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Phase transitions in $M(ClO_4)_2 \cdot 6H_2O$ (M = Mg, Zn). Investigations by adiabatic calorimetry and infrared spectroscopy[a)]

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Infrared spectra of $Mg(ClO_4)_2 \cdot 6H_2O$ at 10 K indicate a complex structure containing at least 16 distinct types of water protons. At 107.9 K this structure transforms sharply to a much simpler disordered form ($\Delta S_{trans} = 7.754\ J\ K^{-1}\ mol^{-1}$), and at 273.2 K it transforms more gradually to a form in which all water protons are equivalent ($\Delta S_{trans} = 8.25\ J\ K^{-1}\ mol^{-1}$). There is also a phase transition at 325.36 K ($\Delta S_{trans} = 21.9\ J\ K^{-1}\ mol^{-1}$). Infrared spectra of $Zn(ClO_4)_2 \cdot 6H_2O$ at 10 K indicate a disordered structure, with a continuum of proton environments, probably related to the structure of the Mg compound above 107.9 K. The phase transitions in the Zn compound at 70.1, 209.8, 290.5, and 349.0 K ($\Delta S_{trans} = 3.70, 0.08, 9.50$, and $21.6\ J\ K^{-1}\ mol^{-1}$, respectively) occur without a major change in the infrared spectrum. The measured entropy changes in the Mg, Zn, and Cd compounds appear to be related to the number of distinguishable types of water protons that already exist at 10 K.

I. INTRODUCTION

In molecular or ionic species with weak orientational forces, and therefore many positional potential minima, solid state phase tranformations are well known. The determination of the phase diagrams of such materials, in conjunction with the investigation of the microscopic processes that give rise to the phase transformations, can lead to a better understanding of weak intermolecular interactions. The purpose of this paper is to describe the experimental investigation of phase transitions in a series of compounds that exhibit solid state polymorphism.

Phase transitions in salts of the general formula $M(ClO_4)_2 \cdot 6H_2O$ (M = Mg,Zn,Cd) have been studied by electron paramagnetic resonance,[1-8] ^1H NMR,[9-11] infrared,[12,13] and Raman[14] spectroscopy, and adiabatic calorimetry.[13,15,16] The overall structure of these solids is known[17] to be hexagonal with octahedrally coordinated $[M(OH_2)_6]^{2+}$ units surrounded by ClO_4^- ions, and, in principle, there could be several phase transitions in $M(ClO_4)_2 \cdot 6H_2O$, associated with rearrangements of the waters of hydration, disorder of the perchlorate ions, and tumbling of the $[M(OH_2)_6]^{2+}$ units.

In a series of compounds such as this, it is quite common to see general trends in phase transitions as the metal is changed, and these trends often can be linked to changes in the lattice constants and, therefore, to the binding forces. However, this particular series has another structural variation associated with the change in metal: positional disorder of $[M(OH_2)_6]^{2+}$ along the *c* axis. This can be envisaged most easily by comparison of the structures of $M(ClO_4)_2 \cdot 6H_2O$ with $LiClO_4 \cdot 3H_2O$. In the latter, each Li^+ is octahedrally coordinated to six H_2O such that chains of $[Li(OH_2)_3^+]_x$ run parallel to the *c* axis.[18,19] The structures of the divalent metal perchlorate hexahydrates can be derived from that of $LiClO_4 \cdot 3H_2O$ by the removal of alternate metal ions along the *c* axis in order to compensate for the valency change. The metal ions can be removed at either 1/4 *c* or 3/4 *c*, and in fact different structures exist, depending on which positions the metal ions take.[20,21] In $Cd(ClO_4)_2 \cdot 6H_2O$, all the metals are at the same height in the unit cell, and the structure is the most ordered of the series. In $Mg(ClO_4)_2 \cdot 6H_2O$ there is a complicated but *periodic* arrangement of the metal ions, described by West[17] as "cyclic threeling" (threefold vertical twinning axis), in which the orthorhombic cell consists of Mg atoms at 1/4 *c* in the corner columns and at 3/4 *c* in the central column. Following Ghosh and Ray,[21] we can call this lattice type *A*, and can call the lattice in which metal atoms are at 3/4 *c* in the corner columns and at 1/4 *c* in the central column type *B*. The structure of $Zn(ClO_4)_2 \cdot 6H_2O$ then can be described in terms of indefinite periodicity of *A* and *B* lattices such that a sequence of lattice types along the *b* axis undergoes *random* shifts between *A* and *B*, and the overall periodicity may be, for example, *AAAABBAAABBBBB*.... In this paper we will examine the relationship between the differences in phase diagrams and differences in structures of $Cd(ClO_4)_2 \cdot 6H_2O$, $Zn(ClO_4)_2 \cdot 6H_2O$, and $Mg(ClO_4)_2 \cdot 6H_2O$.

