The paramagnetic resonance absorption spectra of $\text{Bi}_{2(1-x)}\text{Gd}_{2x}\text{Te}_3$ grown by the Bridgman technique have been measured at room temperature. The magnetization measurements have been performed in magnetic-field intensities up to 65 kOe at temperatures of 1.8, 4.2, 16, and 25 K. The EPR data show that the Gd^{3+} site has a C_{3v} symmetry, indicating a true substitution of Bi^{3+} atoms by Gd^{3+} . The curve fitting of the magnetic-field dependence of the magnetization has been performed using a Brillouin function representing isolated magnetic ions. An extra term was introduced to represent the contribution of the pairs. The results indicate a weak antiferromagnetic coupling between the Gd^{3+} ions. This is similar to the one found in the case of $\text{Pb}_{1-x}\text{Gd}_x\text{Te}$. The bond lengths as well as the bond angles in the case of $\text{Bi}_{2(1-x)}\text{Gd}_{2x}\text{Te}_3$ and $\text{Pb}_{1-x}\text{Gd}_x\text{Te}$ are compared. The similarity of the J_p/k_B values (-0.5 K) in the two systems is explained in terms of superexchange interaction via anions between Gd^{3+} .

I. INTRODUCTION

To date, the dilute magnetic semiconductors (DMS) have been prepared using II-VI and IV-VI materials. In II-VI compounds, extensive studies have been performed using Mn magnetic ions,¹⁻⁴ however, some investigations have been carried out with Fe and Co.⁵⁻⁹ On the other hand, little work has been done in the case of IV-VI compounds using transition metals and rare earths as magnetic ions.¹⁰⁻¹² This paper describes the study of another DMS family, $\text{Bi}_{2(1-x)}\text{Gd}_{2x}\text{Te}_3$. Solid solutions in bismuth telluride Bi_2Te_3 represent an important group of semiconductor materials, for applications in thermoelectric devices. The host crystal Bi_2Te_3 is a semiconductor with an indirect band gap, $E_g \approx 0.15$ eV. Its band structure is rather complex. For example, Ure¹³ suggested the existence of double valence and double conduction bands. Furthermore according to Von Middendorff and Landwehr,¹⁴ the second valence band is 15 meV below the upper one. The presence of two minima in the conduction band was also suggested by Mallinson *et al.*¹⁵ Bi_2Te_3 has a rhombohedral unit cell containing three molecules. Bi_2Te_3 belongs to the $R\bar{3}m$ point group and has an anisotropic layer structure.¹⁶ The characteristic cleavage planes are the result of the shorter interlayer bond lengths between the Te atoms, when compared to the intralayer ones. In effect, this anisotropic structure can be seen as a superposition of complex layers—called quintets—in a direction perpendicular to a threefold axis. Each quintet is composed of five layers and each layer consists of identical atoms forming a hexagonal lattice plane. The schematic crystal structure is illustrated in Fig. 1. The layers alternate in the following sequence:



Thus a bismuth atom has three $\text{Te}^{(1)}$ nearest neighbors with a $\text{Te}^{(1)}\text{-Bi}$ bond length of 3.065 Å and three $\text{Te}^{(2)}$ atoms as next nearest neighbors sandwiching the bismuth planes, with a $\text{Te}^{(2)}\text{-Bi}$ bond length of 3.246 Å.¹⁷ It is interesting to mention that the Gd_2Te_3 is orthorhombic as well, with the following crystallographic characteristics: $a = 11.98$ Å, $b = 11.75$ Å, and $c = 4.29$ Å. The structure consists of zigzag chains—Gd-Te-Gd—oriented along the c axis. Several questions are posed on the position of Gd ions when it is diluted in the host crystal Bi_2Te_3 . The first question is the position of Gd within the host. As a result, how is the magnetic exchange affected in terms of indirect exchange between the Gd ions? Consequently, in case of Gd acting as a donor, one could have a RKKY interaction; on the other hand, if it is neutral, one could have a superexchange interaction.

