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Experimental and theoretical investigations of the magnetic susceptibility and anisotropy of $Na_3Pr(C_4H_4O_5)_3 \cdot 2NaClO_4 \cdot 6H_2O$

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The results of an experimental study of the magnetic susceptibility and anisotropy of a rarely studied single crystal, viz., trigonal trisodium praseodymium tris(oxydiacetate)di(sodium perchlorate)hexahydrate [i.e., $Na_3Pr(C_4H_4O_5)_3 \cdot 2NaClO_4 \cdot 6H_2O$] are reported here. The anisotropy of PrODA shows unusual behavior with the variation of temperature. The crystal-field energy levels and the magnetic susceptibilities are calculated using the intermediate-coupling formalism under the crystal field D_3. The set of crystal-field parameters giving the best fit to the experimental observation of the optical-absorption spectra [R. W. Schwartz, A. K. Banerjee, A. C. Sen, and M. Chowdhury, J. Chem. Soc. Faraday II **76**, 620 (1980)] and the temperature dependence of the magnetic susceptibility and anisotropy from 300 to 70 K are evaluated to be $A_{20}=150$, $A_{40}=-1570$, $A_{60}=623$, $A_{66}=390$, $A_{43}=1158$, and $A_{63}=330$, all in cm^{-1}. The electrostatic and the spin-orbit coupling parameters are chosen to be the same as those given by previous workers. The crystal-field splitting thus obtained is used to determine the temperature dependence of the Schottky specific heat. The values of the Weiss and Curie constant are also determined.

I. INTRODUCTION

This is the first in a series of reports on magnetic studies of rarely studied single crystals of lanthanide trisoxydiacetates. The rare-earth oxydiacetates of the general formula $Na_3L(C_4H_4O_5)_3 \cdot 2NaClO_4 \cdot 6H_2O$ (LODA), where L is a rare earth, form a series of simple magnetic crystals with interesting magnetic, optical, and thermal properties. The crystals are trigonal with space group $R32$.[1] The site symmetry of the nine-coordinate Pr^{3+} ion is D_3, the immediate environment being based upon a distorted trigonal prism of carboxylic oxygens with the ether oxygens lying on twofold axes outside the rectangular faces of the prism. The horizontal plane of symmetry of the perfect D_{3h} trigonal prism is distorted by rotation of the upper and lower oxygen triangles in the opposite sense around the c axis (in order to reduce the strain in the bonds of the ligand molecule), reducing to the site symmetry D_3 and giving rise to optical rotation. The optical anomaly in this crystal arises from the immediate vicinity of the rare-earth ion. The hexagonal unit cell contains three molecules, but the primitive rhombic unit cell only one. The C_3 axis of the trigonal prism coincides with the threefold axis of the crystal. The nearest-neighbor distance is > 8.9 Å.

The study of optical activity offers the means for finding the extent of magnetic dipole contribution when both magnetic dipole and electric dipole mechanisms contribute simultaneously to the observed intensity. With this in view, the optical rotatory dispersion for the asymmetric rare-earth ion center of optically active single crystals of praseodymium oxydiacetate has been studied and analyzed systematically by Schwartz *et al.*,[1] by observing the optical absorption, circular dichroism, and magnetic circular dichroism (MCD) spectra. No other study has been reported as yet for this compound.

The optical spectra of tripositive praseodymium in other lattices have received considerable attention in recent decades.[2] Studies from the far infrared to the ultraviolet and for both crystal[2] and vapor spectra[3] have offered experimentalists an excellent opportunity to identify the various levels associated with the $4f^2$ subshell characteristic of Pr^{3+}. Polarized absorption, fluorescence, and Zeeman spectra have been reported for Pr^{3+} in single crystals of the lanthanide trihalides, ethyl sulfates, double nitrates, and bromates, as well as in CaF_2, Y_2O_3, and other diamagnetic optically transparent oxides.[2] These spectra recorded between 1.4 and 300 K provided the crystalline electric field (CEF) splitting of the J manifolds which helped in examining the atomic structure beyond the usual Hartree-Fock approximations.[4] More than any other lanthanide ion, Pr^{3+} has received considerable theoretical assessment, beginning with the application of perturbation theory to CEF splitting by Judd[5] and followed by successive developments by Wybourne,[6] by Judd, Crosswhite, and Crosswhite,[7] and by Morrison, Fields, and Carnall.[8] Recent work by Judd[9] and by Newman[10] points out the importance of the correlation crystal field by suggesting models for improving the CEF splitting of the singlet states.

