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Transition Metal Iodates
II. Crystallographic, Magnetic, and Nonlinear Optic Survey of the 3*d* Iodates

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The anhydrous iodates of Cr, Mn, Fe, Co and β-Ni form a single isomorphous family, crystallizing in space group $P6_3$ or $P6_322$ with lattice constants typified by $Mn(IO_3)_2$ of $a = 11.178 \pm 0.002$, $c = 5.035 \pm 0.001$ Å and four formulas per unit cell; in addition, α-$Ni(IO_3)_2$ forms as a second phase. $Mn(IO_3)_2$, $Fe(IO_3)_3$, α-$Ni(IO_3)_2$ and β-$Ni(IO_3)_2$ order antiferromagnetically at 6.5, 17.0, 3.5 and 5.0 K, respectively; $Cr(IO_3)_3$ and $Co(IO_3)_2$ remain paramagnetic to 1.5 K. Below Θ_N, a weak ferromagnetic moment develops in the Mn, α-Ni and β-Ni iodates. All the anhydrous iodates generate second harmonics. $Co(IO_3)_2 \cdot 4H_2O$ and β-$Ni(IO_3)_2 \cdot 4H_2O$ crystallize isomorphously in space group $P2_1/c$, with lattice constants $a = 8.370 \pm 0.005$, $b = 6.572 \pm 0.007$, $c = 8.514 \pm 0.008$ Å, $\beta = 99.8 \pm 0.1°$ for the Co compound. $Co(IO_3)_2 \cdot 2H_2O$ is triclinic, with $a = 6.666 \pm 0.015$, $b = 10.991 \pm 0.025$, $c = 4.913 \pm 0.011$ Å, $\alpha = 93.1 \pm 0.1$, $\beta = 92.1 \pm 0.1$, $\gamma = 98.9 \pm 0.1°$, space group $P\bar{1}$, and $Ni(IO_3)_2 \cdot 2H_2O$ is orthorhombic, $a = 9.14986 \pm 0.00008$, $b = 12.20896 \pm 0.00022$, $c = 6.58353 \pm 0.00013$ Å at 298 K, space group $Pbca$. The Co iodate hydrates are paramagnetic to 1.5 K; both Ni hydrates are antiferromagnetic, the dihydrate also developing a weak ferromagnetic moment. The lattice spacings of all 11 compounds are presented, 9 with indexing.

1. Introduction

The nonbonded electron pair and high refractive index characteristic of the iodate ion favors the formation of acentric crystals with nonlinear optical properties. The iodates of the alkali metals, H, Tl and NH_4 crystallize in acentric point groups; many are optically phase matchable (*1*, *2*). Interest in coupled physical properties (*3*) led to the expectation that replacement of the diamagnetic cation by a paramagnetic transition metal ion might result in iodates with coupled magnetization and polar properties. Accordingly, the 3*d*-transition metal iodates were prepared and characterized as described by Nassau, Shiever and Prescott (*4*) (hereafter Part I) and their crystallographic, magnetic and nonlinear optic properties were surveyed. The present paper contains the results of this survey, except for data on the cupric compounds which will be reported later.

2. Properties of Anhydrous Cr, Mn, Fe, Co and Ni Iodates

a. Crystallographic Properties

The anhydrous iodates of Cr, Mn, Fe, Co and Ni form a single isomorphous family crystallizing in the hexagonal system; in addition, Ni also forms a second anhydrous phase designated α-$Ni(IO_3)_2$. Chemical analysis (see Part I) shows that Cr and Fe are present as trivalent ions, and Mn, Co and Ni as divalent ions. The unit cell dimensions and diffraction symmetry of Mn, Fe, Co and β-Ni iodates were determined by photographic techniques on single crystal material: powders only of Cr and α-Ni iodates were available. The pattern for $Cr(IO_3)_3$ contains some weak unindexable lines. It was not possible to identify these as belonging to a second phase, and hence the possibility remains that the actual unit cell differs from but is related to that given in Table I.