In order to settle conflicting earlier reports concerning phase transitions in these compounds, we have undertaken a systematic study of the solid phase of divalent metal perchlorate hexahydrates by adiabatic calorimetry (to determine definitively the phase diagrams, and also the thermodynamic parameters associated with the phase changes) and infrared spectroscopy (to examine the microscopic changes at the phase transitions). We have already reported the results of adiabatic calorimetric investigations of $Mg(ClO_4)_2 \cdot 6H_2O$,[16] and calorimetric and infrared investigations of $Cd(ClO_4)_2 \cdot 6H_2O$.[13] This paper presents calorimetric results for $Zn(ClO_4)_2 \cdot 6H_2O$, infrared results both

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for the Zn and Mg salts, and an overall comparison of the phase diagrams and phase transitions for $Mg(ClO_4)_2 \cdot 6H_2O$, $Zn(ClO_4)_2 \cdot 6H_2O$, and $Cd(ClO_4)_2 \cdot 6H_2O$.

II. EXPERIMENTAL

For the calorimetric experiment, $Zn(ClO_4)_2 \cdot 6H_2O$ (G. F. Smith Co.) was recrystallized twice from distilled water and then an aqueous solution was allowed to crystallize slowly in a desiccator over H_2SO_4. The resultant large needles were kept in the supernatant until needed, and then the surface moisture was removed by drying between filter papers. Chemical analysis indicated 17.7 ± 0.3 mass %Zn (theoretical: 17.56). For the infrared experiments $Mg(ClO_4)_2 \cdot 6H_2O$ was prepared by recrystallization of $Mg(ClO_4)_2$ (Fisher) from water. Crystals of the Zn and Mg compounds were further recrystallized from an H_2O/D_2O solution of the desired H/D ratio.

The heat capacity of 15.8088 g of $Zn(ClO_4)_2 \cdot 6H_2O$ was measured from $T = 15$ to 370 K by a dc adiabatic calorimeter run in the heat-pulse mode. The overall precision and accuracy of the calorimeter had been determined previously to be $\pm 1\%$.[22]

For the infrared experiments, fluorocarbon or hydrocarbon mulls were prepared under a flow of dry nitrogen and then sandwiched between calcium fluoride or silver chloride windows. The mulls were kept overnight at 0.01 Torr within the cryostat prior to low-temperature spectroscopy. The procedure yielded spectra which clearly corresponded to the pure hexahydrate. (See, for example, Ref. 23.) Spectra were obtained with a Fourier-transform infrared spectrometer (Bomem DA3.02) fitted with a closed cycle helium refrigerator (Displex Model 202, Air Products and Chemicals Co.). The variable-temperature spectral runs were made in the heating mode between 10 K and room temperature. The spectral range examined was 4000 to 500 cm^{-1}. Bands singled out for closer inspection were those corresponding to OD stretching and H–O–D bending fundamentals of isotopically dilute HDO, H–O–H bending fundamental of isotopically dilute H_2O, and the symmetric stretching fundamental of the ClO_4^- ion. These modes yielded directly interpretable structural information concerning water molecules and perchlorate ions and are most likely, because of their relative sharpness, to respond with observable shifts to structural changes in the crystal.[13]

III. RESULTS

A. The phase diagram of $Zn(ClO_4)_2 \cdot 6H_2O$

The experimental molar heat capacities of $Zn(ClO_4)_2 \cdot 6H_2O$ as a function of temperature are illustrated in Fig. 1 and listed in Table I. No sample history effects were observed in the temperature region examined.

The temperatures and associated enthalpy and entropy changes of the four observed phase transformations, determined by the usual methods,[13] are given in Table II. The two higher-temperature phase transitions have been observed previously by EPR,[3,5,7] and although the EPR experiments were carried out down to $T = 77$ K, this is the first report of the two lower-temperature transformations. (It should be noted that although the present results are in conflict with apparent phase transitions detected, by earlier infrared experiments, at 233, 256.5, and 284 K,[23] that IR study is suspect[12] due to the presence of excess water in the hygroscopic samples.)