Magnetic susceptibility measurements of almost all well-known praseodymium compounds,[11–14] except oxydiacetate, have been reported. They show many interesting features which give an insight into the nature of the crystal field. Praseodymium ethyl sulfate is nearly isotropic at 300 K but becomes highly anisotropic at low temperatures. The anisotropy shows a maximum at about 200 K and becomes negative below 140 K.[12] Praseodymium antipyrene tri-iodide single crystals were reported to show a maximum in anisotropy at 156.6 K.[13] Praseodymium magnesium double nitrate shows a reversal of sign in anisotropy, as reported by Hellwege *et al.*[14] All these facts prompted the author to study the magnetic properties of the rarely studied single crystals of praseodymium oxydiacetate. The present paper is a presentation of the magnetic measurement of the average susceptibility and the anisotropy in the temperature range between 300 to 70 K, as well as an attempt is made here to find out the best set of crystal-field parameters for explaining the experimental observation of the optical-absorption spectra[1] and the present magnetic measurements. Using the crystal-field splitting thus obtained, the temperature dependence of the Schottky heat capacity is calculated from 360 to 2 K.

II. EXPERIMENTAL

Trigonal-shaped single crystals of praseodymium oxydiacetate are easily grown out of an aqueous solution at room temperature. Single crystals of masses 17.150 to 10.045 mg were available for experiment. They are light green in color. Experiments are repeated with six crystals of varying masses. A polarizing microscope is used to select perfect crystals and then to mount them for the experiment. The variation in the value of room-temperature magnetic anisotropy from crystal to crystal was found to be within $\pm 0.03\%$, which is negligibly small.

The magnetic anisotropy $(K_{\parallel} - K_{\perp})$ was measured at different temperatures by suspending the crystal with a quartz fiber in a homogeneous magnetic field such that the c axis moved freely in a horizontal plane.[15] The average magnetic susceptibility $\overline{K}$ was measured by filling a quartz capsule with the finely powdered sample and then suspending it between the pole pieces of a sensitive Curie balance. Small capsules are used for packing the powdered samples so that the field gradient is constant over the entire volume. The accuracy of the results is high. Measurements below liquid-nitrogen temperature are taken by making it boil under reduced pressure. Thus, by measuring the anisotropy $(K_{\parallel} - K_{\perp})$ and the average susceptibility $\overline{K} = \frac{1}{3}\,(K_{\parallel} + 2K_{\perp})$, it is possible to get the values of $K_{\parallel}$ and $K_{\perp}$. Measurements are made at different temperatures between 300 and 70 K.

III. THEORY

To get the intermediate-coupled free-ion wave functions and the corresponding energy levels, the following Hamiltonian, comprised of the Coulomb electrostatic interaction and the spin-orbit coupling, is solved:

$$\mathscr{H}_{IC} = \sum_{\substack{i<j \\ i,j}} \frac{e^2}{r_{ij}} + \zeta \sum_i l_i \cdot \mathbf{s}_i \ .$$

The Coulomb interaction between the two $4f$ electrons gives rise to the seven terms ^1S, ^3P, ^1D, ^3F, ^1G, ^3H, and ^1I. The spin-orbit interaction $\zeta(l_1 \cdot \mathbf{s}_1 + l_2 \cdot \mathbf{s}_2)$ splits up each triplet term into three levels. Since it commutes with J, it also couples together levels possessing the same value of J that derive from different terms, thus producing deviations from pure Russell-Saunders (RS) coupling. The diagonalization of the above-written matrix yields energy eigenvalues corresponding to the free-ion levels $^3H_4$, $^3H_5$, $^3H_6$, $^3F_2$, $^3F_3$, $^3F_4$, $^1G_4$, $^1D_2$, $^3P_0$, $^3P_1$, $^1I_6$, $^3P_2$, and $^1S_0$, respectively. The matrix elements of the electrostatic interaction for the $4f^2$ configuration have been expressed in terms of Slater-Condon parameters, F_k's and have been tabulated by Nielson and Koster.[16] The matrix elements of the spin-orbit coupling interaction between the various levels have been calculated by Spedding.[17] The results are utilized here. The effect of the crystal field on the intermediate-coupled states is to split them further into crystal-field energy levels. They are obtained by operating with the following crystal-field potential in the present case of D_3 symmetry:

$$V = A_{20}U_0^2 + A_{40}U_0^4 + A_{60}U_0^6 + A_{66}(U_6^6 + U_{-6}^6) + A_{43}(U_3^4 - U_{-3}^4) + A_{63}(U_3^6 - U_{-3}^6) \ ,$$

where $U_q^k = r^k Y_k^q$ is an irreducible tensor operator. A_{kq} are the crystal-field parameters which are related to the Steven's parameters B_k^q (which are obtained when the operator equivalent method is used) by constant factors as follows:

$$A_{20} = 4\sqrt{\pi/5}B_2^0, \quad A_{40} = \tfrac{16}{3}\sqrt{\pi}B_4^0, \quad A_{60} = 32\sqrt{\pi/13}B_6^0 \ ,$$

$$A_{66} = 32\sqrt{\pi/3003}b_6^6, \quad A_{43} = \tfrac{4}{3}\sqrt{\pi/35}B_4^3 \ ,$$

$$A_{63} = 16\sqrt{\pi/1365}B_6^3 \ .$$

The matrix elements of U_q^k are obtained by the same procedure as given by Elliot *et al.*[18] The eigenfunctions and the energy eigenvalues are evaluated for the different states. This will be communicated in detail. The contribution towards the magnetic susceptibility of the energy levels other than the ground $^3H_4$ term is negligibly small, hence, not considered here. A significant contribution comes from the intermediate-coupled lowest multiplet of $^3H_4$. It contains nine crystal-field states, of which three are doublets and three are singlets. They are substituted in the Van Vleck expression for paramagnetic susceptibility, to get the values of $K_{\parallel}$ and $K_{\perp}$ at various temperatures.[15]

IV. RESULTS AND DISCUSSION

The experimental observation of magnetic anisotropy of the single crystals and the average susceptibility of the powdered samples are plotted in Fig. 1 from 300 to 77 K. At room temperature, the crystal has a small value of magnetic anisotropy (280×10^{-6} emu/mole) which is less than 6% of the average susceptibility. While $(K_{\parallel} - K_{\perp})$ values of compounds of other members of the rare-earth series[15] rise steadily with decreasing temperature, the anisotropy of PrODA shows an unusual behavior with the variation of temperature. The susceptibility along the crystal c axis (Fig. 2) is found to be less than that along the perpendicular axis at room temperature. The crystal rests with the c axis perpendicular to the applied magnetic field. The susceptibility along this axis increases faster than along the a axis with decreasing temperature. The anisotropy shows a maximum at 180 K (Fig. 1). Thereafter it decreases with the drop in temperatures until 100 K where it has a zero line. Below this temperature it increases quite rapidly, with the greater susceptibility along the crystal c axis. The peculiar behavior of the magnetic