TABLE I

PHYSICAL CONSTANTS OF ANHYDROUS IODATES OF Cr, Mn, Fe, Co AND Ni[a]

	$Cr(IO_3)_3$	$Mn(IO_3)_2$	$Fe(IO_3)_3$	$Co(IO_3)_2$	β-$Ni(IO_3)_2$	α-$Ni(IO_3)_2$
a (Å)	10.493 ± 10[b]	11.178 ± 2	10.664 ± 2	10.956 ± 4	10.783 ± 3	[c]
c (Å)	5.174 ± 10	5.035 ± 1	5.228 ± 2	5.082 ± 2	5.147 ± 1	
Vol. (Å^3)	493.4	544.73	514.88	528.31	518.29	
Space group	$P6_3$ or $P6_322$	$P6_3$ or $P6_322$	$P6_3$ or $P6_322$	$P6_3$ or $P6_322$	$P6_3$ or $P6_322$	
Z	$4[Cr_{2/3}(IO_3)_2]$	$4[Mn(IO_3)_2]$	$4[Fe_{2/3}(IO_3)_2]$	$4[Co(IO_3)_2]$	$4[Ni(IO_3)_2]$	
D_x (g cm^{-3})	5.18	4.934	5.232	5.138	5.234	
D_m (g cm^{-3})	—	4.9 ± 2	—	—	—	
Θ_N (K)	—	6.5	17.0	—	5.0[d]	3.5
Θ_p (K)	0	−7.0	−26.0	−14.0	+3.0	−4.0
C_m (cm^3 K/mole)	1.73	4.23	4.11	3.40	1.28	1.09
p_{eff} (obs) (μ_B)	3.72	5.82	5.74	5.22	3.20	2.95
p_{eff} (theor) (μ_B)	3.87	5.92	5.92	3.87	2.83	2.83
N_B (μ_B)	—	0.036	—	—	0.110	0.026
Canting angle (°)	—	0.04	—	—	2.7	0.7
SHG	$\sim 10^0$	$\sim 10^0$	$\sim 10^2$	$\sim 10^2$	$\sim 10^{-1}$	$\sim 10^{-1}$

[a] Note that Cr and Fe form tri-iodates, Mn, Co and Ni di-iodates; a and c are lattice constants, D_x and D_m are X-ray and measured densities, Θ_N is the Néel and Θ_p the paramagnetic Curie temperatures, C_m the Curie–Weiss constant, p_{eff}(obs) and p_{eff} (theor) the observed and theoretical spin-only paramagnetic moment, N_B the ferromagnetic moment and SHG is the ratio of second harmonic generation at 1.06 μm of the powdered iodate to that of quartz.

[b] Error values without decimal point correspond to the least significant digit in function value.

[c] The powder pattern of α-$Ni(IO_3)_2$ is not unambiguously indexed (see Table II).

[d] A small paramagnetic impurity phase is assumed present (see text).

The lattice constants for each compound (see Table I) were obtained from least squares refinement of spacings measured on Debye–Scherrer photographs with CrK radiation, and are given in Table II. These constants correspond to unit cell volumes that decrease linearly for the Mn, Co and β-Ni iodates with the 3d contraction in divalent metal ion radius. The a-axis lattice constants similarly decrease, in contrast with the increase in c-axis, as the atomic number increases. The powder pattern of α-$Ni(IO_3)_2$ (Table II) was not unambiguously indexed, hence the unit cell is not given in Table I.

It is to be noted that both divalent (Mn, Co and Ni) and trivalent (Cr and Fe) 3d-metal iodates have isomorphous unit cells containing eight IO_3^{2-} ions, together with either four divalent or 8/3 trivalent metal ions, i.e., $Cr(IO_3)_3$ and $Fe(IO_3)_3$ each contain an additional 4/3 vacant metal sites per unit cell. No evidence for ordering among the partially occupied metal sites was observed.

b. Magnetic Properties

The magnetic susceptibility of each anhydrous iodate was measured in the temperature range 1.4–300 K with applied fields between 0 and 15 kOe. The magnetization as a function of temperature is shown in Fig. 1. The inverse magnetic susceptibility of $Cr(IO_3)_3$ follows Curie law behavior, with zero intercept. The paramagnetic Cr^{3+} moment (Table I) is close to the spin-only value.

$Mn(IO_3)_2$ orders antiferromagnetically below 6.5 K, but with a weak net ferromagnetic moment. The effective Mn^{2+} moment in the high temperature paramagnetic phase is not significantly different from the spin-only value of 5.92 μ_B. Assuming the Landé splitting factor g is 2, the corresponding Mn^{2+} moment in the ordered state is 4.90 μ_B. The observed ferromagnetic moment of a loosely held microcrystalline sample cooled in a field may be accounted for by a canting angle of 0.4° of the antiferromagnetic moments from collinearity.

