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The Structures and Crystal Chemistry of Magnesium Chloride and Cadmium Chloride

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The crystal structures of $MgCl_2$ and $CdCl_2$ have been refined using powder X-ray diffraction data. They have space group $R\bar{3}m$. For magnesium chloride a = 3.6363(1) Å, c = 17.6663(5) Å, V = 202.31 $Å^3$, D_x = 2.35 g cm^{-3}, Mg 0,0,0; Cl 0,0,0.25784(8), and for cadmium chloride a = 3.8459(1) Å, c = 17.4931(4) Å, V = 224.07 $Å^3$, D_x = 4.08 g cm^{-3}, Cd 0,0,0; Cl 0,0,0.2520(1). d (Mg–Cl) = 2.4873(6) Å (6 ×), d (Cd–Cl) = 2.637(1) (6 ×). The structures and their relationship to that of fluorite are discussed within the framework of a simple Born–Mayer model.

Introduction

In contrast to the alkali halides, the alkaline earth halides adopt a wide variety of structures with metal coordination numbers ranging from 4 to 9 (*1*). Thus the equilibrium structures of $BeCl_2$, $MgCl_2$, $CaCla_2$, $SrCl_2$, and $BaCl_2$ are all different. Collectively they provide a much more stringent test of models, such as the Born–Meyer ionic model, of interatomic forces than do those of the alkali halides. Other than the fluorite structure of CaF_2, SrF_2, BaF_2, and $SrCl_2$, the structures of MgF_2 (with the rutile structure) and of $MgCl_2$ (with the $CdCl_2$ structure) are the simplest, being determined by two lattice parameters and one internal positional parameter. The interpretation of the details of the rutile structure remains a topic of lively debate (*2, 3*) and the structures of a number of rutiles have been the subject of accurate refinements. It is somewhat surprising therefore that the structures of $MgCl_2$ and $CdCl_2$ have not been quantitatively determined although the structures of some isostructural transition metal halides have been refined (*4, 5*). However, it is known (*6, 7*) that for rutile-structure fluorides of the transition metals the structural details are influenced by the open *d* shell and one might expect similar effects in the chlorides. Accordingly we have undertaken a refinement of the $MgCl_2$ and $CdCl_2$ structures (with d^0 and d^{10} cations). The simplicity of the structures led us to expect that they could be accurately refined using modern powder X-ray diffraction techniques.

The structure type of $MgCl_2$ and $CdCl_2$ is usually known as the $CdCl_2$ or *C*19 type and has been described (*8*) as consisting of cubic eutaxy ("close packing") of Cl atoms with Mg in the octahedral interstices of alternate layers. This description emphasizes the layer nature of the structure. We find, however, that the departure from ideal eutaxy is significant and that the coordination octahedra are far from regular.

Experimental

Magnesium chloride powder from Aldrich Chemical Co. with a stated water content of

0022-4596/91 $3.00

less than 1.5% was used. The crystals have an extremely tabular, almost micaceous, habit as might be expected of a layer structure. The cadmium chloride sample came from Johnson Matthey and was reported to be anhydrous and have a purity of 99.995%. Both $CdCl_2$ and $MgCl_2$ are very hygroscopic so they were always maintained under a purified argon atmosphere.

Ground samples of the materials were loaded into an environmental cell with a kapton window (*9*) and X-ray data collected on a Rigaku D/max IIB spectrometer using $CuK\alpha_1$ radiation. The data consisted of two sets, each being a sum of 10 step scans, one of 0.02° steps at a rate of 3.0°/min for the $2\theta = 5°$ to 80° set, and the other of 0.04° steps and 3.0°/min for the $2\theta = 80°$ to 140° set.

The structure refinement using program GSAS (*10*) was not entirely straightforward for the magnesium chloride data. Despite our efforts there was substantial preferred orientation to be corrected for: $R_0 = 0.79$ for the best data set, where R_0 is defined (*10*) in terms of $O_{p,h}$ the preferred orientation coefficient of Dollase (*11*). An initial refinement in space group $R\bar{3}m$ gave reasonable coordinates but unrealistic thermal parameters. A difference Fourier synthesis at this stage showed substantial electron density in the region between the $MgCl_2$ layers (which we had supposed to be empty). After considering and rejecting several models (such as Mg disorder, or possible intercalated water) we finally concluded that the origin of the effect was the presence of antiphase boundaries in the material as illustrated schematically in Fig. 1. This was modeled by dividing the Mg and Cl atoms into two sets displaced from one another by $0,0,\frac{1}{2}$. Allowing the occupancies of the two sets to vary, subject to the constraint that their sum was one, resulted in a satisfactory refinement with the relative occupancies of 0.89 : 0.11 for the two sets. We were now able to obtain reasonable anisotropic temperature factors.