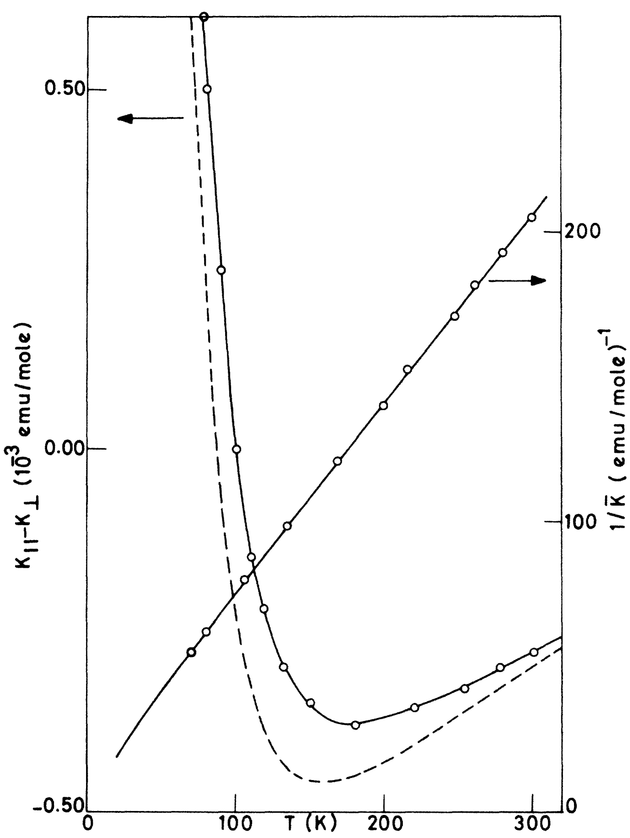

FIG. 1. Temperature dependence of the anisotropy and the inverse of average susceptibility of PrODA. (○) represents the experimental observation. The solid and dashed lines indicate calculated values using crystal-field parameters of the present work and that by Schwartz *et al.* (Ref. 1), respectively.

anisotropy with the drop in temperature from 300 to 70 K indicates the effect of the crystal field to be the major factor governing the nature of the compound. However, the low value of anisotropy at room temperature is due to some sort of averaging, resulting from the contributions of the various energy levels which are all populated at this temperature.

In an attempt to explain the experimental findings, a crystal-field calculation with Russell-Saunders coupling between the Pr^{3+} ions was carried out. The crystal-field parameters were chosen to be the same as those prescribed by Schwartz *et al.* The energy-level pattern of the ground $^3H_4$ term thus obtained is not consistent with experiment. The experimental observation is of two singlet levels lying lowest and the third level a doublet, while the calculation gives the first excited level to be a doublet and the second a singlet. Thus, the pattern, as well as the splitting of the lowest three levels, are different from those inferred experimentally. Calculations were extended to obtain the magnetic anisotropy and found that it does not show a reversal of sign anywhere between 300 and 70 K. The crystal-field parameters were varied with no fruitful results. The calculation with RS coupling could explain neither the magnetic susceptibility and anisotropy data nor the optical absorption spectra. The observation of Judd[5] was similar. He concluded that RS coupling was totally inadequate to explain the various multiplets of praseodymium magnesium double nitrate.

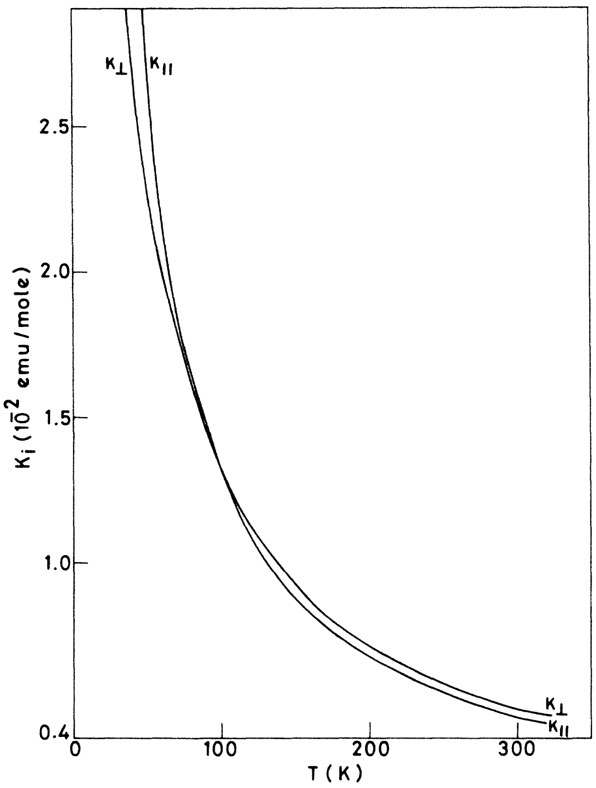

FIG. 2. Temperature dependence of the susceptibilities in directions parallel and perpendicular to the crystal *c* axis.

The effect of intermediate coupling is sufficient to strongly mix states of different *L* and *S*. A calculation within the intermediate-coupling scheme, with the electrostatic and spin-orbit coupling parameters chosen to be the same as those given by Schwartz *et al.*, was conducted. The results are given in Table I. The pattern of the crystal-field energy levels thus obtained is consistent with the optical-absorption experiment. The magnetic anisotropy shows a reversal of sign at 87 K and a maximum at 160 K (Fig. 1). Calculations including intermediate-coupling effects gave fruitful results, yet the temperature dependence of the magnetic anisotropy does not agree with experimental observation. The various A_{mn} parameters are now varied to match the magnetic measurements from 300 to 70 K as well as the crystal-field splitting of the energy levels.[1] The best set of crystal-field parameters thus obtained is given by $A_{20}=150$, $A_{40}=-1570$, $A_{60}=623$, $A_{66}=390$, $A_{43}=1158$, and $A_{63}=330$, all in cm^{-1}.