$Fe(IO_3)_3$ orders antiferromagnetically below $\Theta_N = 17.0$ K (see Fig. 1) without net moment development. The Curie–Weiss law is followed at higher temperatures, with a paramagnetic moment close to that expected for a spin-only moment.

$Co(IO_3)_2$ remains paramagnetic to 1.4 K:

TABLE II

OBSERVED AND CALCULATED *d*-SPACINGS (Å) OF THE ANHYDROUS IODATES OF Cr, Mn, Fe, Co AND Ni

$Cr(IO_3)_3$				$Mn(IO_3)_2$				$Fe(IO_3)_3$				$Co(IO_3)_2$				β-$Ni(IO_3)_2$				α-$Ni(IO_3)_2$	
hkl	d_{obs} (Å)	d_{calc} (Å)	I_{obs}	*hkl*	d_{obs} (Å)	d_{calc} (Å)	I_{obs}	*hkl*	d_{obs} (Å)	d_{calc} (Å)	I_{obs}	*hkl*	d_{obs} (Å)	d_{calc} (Å)	I_{obs}	*hkl*	d_{obs} (Å)	d_{calc} (Å)	I_{obs}	d_{obs} (Å)	I_{obs}
101	4.505	4.496	5	200	4.82	4.84	1	200	4.60	4.62	1	200	4.71	4.74	3	200	4.64	4.67	2	5.06	3
201	3.401	3.414	10	210	3.48	3.49	10	101	4.50	4.55	1	201	3.45	3.47	10	201	3.44	3.46	5	4.43	1
—[a]	3.134		2	220	2.80	2.79	7	201	3.45	3.46	10	220	2.73	2.74	10	220	2.69	2.70	8	3.72	8
—[a]	2.962		2	002	2.51	2.52	2	300	3.16	3.08	1	002	2.54	2.54	2	002	2.56	2.57	1	3.63	10
220	2.619	2.623	8	221	2.44	2.44	2	220	2.66	2.67	4	221	2.40	2.41	1	221	2.38	2.39	1	3.44	2
002	2.585	2.587	2	311	2.35	2.37	1	301		2.65		400	2.37	2.37	1	400	2.33	2.33	1	3.29	7
221	2.341	2.340	2	401	2.19	2.18	5	002	2.61	2.61	2	202	2.23	2.24	1	202	2.25	2.25	1	3.13	1
311	2.266	2.266	6	222	1.873	1.870	5	221	2.37	2.38	2	401	2.14	2.15	5	401	2.12	2.13	7	2.71	3
—[a]	2.183		2	421	1.726	1.719	3	400	2.31	2.31	1	222	1.860	1.863	7	222	1.860	1.861	8	2.67	10
401	2.083	2.080	8	412	1.619	1.618	1	311		2.30		402	1.732	1.734	1	402	1.728	1.729	2	2.39	3
—[a]	2.015		2	203	1.586	1.586	1	202	2.27	2.27	2	421	1.688	1.691	6	421	1.668	1.669	10	2.31	5[b]
—[a]	1.962		1					401	2.11	2.11	5	203	1.594	1.595	1	203	1.609	1.610	2	2.24	2[b]
411	1.851	1.852	9					410	2.04	2.02	2	600	1.580	1.581	2	600	1.585	1.556	5	2.11	10[b]
420	1.717	1.717	3					321	1.975	1.964	2									1.86	2[b]
402	1.708	1.707	2					222	1.866	1.866	6										
								402	1.729	1.730	2										
								421	1.654	1.655	5										
								203	1.630	1.630	3										

[a] Not indexable on basis of unit cell given in Table I.

[b] Diffuse.