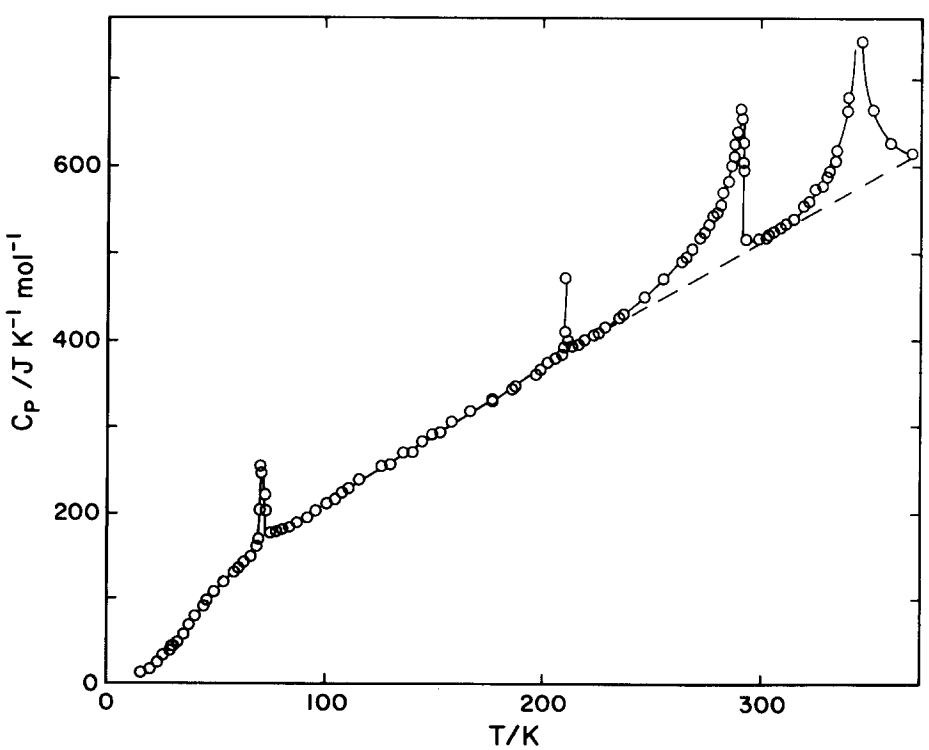

FIG. 1. The experimental heat capacity of $Zn(ClO_4)_2 \cdot 6H_2O$ as a function of temperature. Circles: experimental points; broken line: the base line heat capacity used to evaluate the transition enthalpies and entropies.

TABLE I. The experimental values of the heat capacity C_p of $Zn(ClO_4)_2 \cdot 6H_2O$.