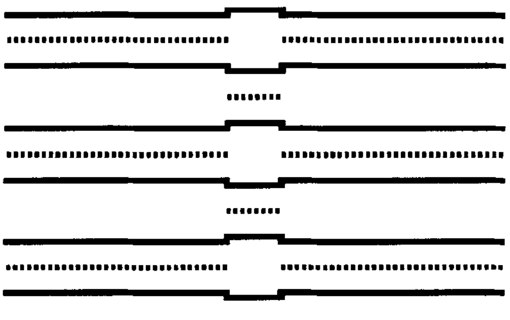

FIG. 1. A possible antiphase boundary in $MgCl_2$. Layers of magnesium and chlorine are shown as dashed and solid lines respectively.

In the refinement of the cadmium chloride data, it was evident that a trace of the second phase was present. The second phase was identified as $CdCl_2 \cdot H_2O$ and estimated to consist of less than 4 mole% of the total sample.

The final refinement of the magnesium chloride data used 4798 data points for 72 reflections; $\chi^2 = 5.00$, $R_{wp} = 0.15$, and $R_p = 0.10$ for a total of 29 parameters. The cadmium chloride data used 3998 data point for 74 reflections; $\chi^2 = 2.92$, $R_{wp} = 0.10$, and $R_p = 0.07$ for a total of 38 parameters. Structural parameters are reported in Table I and selected interatomic distances and angles in Table II. A surprisingly wide range of lattice parameters has been reported in the literature for $MgCl_2$; our results (Table I) are in good agreement with a recent determination (*12*). See Figs. 2 and 3 for a final fit to data.

Discussion

The structure would consist of perfect cubic eutaxy (close packing) of the Cl atoms if $c/a = \sqrt{24} = 4.898\ldots$, and $z_{Cl} = \frac{1}{4}$. The observed values are $c/a = 4.858$ and $z_{Cl} = 0.2578$ for $MgCl_2$ and $c/a = 4.549$ and $z_{Cl} = 0.2520$ for $CdCl_2$. Because of the large c axis, the apparently small departure of z_{Cl} from $\frac{1}{4}$ represents a significant distortion of

TABLE I

STRUCTURAL DATA FOR $MgCl_2$ AND $CdCl_2$[a]

	Atom	x	y	z	U_{11}	U_{33}	U_{12}
$MgCl_2$	Mg	0	0	0	0.025(2)	0.027(2)	0.012(2)
	Cl	0	0	0.25784(8)	0.045(2)	0.003(1)	0.0220(9)
$CdCl_2$	Cd	0	0	0	0.015(2)	0.027(2)	0.007(9)
	Cl	0	0	0.2520(1)	0.017(2)	0.012(2)	0.009(1)

[a] Space group $R\bar{3}m$, $MgCl_2$: $a = 3.6363(1)$ Å, $c = 17.6663(5)$ Å; $CdCl_2$: $a = 3.8459(1)$ Å, $c = 17.4931(4)$ Å. Temperature factors in Å^2: $U_{22} = U_{11}$, $U_{13} = U_{23} = 0$.

the octahedra. The octahedra that are occupied by Mg are flattened (edges perpendicular to the threefold axis are longer than the others) and the empty octahedra are elongated. The ratio of the short and long edges of the occupied octahedra in $MgCl_2$ is $\rho = 0.934$. The corresponding measure of the elongation of the empty octahedra is the ratio of the long and short edges $\sigma = 1.057$. In $CdCl_2$ both the occupied and the empty layers are flattened, although the occupied layers are slightly more so; $\rho = 0.938$ and $\sigma = 0.968$. In Table III these quantities ρ and σ are compared for $MgCl_2$, $CdCl_2$, $CoCl_2$, $NiCl_2$, $FeCl_2$, and $SrCl_2$ (with the fluorite structure).