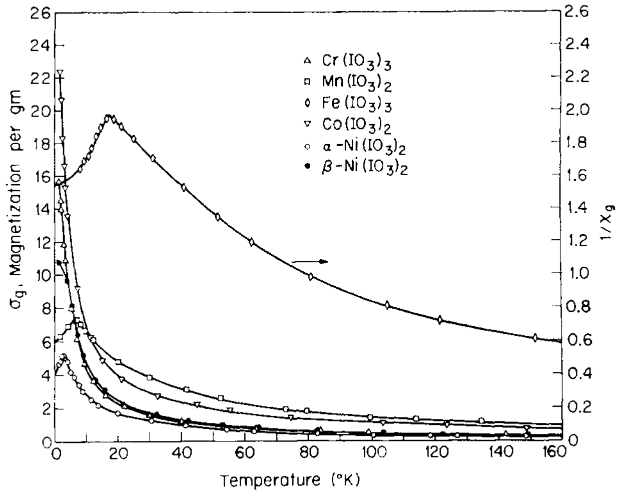

FIG. 1 .Magnetic susceptibility of the anhydrous iodates of Cr, Mn, Fe, Co and Ni between 1.5 and 150 K. The ordinate for $Fe(IO_3)_3$ is at right, all others are at left.

the paramagnetic moment contains a substantial orbital contribution, as is commonly found for the Co^{2+} ion.

β-$Ni(IO_3)_2$ shows basic antiferromagnetic behavior, in spite of the magnetic susceptibility not reaching a maximum (see Fig. 1). Although evidence of a second phase was not present in the powder pattern (Table II), a paramagnetic impurity of about 5% by weight (which could be imperceptible) could suffice to obscure the susceptibility maximum and replace it by the observed inflection at 5 K. The weak observed ferromagnetic moment thus corresponds to a noncollinear antiferromagnet, with canting angle of 2.7° based on a moment gJ of 2.35 μ_B (assuming $g = 2$).

α-$Ni(IO_3)_2$ orders antiferromagnetically below 3.5 K, developing a weak ferromagnetic moment (Table I). The paramagnetic moment is closer ~~to spin~~-only than for β-$Ni(IO_3)_2$. The resulting moment of 2.11 μ_B corresponds to a canting angle of about 0.7° from collinearity below Θ_N.

c. *Nonlinear Optical Properties*

The nonlinear optical property of second harmonic generation was sought, and found, in each of the anhydrous iodates listed in Table I. The efficiency of generation in powdered samples is given in terms of the response found in microcrystalline quartz; conversion is highest in $Fe(IO_3)_3$ and lowest in β-$Ni(IO_3)_2$.

3. Properties of Hydrated Co and Ni Iodates

a. *Crystallographic Properties*

The only 3*d*-transition metals, in addition to Cu, that form hydrated iodates (see Part I) are Co and Ni, both of which give a stable dihydrate and tetrahydrate. Ni also forms a second, metastable, tetrahydrate: the cupric iodates will be discussed in a later report. The stable tetrahydrates crystallize isostructurally in the monoclinic system, with point group $2/m$ and lattice constants and space group as given in Table III. The relative decrease in unit cell volume between $Co(IO_3)_2 \cdot 4H_2O$ and β-$Ni(IO_3)_2 \cdot 4H_2O$ is 1.5% compared to 1.9% between $Co(IO_3)_2$ and β-$Ni(IO_3)_2$ (see Sect. 2a).

$Co(IO_3)_2 \cdot 2H_2O$ is triclinic, with two formulas in the centrosymmetric unit cell and lattice constants as given in Table III.

$Ni(IO_3)_2 \cdot 2H_2O$ crystallizes readily from boiling water solution (see Part I) in the orthorhombic system. The lattice constants of Table III were measured on a single crystal, as part of a complete structure determination (*5*). An independent measurement gave (*6*) $a = 9.158 \pm 0.001$, $b = 12.206 \pm 0.002$ and $c = 6.584 \pm 0.001$ Å. The efficiency of packing in $Ni(IO_3)_2 \cdot 2H_2O$, as indicated by the density, is significantly less than in the triclinic $Co(IO_3)_2 \cdot 2H_2O$ structure. It is noteworthy that the 6.6 Å repeat is common to the lattice dimensions of all four stable iodate hydrates. The point group for $Ni(IO_3)_2 \cdot 2H_2O$

TABLE III

PHYSICAL CONSTANTS OF THE HYDRATED Co AND Ni IODATES[a]