II. EXPERIMENTAL RESULTS AND INTERPRETATION

The $\text{Bi}_{2(1-x)}\text{Gd}_{2x}\text{Te}_3$ alloys, with $0 < x < 1$, have been prepared by melting its elements. The former alloys were annealed for about fifteen days. Their composition is then verified by x-ray powder diffraction. The solid solution takes place in a very short composition range, not more than 5% atomic. Single crystals were prepared using the Bridgman technique. Two ingots were grown, the starting elemental composition being 1 and 5 mol % of Gd. The single resulting crystals were 50–60 mm long and 10 mm in diameter and could easily be cleaved. The trigonal c axis was perpendicular to the pulling direction; thus, the (0001) plane was parallel to the growth direc-

tion. The orientation of the cleavage faces were verified by x-ray diffraction. The hexagonal lattice parameters of the highest concentration of Gd powdered sample were $a=4.39\pm 0.01 \text{ \AA}$ and $c=30.63\pm 0.04 \text{ \AA}$ indicating a lattice volume (512 \AA^3) slightly bigger than that of Bi_2Te_3 's composition ($a=4.386 \text{ \AA}$; $c=30.497 \text{ \AA}$, and $V=508 \text{ \AA}^3$).

The two ingots *A* and *B*, at room temperature, were *p* type with carrier concentrations of $p=2\times 10^{18} \text{ cm}^{-3}$, with a carrier mobility of $\mu=200 \text{ cm}^2/\text{V s}$ and the Seebeck coefficient of $S=200 \text{ \mu V/K}$. A pure Bi_2Te_3 grown under the same conditions had $p=1.2\times 10^{18} \text{ cm}^{-3}$, $\mu=250 \text{ cm}^2/\text{V s}$, $S=220 \text{ \mu V/K}$. The comparison of the above-mentioned transport properties of the pure Bi_2Te_3 and its Gd alloys clearly indicates that Gd does not act as a donor, as usually is the case in the II-VI compounds.

Paramagnetic resonance absorption measurements in the *X* band region (9.8 GHz) were carried out at room temperature, on the two crystals. The trivalent gadolinium ion has seven electrons resulting in a half-filled $4f$ shell; it also has a $^8S_{7/2}$ ground state. The crystal field

can affect its energy levels only through high order interactions; thus, the initial splitting of the $^8S_{7/2}$ levels is expected to be very small. Generally, seven lines can be observed; they correspond to the transitions in which the projection of the angular momentum on the symmetry axis changes by one unit. The spacing between these transitions, and their variations with the orientation of the external magnetic field relative to the crystal axis, provide sufficient information to experimentally verify the form of the crystal field. The measurements are interpreted in terms of a spin Hamiltonian. The spin Hamiltonian for zero magnetic field must show the same symmetry as the symmetry site of the Gd^{3+} ion (i.e., C_{3v}):¹⁸

$$H = g\mu_B B \times S + B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^0 O_6^0 + B_6^6 O_6^6 + B_4^3 O_4^3 + B_6^3 O_6^3, \quad (1)$$

where g is the effective Lande factor of the magnetic ion, μ_B is the Bohr magneton.

The angular spin momentum operators O_2^0 , O_4^0 , and O_6^0 in the above Hamiltonian are considered as simple operators with the same transformation properties as the corresponding spherical harmonics, Y_n^m , necessary for the expression of the C_{3v} crystal field potential. To reduce the numerical values, it is customary to redefine the constants B_2^0 , B_4^0 , B_6^0 , B_6^6 , B_4^3 , and B_6^3 in the spin Hamiltonian as follows:

$$b_2^0 = 3B_2^0, \quad b_4^0 = 60B_4^0, \quad b_6^0 = 1260B_6^0, \quad (2)$$

$$b_4^3 = 3B_4^3, \quad b_6^3 = 36B_6^3, \quad b_6^6 = 1260B_6^6. \quad (3)$$

Strong distortions (dysonian lines) of the signals are observed, even in very small samples; see Fig. 2. This might