It has long been recognized (*13*) that there is a simple relationship of the fluorite structure to that of $CdCl_2$ (and of rutile). Specifically the fluorite structure may be considered a special case of the $CdCl_2$ structure with $c/a = \sqrt{6} = 2.449\ldots$, $z = 0.25$, and $\rho = \sigma = 1/\sqrt{2} = 0.707\ldots$. This relationship is illustrated in Fig. 4. The interesting questions that are to be answered are what factors determine which structure is adopted and what determines the observed parameters. Here we use the simplest possible nontrivial ionic model to get some insight into these questions.

In the ionic model, in addition to the electrostatic energy, one must include a repul-

TABLE II

INTERATOMIC DISTANCES AND ANGLES[a] IN $MgCl_2$ AND $CdCl_2$

$MgCl_2$			
Mg–Cl	2.4873(8) (6×)	Cl–Mg–Cl	86.06(4) (6×)
			93.94(4) (6×)
Cl–Cl	3.395(2) (3×)[b]	Mg–Cl–Mg	93.94(4) (3×)
	3.845(2) (3×)[c]		
	3.6363(1) (6×)		
$CdCl_2$			
Cd–Cl	2.637(1) (6×)	Cl–Cd–Cl	86.36(5) (6×)
			93.64(5) (6×)
Cl–Cl	3.609(1) (3×)[b]	Cd–Cl–Cd	93.64(5) (3×)
	3.721(1) (3×)[c]		
	3.8459(1) (6×)		

[a] Å and degrees.

[b] Occupied octahedron.

[c] Empty octahedron.