	$Co(IO_3)_2 \cdot 4H_2O$	$Co(IO_3)_2 \cdot 2H_2O$	β-$Ni(IO_3)_2 \cdot 4H_2O$	$Ni(IO_3)_2 \cdot 2H_2O$[b]
a (Å)	8.370 ± 5	6.700 ± 15	8.268 ± 8	9.14986 ± 8
b (Å)	6.572 ± 7	10.980 ± 25	6.562 ± 6	12.20896 ± 22
c (Å)	8.514 ± 8	4.923 ± 11	8.532 ± 8	6.58353 ± 13
α	(90°)	91°45′ ± 5′	(90°)	(90°)
β	99°47′ ± 5′	92°42′ ± 5′	100°42′ ± 5′	(90°)
γ	(90°)	98°43′ ± 5′	(90°)	(90°)
Vol. (Å^3)	461.52	357.33	454.85	735.45
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$Pbca$
Z	2	2	2	4
D_x (g cm^{-3})	3.459	4.161	3.508	4.014
Θ_N (K)	—	—	3.0	3.1
Θ_p (K)	−2.0, −9.0[c]	−3.0, −14.0[d]	−2.0	−3.0
C_m (cm^3 K/mole)	2.40, 3.34	2.22, 3.07	1.28	1.25
p_{eff} (obs) (μ_B)	5.17	4.96	3.20	3.16
N_B (μ_B)	—	—	—	0.187
Canting angle (°)	—	—	—	4.64
SHG	0	0	0	0

[a] See footnote *a* to Table I for definitions of abbreviations.

[b] See Ref. (*5*).

[c] A break in the inverse susceptibility at about 16 K gives two Curie-Weiss constants and Curie points.

[d] As in footnote *c* but with a break at about 28 K.

is the centrosymmetric *mmm*, and that for $Co(IO_3)_2 \cdot 2H_2O$ either 1 or $\bar{1}$. Lack of second harmonic generation (see below) eliminates the acentric possibility, hence all these hydrates are centrosymmetric.

Lattice constants and other measurements were not made on α-$Ni(IO_3)_2 \cdot 4H_2O$, which was unobtainable in pure form. Lattice spacings, from Debye-Scherrer photographs taken with Cr*K* radiation, for this and the remaining hydrates are given in Table IV.

b. Magnetic Properties

$Co(IO_3)_2 \cdot 2H_2O$ and $Co(IO_3)_2 \cdot 4H_2O$ are both paramagnetic, down to 1.55 K (see Fig. 2). The paramagnetic moment for the two hydrates is considerably higher than the spin-only value, and is comparable with the value in the anhydrous iodate. The inverse susceptibility of both hydrates obeys Curie-Weiss behavior, except for breaks at about 28 K for $Co(IO_3)_2 \cdot 2H_2O$ and at about 16 K for $Co(IO_3)_2 \cdot 4H_2O$. Cooling $Co(IO_3)_2 \cdot 2H_2O$ in a magnetic field of 15.3 kOe does not increase the field-dependent magnetization, in contrast to $Co(IO_3)_2 \cdot 4H_2O$.

β-$Ni(IO_3)_2 \cdot 4H_2O$ is basically antiferromagnetic but, like β-$Ni(IO_3)_2$, the maximum in susceptibility at about 3 K is obscured by a small paramagnetic impurity. The field-dependent magnetization of β-$Ni(IO_3)_2 \cdot 4H_2O$ is appreciably increased on cooling a loose microcrystalline sample in a field. The paramagnetic moment (Table III) is identical to that found in β-$Ni(IO_3)_2$.

Magnetization measurements on $Ni(IO_3)_2 \cdot 2H_2O$, shown in Fig. 3, were made at 1.5 K on a large prismatic single crystal (*7*) [8 × 5 × 4 mm, elongated along [100] and bounded by (021) and (02$\bar{1}$) faces] as well as on a microcrystalline sample (Fig. 2). Earlier measurements (*8–10*) showed $Ni(IO_3)_2 \cdot 2H_2O$ to be a weak ferromagnet below 3.08 K, with a canting angle of about 1.5° between the nearly antiparallel spins. The present work confirms the Néel temperature, but the net ferromagnetic moment of 0.187 μ_B/Ni^{2+} below Θ_N (Table III) corresponds to a canting angle of 4.6°. A powder neutron diffraction study (*6*) suggests the antiferromagnetic spins lie primarily in the *ab*-plane, with the major spin component (about 2 μ_B) along *a*, and a smaller (0.5 μ_B) component along *b*.