T(K)	C_p (J K^{-1} mol^{-1})	T(K)	C_p (J K^{-1} mol^{-1})	T(K)	C_p (J K^{-1} mol^{-1})	T(K)	C_p (J K^{-1} mol^{-1})
15.26	13.90	75.78	171.6	206.02	380.0	286.24	599.4
19.52	18.98	76.04	173.1	206.65	383.4	287.14	612.1
19.65	20.33	77.07	177.9	207.85	383.2	288.46	627.3
22.59	26.47	78.58	176.9	208.06	384.8	289.40	639.9
22.70	27.16	79.00	176.4	208.17	385.6	290.12	650.8
25.14	34.36	79.77	182.5	208.31	382.1	290.63	666.8
29.48	38.52	81.13	179.4	209.44	389.6	291.04	655.3
30.70	44.17	82.61	182.6	209.63	409.5	291.32	626.4
32.27	49.45	84.38	181.3	209.85	472.0	291.35	604.8
34.92	58.12	87.12	189.6	209.99	399.9	291.88	595.2
35.67	63.33	91.14	196.8	210.22	389.4	292.46	519.5
37.22	68.55	95.42	204.4	211.71	394.4	292.96	516.3
40.42	80.80	96.65	202.8	211.80	391.3	299.35	517.8
41.01	82.10	99.39	212.8	213.25	391.5	301.72	518.3
43.93	92.74	102.79	215.8	216.07	395.0	302.48	516.5
45.24	97.12	106.68	225.6	218.86	399.7	303.11	517.4
48.30	107.60	110.26	228.1	221.61	405.5	304.06	520.4
49.08	110.10	115.40	239.5	224.78	410.0	306.51	525.2
52.97	119.70	125.81	255.7	224.97	411.1	309.25	529.7
55.17	125.30	129.27	256.7	227.60	415.2	310.88	535.0
55.70	125.80	135.41	270.2	234.59	427.6	312.07	531.5
57.96	132.90	138.64	269.9	236.74	431.8	315.05	539.1
58.98	134.70	144.54	283.8	236.89	432.4	319.55	556.0
59.14	136.50	148.47	291.9	245.89	449.1	321.83	560.0
62.14	143.60	151.94	293.7	245.98	450.8	321.89	557.3
63.10	144.90	157.26	306.0	254.25	468.7	324.33	575.0
63.44	144.50	166.47	319.9	255.30	471.9	327.83	576.2
63.77	145.20	176.02	333.6	263.17	492.6	329.30	590.4
64.71	147.30	176.97	330.8	264.68	495.6	331.69	594.1
65.63	149.50	177.81	334.4	265.78	501.0	334.38	607.2
65.73	155.90	186.32	343.7	268.31	505.2	334.52	619.3
66.55	158.70	186.55	349.0	268.36	508.4	340.05	664.4
67.58	162.80	187.93	348.8	270.74	518.0	340.83	679.9
68.66	170.30	195.78	358.8	273.27	524.1	344.68	766.6
68.94	205.40	196.20	361.6	275.09	529.7	347.76	1006.0
69.66	254.00	198.51	367.1	276.02	533.3	349.12	11750.0
70.64	248.50	198.85	367.4	277.29	543.1	350.04	1368.0
71.21	222.00	200.33	371.2	278.89	547.8	352.54	665.0
71.68	203.20	201.69	374.9	281.19	556.5	359.77	626.9
73.45	170.10	202.97	372.9	282.53	570.3	369.27	615.5
73.70	176.60	204.95	377.0	284.85	584.6		
75.74	177.20	205.13	380.5	285.62	598.7		

B. Infrared spectra of $Mg(ClO_4)_2 \cdot 6H_2O$

1. Water vibrations

At 10 K the OD stretching fundamental of isotopically dilute HDO is a very complex multiplet consisting of a large number of partly resolved components of widely varying intensity, with a centroid at 2593 ± 1 cm^{-1} (Fig. 2). About 16 peaks and shoulders can be counted; this appears to be the most complex OD stretching spectrum so far reported for any crystalline hydrate.[25,26] One-to-one correspondence

TABLE II. Phase transitions in $M(ClO_4)_2 \cdot 6H_2O$.

M	T_{trans} (K)	ΔH_{trans} (J mol^{-1})	ΔS_{trans} (J K^{-1} mol^{-1})	Shape[a]	Reference
Cd	124.8 ± 0.1	2530 ± 12	20.3 ± 0.1	s	13
	238.45 ± 0.05	1260 ± 90	6.1 ± 0.4	g	13
	271.62 ± 0.05	1505 ± 15	5.54 ± 0.06	s	13
Mg	107.9 ± 0.1	800.4 ± 0.3	7.754 ± 0.003	s	16
	273.2 ± 0.1	2132 ± 3	8.25 ± 0.01	g	16
	325.36 ± 0.02	7120 ± 90	21.9 ± 0.3	g	16
Zn	70.1 ± 0.2	261 ± 1	3.70 ± 0.01	s	this work
	209.8 ± 0.1	16 ± 3	0.08 ± 0.01	s	this work
	290.5 ± 0.2	2580 ± 20	9.50 ± 0.07	g	this work
	349.0 ± 0.5	7550 ± 150	21.6 ± 0.4	g	this work

[a] s = sharp; g = gradual.