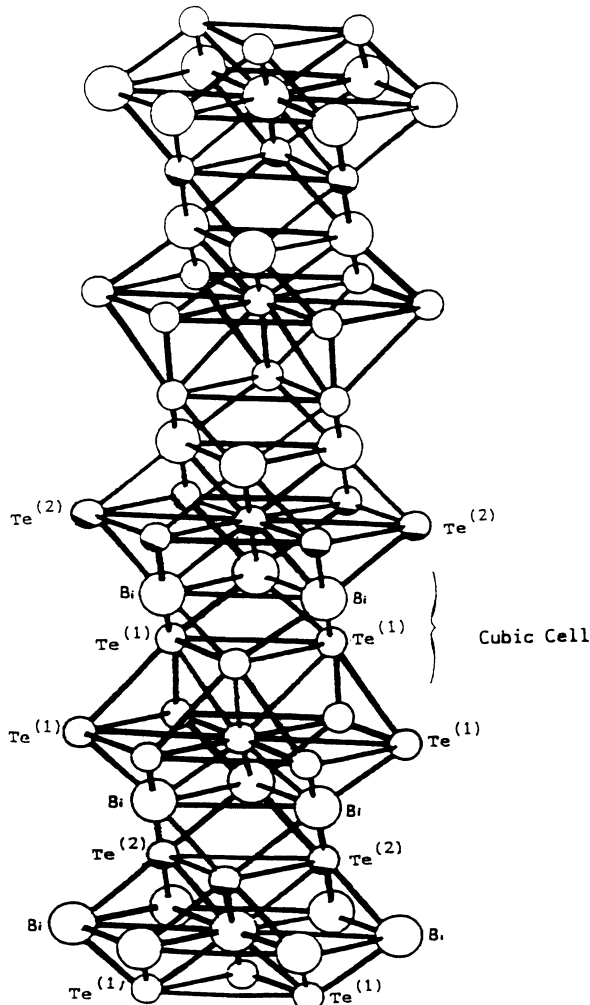


FIG. 1. Representation of the crystal structure of Bi_2Te_3 showing hexagonal cell (Ref. 17).

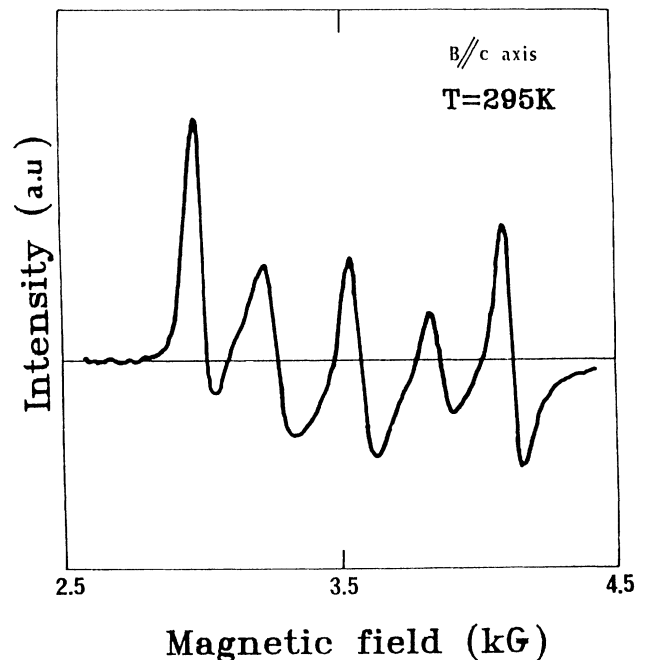


FIG. 2. Gd^{3+} EPR spectrum in Bi_2Te_3 single crystal at 295 K. Central magnetic field $3.5\pm 1 \text{ kG}$. Microwave frequency 9.8 GHz.

be due to a large skin effect related to an important electrical conductivity of the material. Independent of the starting compositions (1 or 5 mol %), the half width of the line is too large (≈ 80 G) to allow an accurate estimation of their position, and at the same time take into account second-order corrections. To eliminate certain asymmetries resulting from the second-order effects, the values of b_2^0 , b_4^0 , and b_6^0 were calculated from the spacing between corresponding lines on either side of the central line. The values of the spin Hamiltonian parameters deduced from our experimental EPR spectra were

$$\begin{aligned} g &= 2.020 \pm 0.005, \\ b_2^0 &= 109 \times 10^{-4} \text{cm}^{-1}, \\ b_4^0 &= -4.7 \times 10^{-4} \text{cm}^{-1}, \\ b_6^0 &= 1.8 \times 10^{-4} \text{cm}^{-1}. \end{aligned}$$

The overall zero field splitting was 0.13 cm^{-1} .