TABLE IV

OBSERVED AND CALCULATED d-SPACINGS OF THE HYDRATED Co AND Ni IODATES

$Co(IO_3)_2 \cdot 4H_2O$				$Co(IO_3)_2 \cdot 2H_2O$				β-$Ni(IO_3)_2 \cdot 4H_2O$				$Ni(IO_3)_2 \cdot 2H_2O$				α-$Ni(IO_3)_2 \cdot 4H_2O$[a]	
hkl	d_{obs} (Å)	d_{calc} (Å)	*I*	*hkl*	d_{obs} (Å)	d_{calc} (Å)	*I*	*hkl*	d_{obs} (Å)	d_{calc} (Å)	*I*	*hkl*	d_{obs} (Å)	d_{calc} (Å)	*I*	d_{obs} (Å)	*I*
110	5.07	5.14	5	100	6.62	6.61	1	110	5.08	5.10	3	200	4.57	4.59	3	13.85	10
$11\bar{1}$	4.56	4.61	2	110	5.30	5.30	3	$11\bar{1}$	4.57	4.61	1	021	4.44	4.48	7	8.64	2
200	4.16	4.12	6	001	4.83	4.91	1	002 111	4.16	4.19 4.15	10	220	3.66	3.67	1	7.11	1
210	3.46	3.49	5	$\bar{1}01$	4.00	4.05	3	200	4.05	4.06	1	002 131	3.27	3.30 3.24	3	5.35	2
$11\bar{2}$	3.40	3.43	5	101	3.84	3.85	5	$11\bar{2}$	3.43	3.44	6	221	3.19	3.21	10	4.86	6
$21\bar{1}$	3.37	3.40	1	$1\bar{1}1$	3.81	3.77	8	$21\bar{1}$	3.37	3.39	2	040 230	3.04	3.05 3.04	2	4.39	2
$20\bar{2}$	3.20	3.23	1	$\bar{1}\bar{1}1$	3.72	3.72	5	020	3.28	3.28	1	022	2.88	2.90	3	3.88	3
021	3.06	3.06	2	030	3.65	3.62	3	202	3.20	3.23	3	202 141	2.66	2.68 2.65	4	3.64	2
120	3.03	3.05	3	111	3.46	3.50	4	112 021 120 211	3.05	3.07 3.06 3.04 3.03	7	240 321	2.53	2.54 2.53	3	3.53	2
$12\bar{1}$ $21\bar{2}$	2.91	2.93 2.90	6	$\bar{2}10$	3.31	3.31	10	$12\bar{1}$ $21\bar{2}$	2.91	2.93 2.90	4	400 331	2.29	2.30 2.29	3	3.38	6
300 202	2.73	2.75 2.72	10	200	3.27	3.31	7	300	2.69	2.71	8	042 232	2.23	2.24 2.24	10	3.27	5
113 220 013 $12\bar{2}$	2.56	2.57 2.57 2.57 2.55	4													3.18	7
																3.12	2
																3.04	1
																3.01	3
																2.94	3

[a] The powder pattern of α-$Ni(IO_3)_2 \cdot 4H_2O$ was not unambiguously indexed.