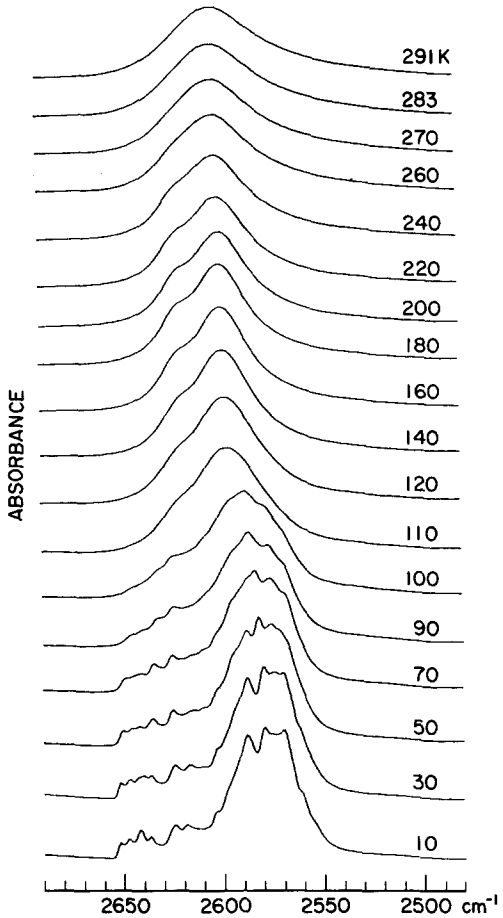

FIG. 2. OD stretching fundamental of isotopically dilute HDO in $Mg(ClO_4)_2 \cdot 6H_2O$ (3% D) at different temperatures.

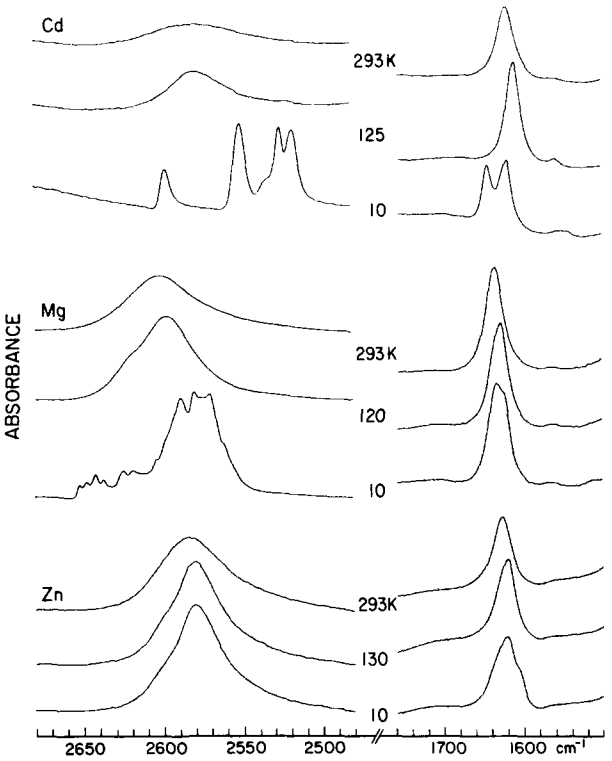

FIG. 3. Left panel: OD stretching fundamental of isotopically dilute HDO in $Cd(ClO_4)_2 \cdot 6H_2O$, $Mg(ClO_4)_2 \cdot 6H_2O$, and $Zn(ClO_4)_2 \cdot 6H_2O$ (1%–3% D) at three temperatures. Right panel: H–O–H bending fundamental of isotopically isolated H_2O in the same three compounds ($\sim$70 % D).

between OD stretching features and crystallographically distinct water hydrogens is well established,[25–27] so that the large number of spectral features implies a very complex structure with about 16 distinct hydrogens. The half-widths of many of the components are less than about 5 cm^{-1}. (Half-width is defined as full width at half-maximum.) The large range of OD frequencies, extending from 2556 to 2652 cm^{-1}, indicates a very wide variation of hydrogen-bond strengths, some of the hydrogen bonds being unusually weak.

With increasing temperature, the components of the OD stretching multiplet broaden until at 105 $\pm$ 5 K the multiplet collapses into a broad doublet centered near 2606 cm^{-1}, its main peak being at 2596 cm^{-1}, with half-width of the order of 40 cm^{-1}; a weaker component is observed at 2622 cm^{-1}. The collapse of the multiplet to a doublet appears to correspond to the phase transition at 107.9 K detected calorimetrically. The doublet indicates the existence of two distinct hydrogens, but the large width of the two components indicates either static or dynamic disorder. The 13 cm^{-1} shift of the band centroid to higher frequency above 107.9 K implies that hydrogen bonding is, on average, weaker than in the low-temperature phase.

At increasing temperatures the doublet broadens further and near 270 K it becomes a singlet. It is not clear whether this spectral change corresponds to the phase transition observed calorimetrically at 273.2 K. The occurrence of one band at room temperature is consistent with a structure in which all hydrogens and all water molecules are effectively equivalent; its large half-width indicates disorder.