The observed EPR spectrum perpendicular to the axis ($\theta = 90^\circ$) is markedly asymmetric due to second-order effects. Variations in the spectrum have threefold symmetry as expected in a site C_{3v} . These results indicate that Gd^{3+} ions is in a substitutional position of the Bi^{3+} ion and there is a high probability of electron-spin interaction. This might explain why Gd^{3+} is not a donor as in the case of II-VI or IV-VI compounds.

Magnetization measurements were performed with a squid system, where the magnetic field B varied from 0 to 65 kOe. The results of the two samples A and B are depicted in Figs. 3 and 4. The magnetic field was applied along the c axis for sample A and along the basis for the sample B . The experimental magnetization curves were fitted with a high degree of accuracy by taking into account the isolated magnetic ions contributions, and the pair contribution:^{19,20}

$$M = M_s + M_p + \chi_d B, \quad (4)$$

$$M_s \text{ for single,}$$

$$M_p \text{ for pair,}$$

$$\chi_d \text{ for diamagnetic lattice contribution.}$$

$$\begin{aligned} M_p = (\frac{1}{2})M_0 y_2 \left\{ \sum_{m=0}^{m=S_{\max}} [(m + \frac{1}{2}) \cosh(m + \frac{1}{2})z - \frac{1}{2} \sinh(m + \frac{1}{2})z \coth(\frac{1}{2}z)] \exp \left[\frac{J_p}{k_B} \frac{m(m+1)}{T} \right] \right. \\ \left. \times \left[\sum_{m=0}^{m=S_{\max}} \sinh(m + \frac{1}{2})z \exp \left[\frac{J_p}{k_B} \frac{m(m+1)}{T} \right] \right]^{-1} \right\} \end{aligned}$$

and

$$z = \frac{g\mu_B B}{k_B T}.$$

Here S is the magnetic-ion spin ($S = \frac{7}{2}$ for Gd^{3+}), N_0 is the number of cation sites per gram, k_B is the Boltzmann

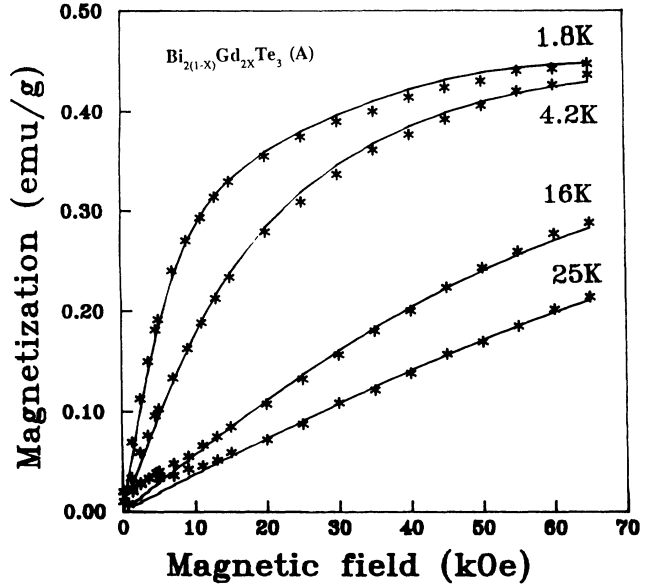


FIG. 3. Magnetization curve of $\text{Bi}_{2(1-x)}\text{Gd}_{2x}\text{Te}_3$ of sample A , as a function of magnetic field at 1.8, 4.2, 16, and 25 K. Symbols: Experimental points. Solid lines: Theoretical curve with isolated and pair Gd^{3+} ions contribution.

M_s is given by

$$M_s = M_0 S y_1 B_s(\zeta)$$

and

$$M_0 = g\mu_B N_0,$$

$B_s(\zeta)$ is a Brillouin function,

$$B_s(\zeta) = \frac{2S+1}{2S} \coth \left[\frac{2S+1}{2S} \zeta \right] - \frac{1}{2S} \coth \left[\frac{\zeta}{2S} \right],$$

and

$$\zeta = \frac{g\mu_B B S}{k_B T}.$$

M_p is given by

constant, T the operating temperature, $\chi_d = 4.2 \times 10^{-7}$ emu/g Oe,²¹ J_p is the pair exchange parameter, $S_{\max} = 2S$, y_1 and y_2 are the respective fractional concentrations of the magnetic ions in the singles and in the pairs, and g and μ_B were defined previously. Usually T is replaced by $T_{\text{eff}} = T + T_0$, where T_0 is a phenomenological parameter including the contribution due to the ex-