It is noted that the values of A_{40}, A_{60}, A_{66}, A_{43}, and A_{63} differ from the corresponding values given by Schwartz by 4%, 1%, 6%, 2.6%, and 7%, respectively. None of these deviations is appreciable, yet the present crystal field gives an elegent match with the experiments. It may be recalled that Schwartz put no emphasis on the

TABLE I. Crystal-field splitting and the eigenfunctions of the ground $^3H_4$ term in PrODA. μ denotes the crystal quantum numbers.

Experimental observation[a]		Using Schwartz parameters[a]				Result of present work		
		First-order calculation		Calculation including intermediate coupling				
D_3 states	Energy levels (cm^{-1})	μ	Energy levels (cm^{-1})	μ	Energy levels (cm^{-1})	μ	Energy levels (cm^{-1})	Eigenfunctions
$1A_1$	0	3	−149.2073	3	−153.1600	3	−161.6159(0)	$-0.7071\,\|3\rangle-0.7071\,\|-3\rangle$
A_2	20	±1	−146.3130	0	−144.4724	0	−148.6057(13.0)	$-0.6406\,\|3\rangle+0.4234\,\|0\rangle+0.6406\,\|-3\rangle$
$1E$	28	0	−129.2250	±1	−143.9452	±1	−147.7739(14.0)	$0.0321\,\|\pm4\rangle+0.1370\,\|\pm1\rangle+0.9901\,\|\mp2\rangle$
$2E$		±1′	−67.4390	±1′	−66.5272	±1′	−68.3131(93.3)	$-0.6147\,\|\pm4\rangle+0.7838\,\|\pm1\rangle-0.0885\,\|\mp2\rangle$
$2A_1$		0′	220.0436	0′	222.8280	0′	229.0615(390.7)	$0.2994\,\|3\rangle+0.9059\,\|0\rangle-0.2994\,\|-3\rangle$
$3E$		±1″	242.9473	±1″	247.7808	±1″	256.5733(418.2)	$0.7881\,\|\pm4\rangle+0.6057\,\|\pm1\rangle-0.1093\,\|\mp2\rangle$

[a] Reference 1.

best set of crystal-field parameters; rather, an attempt was made to produce a reasonable set of parameters which would allow the maximum number of transitions to be assigned. The influence of J mixing is negligibly small on the ground $^3H_4$ term and hence is omitted from the present calculation. By carrying out calculations including intermediate-coupling effects, accurate descriptions of the states corresponding to the observed transitions are obtained. The lowest intermediate-coupled free-ion state in Pr^{3+} is

$$\psi=0.9921\,|^3H_4\rangle+0.1233\,|^1G_4\rangle-0.0228\,|^3F_4\rangle\ .$$

Schwartz *et al.* reported the positions and crystal-field splittings of the six states $^3P_0$, $^3P_1$, $^3P_2$, $^1D_2$, $^1I_6$, and $^3H_4$. It is quite unfortunate that the $^3F_3$ levels were not observed, while the presence of $^3P_1$ in the above list is of particular interest. Since they are the only levels in f^2 possessing J values of three and one, respectively, their positions are thus unaffected by deviations from RS coupling and are used as positions of reference in the configuration.

It is seen from Table I that the positions of two experimentally observed excited levels are different from their respective calculated values, using the present crystal field. The difference is not much, in view of the fact that an error of $\pm10\ cm^{-1}$ was included in the experimental determination of energy levels by Schwartz *et al.* The calculated value of energy for the first excited state is well within the limit of experimental error. The value for the second excited one differs appreciably from its experimental value. It is to be noted that the spectral measurements by Schwartz *et al.* were performed at low temperatures, where the site symmetry is lower than D_3 and each degenerate level is split. The second excited state was observed to split to levels at 24 and 32 cm^{-1}.[1] Hence, the energy-level diagram presented by Schwartz does not exactly depict the situation at higher temperatures. Any attempt to make the difference small yields anisotropy values which are definitely outside the range of experimental error.