The corresponding H–O–D bending fundamental at low temperature has a band shape consistent with its being an unresolved multiplet. At 10 K the main peak is centered at 1438 cm^{-1}. At 105 $\pm$ 5 K this band sharpens and becomes a well-shaped singlet, or possibly a very close unresolved multiplet, at about 1436 cm^{-1}. An unresolved doublet would be expected from the observation of a doublet in the OD stretching region. By room temperature this band has shifted to about 1442 cm^{-1}.

At 10 K, the H–O–H bending fundamental of isotopically dilute H_2O (Fig. 3) is a complex, poorly resolved band, showing at least three components, near 1634, 1630, and 1624 cm^{-1}. This indicates the occurrence of at least three distinct water molecules and is consistent with eight or more, as implied by the presence of 16 OD stretching components. At increasing temperatures the components of the multiplet gradually coalesce and at 110 $\pm$ 5 K the band sharpens into a well-shaped singlet centered at 1629 cm^{-1}, corresponding to a structure containing only one distinguishable water molecule. Above this temperature the band gradually shifts to higher wave numbers and by room temperature it has shifted to 1635.5 cm^{-1}.

2. Perchlorate vibrations

In the 10 K spectrum the degenerate stretching fundamental of ClO_4^-, $\nu_3(F)$, is a complex absorption centered at about 1100 cm^{-1} and extending over 300 cm^{-1}. The symmetric stretching fundamental ν_1 appears as a small absorption band at 933.5 cm^{-1}, with a half-width of about 8 cm^{-1} and a total intensity of the order of 1/1000 of that of ν_3. The single absorption peak in the ν_1 region implies the occurrence of either just one distinct perchlorate ion, or possibly several perchlorate ions in chemically similar sites, so that their ν_1 bands coincide within 4 cm^{-1}. The latter is more likely in view of the complex structure indicated by the water spectra. The appreciable intensity of the ν_1 band, which is infrared inactive under ideal T_d symmetry of the ClO_4^- tetrahedron, indicates distortion from tetrahedral symmetry.

Between 10 and 100 K the ν_1 fundamental undergoes little change in frequency or intensity. Between 100 and 110 K, a temperature that seems to correspond to the phase transition detected calorimetrically at 107.9 K, the band undergoes a threefold reduction in intensity similar to that observed in the spectrum of the Cd compound near 125 K. This implies a diminution of the ClO_4^- distortion. Above 108 K, the band gradually undergoes a further reduction of intensity and becomes nearly undetectable by room temperature. It is not possible to determine whether a spectral discontinuity occurs near 273.2 K, the temperature of the calorimetrically determined phase transition.

C. Infrared spectra of $Zn(ClO_4)_2 \cdot 6H_2O$

1. Water vibrations

At 10 K the OD stretching fundamental of isotopically dilute HDO is a broadband with the main maximum at 2580.2 cm^{-1} and a half-width of about 40 cm^{-1}, exhibiting a barely discernible shoulder at about 2595 cm^{-1} (Fig. 2). The corresponding H–O–D bending fundamental is a broad singlet with a maximum at 1426.5 cm^{-1} and a half-width of about 20 cm^{-1}. The H–O–H bending fundamental of isotopically dilute H_2O (Fig. 2) is a broadband with a maximum at 1622.5 cm^{-1} and a half-width of about 40 cm^{-1}, with a shoulder at about 1607 cm^{-1}. The large widths of all three of these bands are consistent with severe disorder. Their positions and half-widths, as well as their temperature shifts, resemble closely those of $Cd(ClO_4)_2 \cdot 6H_2O$ above the transition at 124.8 K.

Between 10 K and room temperature all three of these bands shift gradually to higher frequency. There are no discontinuities in the spectrum of the Zn compound corresponding to the phase transition at 124.8 K for the Cd compound and at 107.9 K for the Mg compound. The water fundamentals in the low-temperature spectra of the Zn compound do not split into sharp components as do those of the Cd and Mg compounds. However, the observed band shapes, especially the additional shoulders observed for the OD stretching and the H–O–H bending of the Zn compound at 10 K, indicate that these fundamentals also consist of several unresolved components. The shoulders disappear by about 75 K.