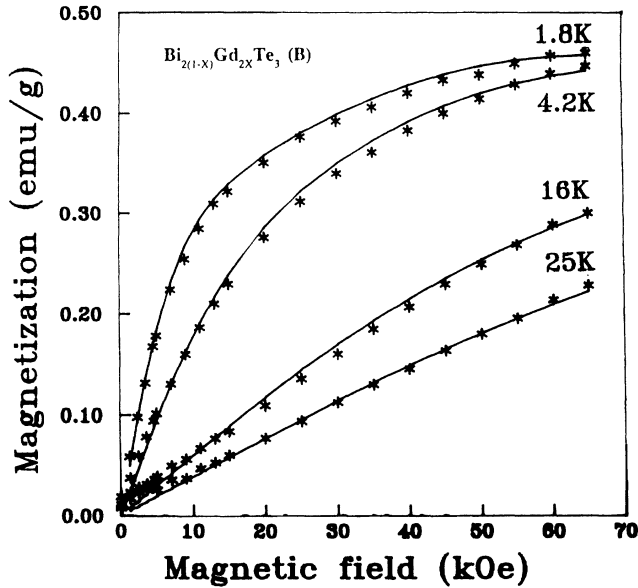


FIG. 4. Magnetization curve of $\text{Bi}_{2(1-x)}\text{Gd}_{2x}\text{Te}_3$ of sample *B*, as a function of magnetic field at 1.8, 4.2, 16, and 25 K. Symbols: Experimental points. Solid lines: Theoretical curve with isolated and pair Gd^{3+} ions contribution.

change from the clusters.²² In our case we used $T_{\text{eff}} = T$, because the contribution of the pairs is included through M_p , so the contribution of the other clusters should be small. On the other hand the value of the saturated magnetization for the largest fields is required to determine T_0 , and it is not reached in our case.

However, it is well known that the value of J_p/k_B obtained from the three fitting parameters (y_1, y_2, J_p) is slightly smaller than those obtained from the four fitting parameters (y_1, y_2, J_p, T_0). Using three parameters one obtained an "average" of the pair exchange and a smaller antiferromagnetic exchange parameter. In addition, for the two samples used the Gd concentration is small; the weaker the Gd concentration, the weaker the clusters contribution, other than pairs.²⁰ A summary of the fitting parameters, for the two samples studied, is given in Tables I and II.

The nearest-neighbor exchange interaction in $\text{Bi}_{2(1-x)}\text{Gd}_{2x}\text{Te}_3$ is antiferromagnetic, with the value of J_p/k_B of -0.5 K. This is very similar to the one obtained in $\text{Pb}_{1-x}\text{Gd}_x\text{Te}$ (-0.45 K) and $\text{Pb}_{1-x}\text{Eu}_x\text{Te}$ (-0.46 K).^{2,20} From Tables I and II, one can deduce for the two samples *A* and *B* that $y = y_1 + y_2$ is about the

TABLE I. Magnetization curve fitting parameters of $\text{Bi}_{2(1-x)}\text{Gd}_{2x}\text{Te}_3$ of sample *A*, at T from 1.8 to 25 K for a varying magnetic field of $B = 0-65$ kOe.

T (K)	y_1	y_2	J_p/k_B (K)
1.8	0.0074	0.0025	-0.5
4.2	0.0074	0.0026	-0.5
16	0.0100	0.0	0.0
25	0.0105	0.0	0.0

TABLE II. Magnetization curve fitting parameters of $\text{Bi}_{2(1-x)}\text{Gd}_{2x}\text{Te}_3$ of sample *B*, at T from 1.8 to 25 K for a varying magnetic field of $B = 0-65$ kOe.