The crystal-field splitting of the ground $^3H_4$ J manifold of PrODA is obtained as 419 cm^{-1}. This is larger than the splitting in other compounds of praseodymium. The average magnetic moment is obtained as 3.42 Bohr magnetons at 300 K, which is lower than the value 3.62 Bohr magnetons expected from its free-ion ground term. These observations indicate the importance of the crystal-field effect in this compound.

The temperature dependence of the susceptibilities (Figs. 1 and 2) obey the Curie-Weiss law over a large temperature range as given below:

$$K_{\parallel}=1.4516/(T+11\ \mathrm{K})\quad(300-100\ \mathrm{K})\ ,$$

$$K_{\perp}=1.5385/(T+15\ \mathrm{K})\quad(300-20\ \mathrm{K})\ ,$$

$$\bar{K}=1.5228/(T+17\ \mathrm{K})\quad(300-70\ \mathrm{K})\ .$$

The Weiss constant is different along different crystallographic axis directions. The values of the Curie constant are lower than the free-ion value 1.63. These are purely crystal-field effects.

Figure 3 shows the temperature dependence of the Schottky heat capacity. A flat maximum occurs at 200 K

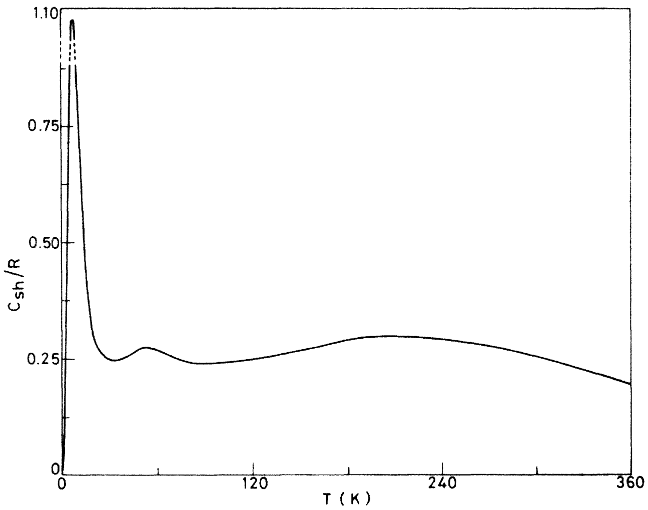

FIG. 3. Temperature dependence of the Schottky heat capacity from 360 to 2 K.

and a small maximum at 50 K. With a further decrease of temperature, the Schottky contribution rises abruptly and there is a sharp peak at 8 K. Thereafter, it falls rapidly with the decrease of temperature, up to 2 K. The positions of the maxima could not be confirmed due to a lack of experimental data.

V. CONCLUSION

Schwartz assumed a second-order crystalline phase transition at low temperatures.[1] The crystal was assumed to undergo a gradual $R32 \rightarrow P3_121$ (or $P3_221$) transformation, owing to the movement of a Na^+ ion off the threefold axis. It lowered the lanthanide site symmetry to C_2, which was considered responsible for the lifting off of the degeneracy of the states at 77 K. I explored this possibility but failed to notice any development of anisotropy in the isotropic (001) plane perpendicular to the *c* axis. The macroscopic crystal symmetry retains the threefold axis even at 70 K. The crystal-field calculation within the D_3 point group gives a reasonably good fit of the experimentally observed energy levels and supports the assignments of the crystal-field components by Schwartz.

It is recalled that only small distortions from D_3 symmetry were observed at the lanthanide sites by Schwartz, and no strain was observed in crystals at low temperatures. Polarization behavior in absorption, the EPR results, and the polarized Zeeman data all indicated that the axes of spin quantization and polarization of the molecule lie only a few degrees from the crystal threefold axis and not along C_2. The MCD data are also consistent with this interpretation. Recent reinvestigation of the crystal structure of Cerium oxydiacetate by Albertsson and Elding[19] has not revealed any such phase transition. Hence, the low-symmetry crystal field is small, allowing C_2 symmetry to be treated as a small perturbation on the D_3 symmetry. It is concluded that the microscopic distortion, without disturbing the macrosymmetry of the crystal, takes place at low temperatures.

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