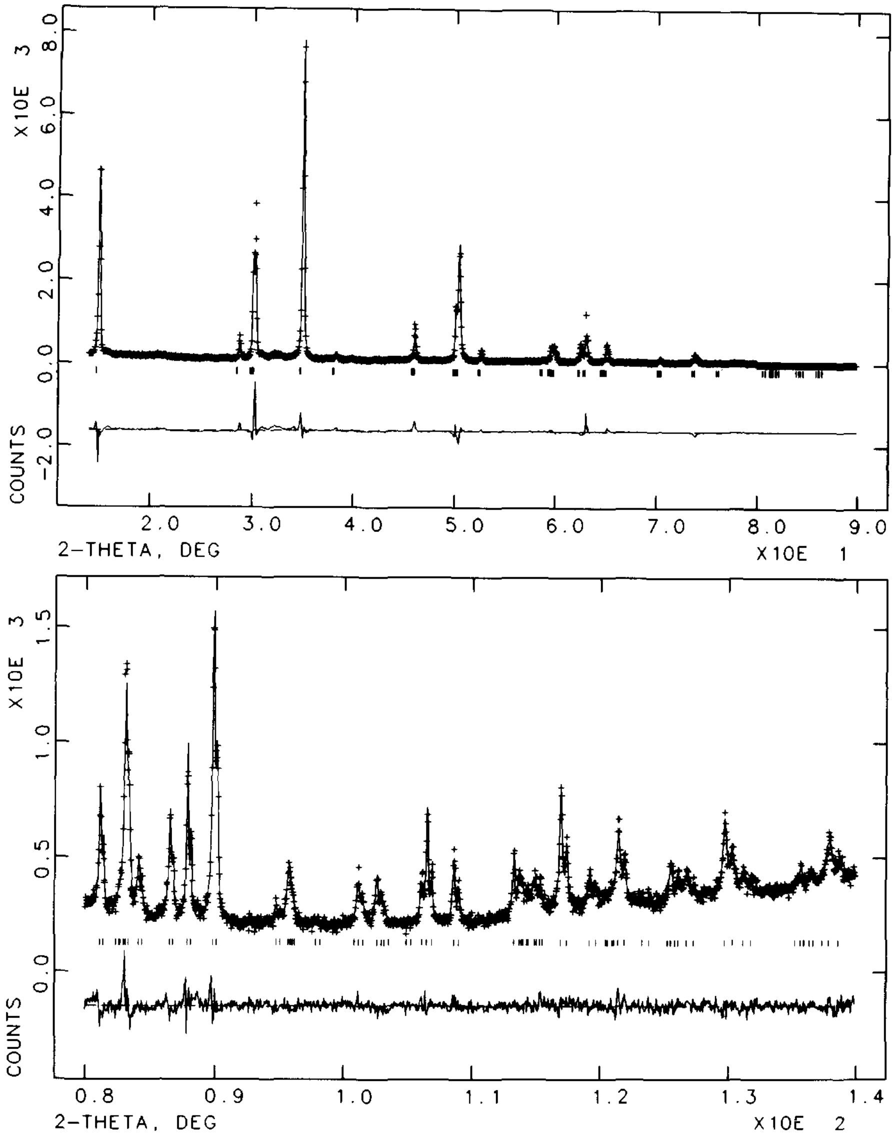

FIG. 2. X-ray diffraction profile fit for $MgCl_2$. The data from 80° to 90°are omitted on histogram 1. The data are shown as (+). The solid line is the calculated profile and the difference curve is shown at the bottom on the same scale. Reflections resulting from both $K\alpha_1$ and $K\alpha_2$ are shown.

sive term to stop the crystal collapsing. In MCl_2 (M = Mg, *etc.*) one must consider at least M . . . Cl and Cl . . . Cl terms. The stoichiometry ensures that M . . . M distances are substantially greater. For the Cl . . . Cl interaction we use the Dashevsky potential quoted by Kitaigorodsky (*14*) as Dashevsky's potentials have been shown to be applicable to simple crystal structures in similar contexts [e.g., Ref. (*2*)]. The Cl . . . Cl repulsive energy is $E_{\mathrm{rep}} = B_{\exp}(-\alpha d)$ with (rounded to two digits) B =