2. Perchlorate vibrations

As in the spectrum of the Mg compound, the symmetric stretching fundamental of the perchlorate ion $\nu_1(A_1)$ appears at 10 K as a very small absorption band at 933.0 cm^{-1} with a half-width of 6 cm^{-1} (Fig. 2). With increasing temperature, the 933 cm^{-1} band diminishes in intensity, but does so gradually, with no indication of discontinuities. In this behavior, again, the spectrum of the Zn compound resembles that of the Mg compound above 107.9 K and that of the Cd compound above 124.8 K.

IV. DISCUSSION

A. Phase transitions in $Mg(ClO_4)_2 \cdot 6H_2O$

The phase transition at 107.9 K is sharp and associated with a rather large entropy change (7.754 $J\,K^{-1}\,mol^{-1}$). The infrared experiments show that below the phase transformation there are 16 types of hydrogens and at least eight crystallographically distinct water molecules. Above the transition, there are only two types of hydrogens, and the two hydrogens on each water molecule are inequivalent and disordered. This transformation, which has previously been observed by EPR,[2] is therefore primarily due to increased disorder of the waters of hydration, although there is also some decrease in perchlorate ion distortion.

The phase change at 273.2 K also involves a substantial entropy change (8.25 $J\,K^{-1}\,mol^{-1}$), although in this case the transition is gradual, as seen in the calorimetric experiment, and also in the earlier EPR study.[2] The infrared spectra show that above this transformation all the hydrogens and all the water molecules are effectively equivalent, and highly disordered, and therefore this transition can be assigned to further disorder involving water.

The highest-temperature phase transformation in the Mg compound occurs at 325.36 K, beyond the range of the infrared experiment. However, from the calorimetric experiment it appears that this is an order–disorder transition (since it is very gradual); earlier Raman work[14] attributes this transition to increased disorder of the perchlorate ions.

B. Phase transitions in $Zn(ClO_4)_2 \cdot 6H_2O$

The phase transition at 70.1 K, detected for the first time in these experiments, is sharp and has a relatively small associated entropy change (3.70 $J\,K^{-1}\,mol^{-1}$). Even below this transition, the infrared spectra show broad featureless bands, consistent with considerable disorder of the water molecules. At about 75 K shoulders in the OD stretching and H–O–H bending spectra disappear, indicating a small increase in disorder of the water molecules at this transition.

The phase transition at 209.8 K is very sharp and involves an extremely small entropy change (0.08 $J\,K^{-1}\,mol^{-1}$), indicating that it is likely due to a subtle first-order structural change. This transformation, which has not been reported previously, does not manifest itself in changes in the infrared spectra.

The next transition in the Zn compound, at 290.5 K, is gradual and involves a rather large entropy change (9.50 $J\,K^{-1}\,mol^{-1}$). Since the water molecules are known to be disordered already below this transition, it is not surprising

that there are no drastic changes in the infrared spectra around 290 K. EPR experiments[7] leave open the possibilities of either increased perchlorate disorder or disorder of $Zn(H_2O)_6^{2+}$ as the source of this transition. We favor the latter explanation in light of comparison with the Mg salt. (See below.)

The highest-temperature transition in $Zn(ClO_4)_2 \cdot 6H_2O$ occurs at 349.0 K, again outside the temperature range of the infrared experiment. However, this transition, which is gradual and involves a very large entropy change (21.6 $J\,K^{-1}\,mol^{-1}$), has been observed in EPR experiments.[3] Based on the similarity with the transitions in the Mg compound (see below), it is likely that this transition involves disorder of the perchlorate ions.

C. Generalizations concerning phase transitions in $M(ClO_4)_2 \cdot 6H_2O$

The infrared spectra of the Mg compound between 10 and 108 K seem to correspond to those of the Cd compound between 10 and 125 K[13] but with the Mg compound having weaker average hydrogen bonding and a much more complex structure, containing at least eight distinct water molecules with a wide variety of hydrogen-bond strengths. The spectral changes occurring near 108 K for the Mg compound parallel those near 125 K for the Cd compound, and correspond to an increase of effective crystal symmetry, onset of equivalence of all water molecules, diminished distortion of the perchlorate tetrahedra, and reduction in the average hydrogen-bond strength. However, the doublet observed in the OD stretching spectrum of $Mg(ClO_4)_2 \cdot 6H_2O$, contrasted with a singlet in the spectrum of the Cd compound, indicates that in the Mg compound the two hydrogens on each water molecule are nonequivalent. This implies the point group symmetry $D_{3d}(b)$ or S_6 for the hexahydrated cation, rather than $D_{3d}(a)$ as in the Cd compound. (See Table III in Ref. 13 for the definitions of the symmetry symbols.) The spectral changes near 273 K in the spectrum of the Mg compound are not clear, and it is not certain whether they correspond to those near 271 K for the Cd compound. From the infrared spectra, at room temperature the structures of the Mg and Cd compounds appear to be similar, with effective $D_{3d}(a)$ point group symmetry for the $M(OH_2)_6^{2+}$ ion. However, hydrogen bonding is appreciably weaker in the Mg compound.