T (K)	y_1	y_2	J_p/k_B (K)
1.8	0.0073	0.0028	-0.5
4.2	0.0073	0.0030	-0.5
16	0.0105	0.0	0.0
25	0.0110	0.0	0.0

same, i.e., around 1%; here y is the total fractional concentration of Gd ions, $x = y/2$ of $\text{Bi}_{2(1-x)}\text{Gd}_{2x}\text{Te}_3$ since there is 2 Gd in a molecule of Gd_2Te_3 . These results agree with the paramagnetic absorption curves which illustrate the same spectra for the two samples. Thus it is clear that, for these two samples, all of the Gd could not be introduced into substitutional positions of the crystal. Assuming a random distribution in a hexagonal lattice, the y_1 and y_2 values can be substantiated by pure statistical means. We calculated the probability of finding ions in isolated sites S , or in pairs P , for a structure like Bi_2Te_3 , which is close packed hexagonal but with a different number of Bi atoms and Te atoms in an unit cell, and thus a plane sequence different from usual close packed hexagonal structures like CdSe (see Fig. 1). One found that

$$S = (1-y)^6, \quad (5)$$

$$P = \frac{54}{13}y(1-y)^8. \quad (6)$$

If we assume that $y = 1\%$, and that the random distribution is stated as expressed above, one then finds

$$S = 0.94, \quad P = 0.04.$$

Thus

$$y_1 = yS = 0.0094, \quad y_2 = yP = 0.0004.$$

These results show a large discrepancy between the values of y_1 and y_2 deduced from the curve fitting of the magnetization and the ones calculated by the above expression. The expressions (5) and (6) assume implicitly for the pairs that the exchange interaction is a direct one.

If we assume that the exchange interaction is superexchange via Te, as in the case of $\text{Pb}_{1-x}\text{Gd}_x\text{Te}$,^{2,20} we cannot consider two Gd atoms separated by a Te plane as isolated but they could be in a pair. In that case S and P are

$$S = (1-y)^6 - \frac{2874}{169}y(1-y)^{12}, \quad (7)$$

$$P = \frac{54}{13}y(1-y)^8 + \frac{2874}{169}y(1-y)^{12}; \quad (8)$$

with the same concentration of Gd, i.e., 1%, one found

$$S = 0.79, \quad P = 0.19.$$

These results are in rather good agreement with the values deduced from magnetization curve fitting:

$$S_A = 0.71, \quad P_A = 0.25 \text{ for sample } A,$$

$$S_B = 0.67, \quad P_B = 0.27 \text{ for sample } B.$$

The small difference could be probably due to the fact that in the curve fitting the triangles are not included, and to a light tendency to clusterization with respect to a pure statistic distribution.

Furthermore, it could be noted that the value of J_p/k_B is very similar to that obtained in $Pb_{1-x}Gd_xTe$ (-0.45 K) where it has been shown that the superexchange interaction via anion is predominant. In $Pb_{1-x}Gd_xTe$, the interatomic distance of Pb-Te is 3.225 Å, while in $Bi_{2(1-x)}Gd_{2x}Te_3$, only a $Te^{(2)}$ anion can be situated between two Bi or two Gd ions; the corresponding bond length of Bi- $Te^{(2)}$ is 3.246 Å. The angles between the Pb-Te bonds or Gd-Te bonds in $Pb_{1-x}Gd_xTe$ are either 90° or 180° . The 90° nearest-neighbor superexchange interaction is comparable to the 180° one.²⁰ The angles between Bi- $Te^{(2)}$ bonds or Gd- $Te^{(2)}$ bonds in $Bi_{2(1-x)}Gd_{2x}Te_3$ differ from the angles in the octahedral coordination by 4.5° ,^{23,24} and are, respectively, 94.5° or 85.5° . Then it is not surprising to find the same value of J_p/k_B in these two classes of compound despite their different structures. It is also interesting to note that the interaction is antiferromagnetic.

III. CONCLUDING REMARKS

The magnetic properties of $Bi_{2(1-x)}Gd_{2x}Te_3$ were studied. It has been found that the average exchange interaction between the Gd^{3+} ions is antiferromagnetic and the value of J_p/k_B equal to (-0.5 K). Although the structures are different, this value is comparable to that of $Pb_{1-x}Gd_xTe$. Furthermore, the results are consistent with the predictions of the model of superexchange interaction via anions in these two compounds. This is a consequence of the cation-anion spacing as well as of the angle between cation-anion-cation bonds, which are about the same. The local symmetry, C_{3v} of the Gd^{3+} ions, has been deduced from EPR experiments.

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