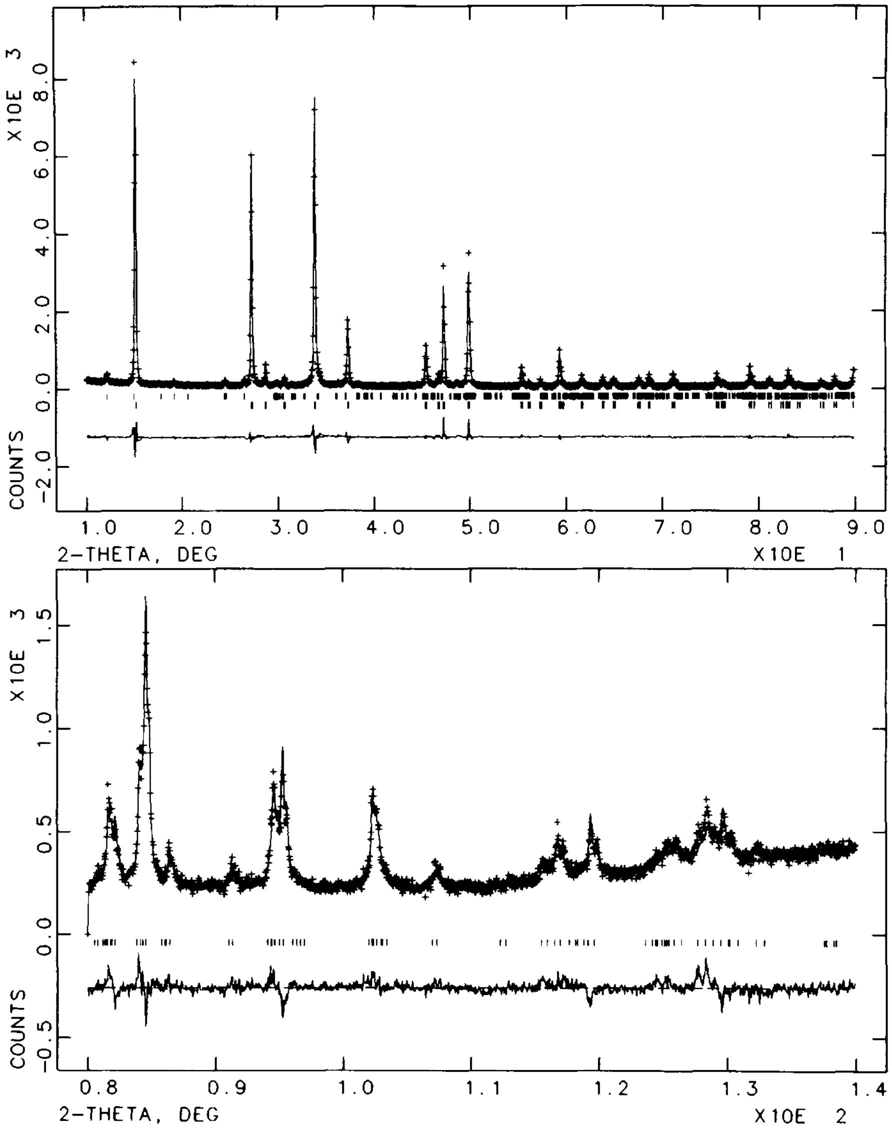

FIG. 3. X-ray diffraction profile fit for $MgCl_2$. The data are shown as (+). The solid line is the calculated profile and the difference curve is shown at the bottom on the same scale. Reflections resulting from both $K\alpha_1$ and $K\alpha_2$ are shown. The lower set of reflection markers is for the second phase, $CdCl_2 \cdot H_2O$.

1.0×10^6 kJ mol^{-1} and $\alpha = 3.5$ Å^{-1}. Here d is the interatomic distance. For the M . . . Cl interaction we take the same exponent. We do this as very similar exponents are appropriate for cation . . . anion repulsions in the alkali halides [e.g., for Na . . . Cl $\alpha = 3.2$ Å^{-1} (*15*)]. We take the preexponential term for the M . . . Cl interaction to be rB where r is a variable, dimensionless parameter and B has the value given above. The value of r is a measure of the "size" of the cation in the sense that the

TABLE III

COMPARISON OF CHLORIDE STRUCTURES[a]

Compound	a	$c/\sqrt{6}a$	ρ	σ	Reference
$NiCl_2$	3.483	2.039	0.970	1.055	(*5*)
$CoCl_2$	3.553	1.995	0.951	1.045	(*4*)
$FeCl_2$	3.603	1.935	0.946	1.012	(*4*)
$MgCl_2$	3.636	1.983	0.934	1.057	This work
$CdCl_2$	3.864	1.857	0.938	0.968	This work
$SrCl_2$	4.926	1.000	0.707	0.707	(Fluorite)

[a] ρ and σ are the ratios of edge lengths of the occupied and unoccupied Cl_6 octahedra as defined in the text.

M–Cl distance in the minimum energy structure increases smoothly with r. The electrostatic energy, E_{el}, is calculated by standard methods (*15*) using integral charges on the ions.

Once B and α are chosen the crystal energy, $E_{el} + E_{rep}$, is a function only of the structural parameters a, c, and z and of r. Figure 5 shows the lattice parameters a and $c/\sqrt{6}$ for the minimum energy structure as a function of r. $c/\sqrt{6}a = 1$ corresponds to the fluorite structure (cubic eutaxy of the cations). Several features of the results are noteworthy. (i) The model predicts that as a increases c will decrease in accord with observation for chlorides (Table III). (ii) The point corresponding to $c/\sqrt{6}a = 2$ (at approximately $r = 0.11$) corresponding to cubic euatxy of the *anions* has no special significance. (iii) There is an abrupt transition to the fluorite structure with increasing r so that compounds with $c/\sqrt{6}a$ not much greater than 1 are not expected to be observed and indeed have not so far been reported; the smallest value of $c/\sqrt{6}a$ in Hulliger's (*16*) compilation of lattice parameters of $CdCl_2$ structure compounds is for Cs_2O with $c/\sqrt{6}a = 1.80$. (iv) Remarkably (considering the simplicity of the model) the magnitudes of the calculated lattice parameters are close to those actually observed for chlorides (see Fig. 5). (v) To high accuracy