The broad water bands in the spectrum of the Zn compound at 10 K show that disorder prevails even at this very low temperature. In fact, there is a striking correlation between each of the structures and the lowest-temperature spectrum of the Cd, Mg, and Zn salts. $Cd(ClO_4)_2 \cdot 6H_2O$, which is known to have the most ordered structure with regard to the placement of the metal ions along the c axis, also has the least disorder in the waters of hydration, and smallest number of distinguishable protons at 10 K. $Mg(ClO_4)_2 \cdot 6H_2O$, which has a complex but periodic arrangement of the metal ions along the c axis, also has a large number of distinguishable protons at 10 K. At the far extreme, $Zn(ClO_4)_2 \cdot 6H_2O$ is known to have considerable disorder in the arrangement of the metal ions along the c axis, and this is reflected in the complex array of disordered waters of hydration, yielding a continuum of OD stretching frequencies at 10 K.

In each of the three salts, there is evidence for increased disorder of the waters of hydration as the temperature is increased. The entropy changes associated with the lowest transition in each compound again reflect the numbers of different types of waters of hydration that already exist at 10 K due to positional disorder in the metals: the entropy change is largest for Cd, intermediate for Mg, and smallest for Zn.

There is a pronounced similarity between the two higher transitions in the Mg compound and those in the Zn compound, in transition shape, transition temperature, and entropy change. It is therefore likely that these transitions have similar origins in $Zn(ClO_4)_2 \cdot 6H_2O$ and $Mg(ClO_4)_2 \cdot 6H_2O$. However, the entropy changes and shapes of the higher transitions in $Cd(ClO_4)_2 \cdot 6H_2O$ make it different from the Zn and Mg salts in the details of its phase changes at higher temperatures.

V. CONCLUSIONS

Experimental studies by adiabatic calorimetry and infrared spectroscopy of compounds of the general formula $M(ClO_4)_2 \cdot 6H_2O$ (M = Mg, Zn, Cd) have revealed several solid–solid phase transformations associated with onset of disorder. Three phase changes are observed for the Mg salt and for the Cd salt, and four transitions are seen in the Zn salt.

The lowest-temperature phase transition in each compound corresponds to an increased disorder in the waters of hydration. Below this transition the numbers of distinguishable protons, as determined from the infrared spectra, are closely correlated with the structures of the salts. At 10 K, $Cd(ClO_4)_2 \cdot 6H_2O$, which has the most ordered crystal structure, has the smallest number of distinguishable protons; $Mg(ClO_4)_2 \cdot 6H_2O$, which has a complex but periodic structure, has the most complex OD stretching spectrum so far reported for a crystalline hydrate; $Zn(ClO_4)_2 \cdot 6H_2O$, which has an indefinite periodicity in its structure, has a continuum of OD stretching frequencies in the lowest-temperature phase. The entropy change at the lowest-temperature transition also reflects the structural order: the entropy change increases on going from $Zn(ClO_4)_2 \cdot 6H_2O$ to $Mg(ClO_4)_2 \cdot 6H_2O$ to $Cd(ClO_4)_2 \cdot 6H_2O$.

Aside from the extremely small entropy transition in the Zn salt at 209.8 K, which is likely due to a very slight structural change, the higher-temperature transitions in the Zn compound appear to correspond to those in the Mg compound; we attribute the lower of these transitions to the onset of further disorder of the waters of hydration, and the upper transition to increased disorder of the perchlorate ions. In contrast, the intermediate transition in $Cd(ClO_4)_2 \cdot 6H_2O$ is due to perchlorate ion disorder, and the highest-temperature transition is due to three-dimensional disorder of the $[Cd(OH_2)_6]^{2+}$ complex.

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