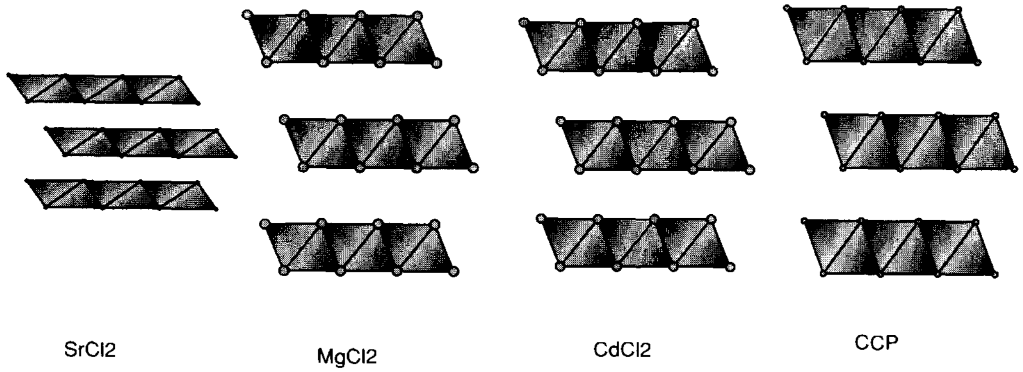

FIG. 4. A comparison of the structures of $MgCl_2$, $CdCl_2$, and $SrCl_2$. The scale is chosen so that the Cl–Cl distances in the close-packed planes are the same in each case.

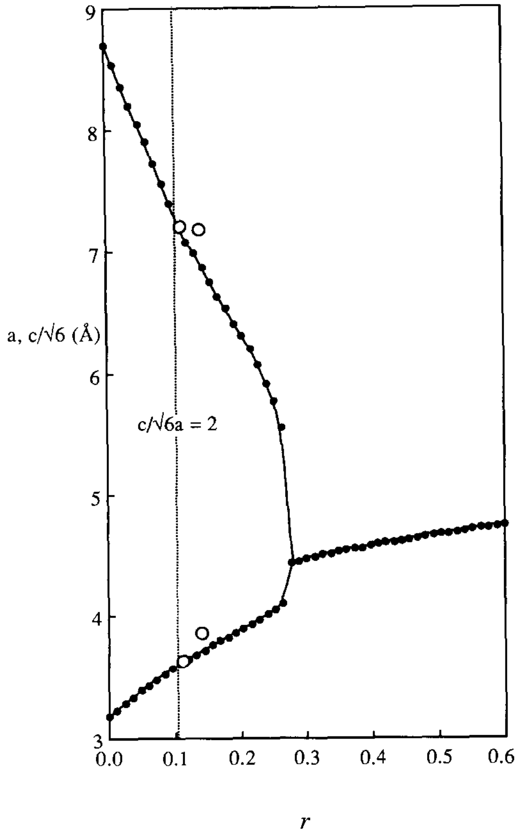

FIG. 5. Predicted evolution of the lattice parameters a and $c/\sqrt{6}$ for the minimum-energy $CdCl_2$ structure with cation "size" parameter r. The range ($r > 0.27$) where $a = c/\sqrt{6}$ corresponds to the fluorite structure. The large open circles are the experimental data for $MgCl_2$ (left) and $CdCl_2$ (right).

the z parameter has a value $\frac{1}{4}$ for the range where $a = c/\sqrt{6}$ and increases for increasing c/a (as observed for $MgCl_2$ and $CdCl_2$).

The bond valence parameters, R, relating bond length, d, and valence, v, in $d = R + b \ln v$ for Mg–Cl, Cd–Cl, Ca–Cl, and Sr–Cl bonds are (with $b = 0.37$ Å) 2.08, 2.23, 2.37, and 2.51 Å, respectively (*17*). Accordingly it is expected that Ca–Cl bonds will be 0.14 Å longer than Cd–Cl bonds and 0.14 Å shorter than Sr–Cl bonds so that $CaCl_2$ should be close to the $CdCl_2$–fluorite transition. It is frustrating that in practice $CaCl_2$ adopts a different structure. The orthorhombic $CaCl_2$ structure is just a small distortion of the tetragonal rutile structure (*18*), and using our simple model we find the rutile structure to be the minimum energy configuration of the $CaCl_2$ structure. This is because we have omitted the attractive (C/d^6) part of the Cl . . . Cl potential which has been shown (*2*) to be necessary to reproduce the details of these structures. It is also found that for $r < 0.6$ the $CaCl_2$/rutile structure is very slightly more stable (energy lower by typically 1%) than the $CdCl_2$/fluorite structure. This observation bolsters our belief that modeling the alkaline earth halide structures will provide a good test of theoretical methods. On the experimental side, the effect of pressure on the structure of, e.g., $MgCl_2$ would be very interesting (to see *inter alia* whether a $CaCl_2$ structure appears). Such studies are planned.

Acknowledgments

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