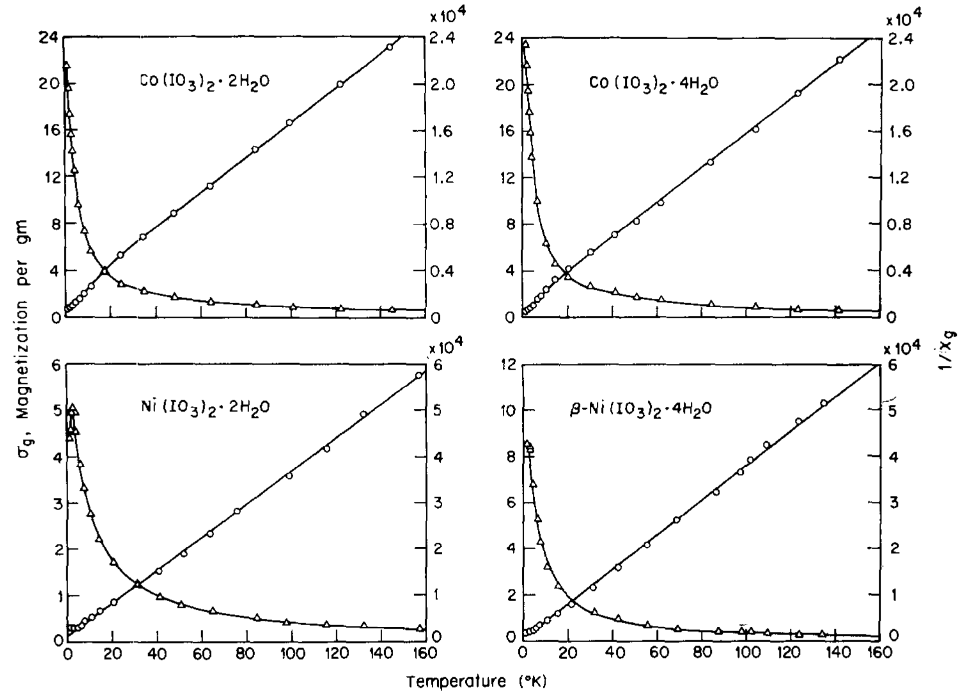

FIG. 2. Magnetic susceptibility of the hydrated iodates of Co and Ni between 1.5 and 150 K: left ordinate is specific magnetization, right is inverse susceptibility.

A magnetization study as a function of field, along each of the three crystallographic axes, at 1.5 K strongly supports the neutron diffraction model. The magnetization per gram is 0.187 μ_B along *c* and zero along *a* and *b* in zero field. At 15 kOe, the magnetization along *b* exceeds that along *a* by the factor 1.6. Hence the antiferromagnetic spins are canted about 4.6° out of the *ab*-plane, and appear to lie closer to [100] than [010].

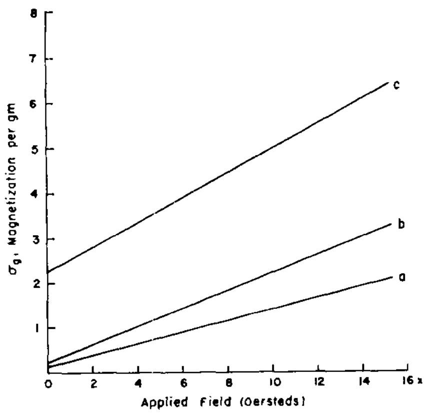

FIG. 3. Magnetization as a function of applied field along the *a*, *b* and *c* axes of Ni(IO$_3$)$_2$·2H$_2$O, at 1.5 K.

c. Nonlinear Optical Properties

No evidence of second harmonic generation was found in Co(IO$_3$)$_2$·2H$_2$O, Co(IO$_3$)$_2$·4H$_2$O, Ni(IO$_3$)$_2$·2H$_2$O nor β-Ni(IO$_3$)$_2$·4H$_2$O. The point groups of the tetrahydrates, determined crystallographically, require zero linear-optical coefficients, but the absence of generation removes the ambiguity from the choice of point groups (1 or $\bar{1}$) for Co(IO$_3$)$_2$·2H$_2$O (see Table III).

4. Summary

The search for new nonlinear optic and magnetic materials has resulted in the preparation and characterization of the anhydrous 3*d*-transition metal iodates. A group of five isostructural iodates containing both di- and trivalent 3*d* metals crystallizes in an optically active point group, and all generate second harmonics. At low temperatures Mn(IO$_3$)$_2$ and β-Ni(IO$_3$)$_2$ develop weak ferromagnetic moments, allowing coupled magnetic and optic interactions. Four stable hydrated 3*d*-transition metal iodates have also been prepared and characterized. All are centrosymmetric; Ni(IO$_3$)$_2$·2H$_2$O develops a weak ferromagnetic moment at low temperatures.

Note added in proof: Drs. J. B. A. A. Elemans and G. C. Verschoor have kindly sent us a preprint of their paper on the crystal structure of β-$Ni(IO_3)_2 \cdot 4H_2O$ and triclinic α-$Co(IO_3)_2 \cdot 2H_2O$ and the unit cells, space groups and magnetization of these two crystals and of $Ni(IO_3)_2 \cdot 2H_2O$, $Co(IO_3)_2 \cdot 4H_2O$ and β-$Co(IO_3)_2 \cdot 2H_2O$, which is now in press in *J. Inorg. Nucl. Chem.* The two sets of lattice constants are in acceptable agreement, although normal probability analysis indicates the pooled standard deviation of the differences between corresponding lattice constants is underestimated by about a factor of 4. It may be noted that our $Co(IO_3)_2 \cdot 2H_2O$ should be designated α-$Co(IO_3)_2 \cdot 2H_2O$: both investigations resulted in the same reduced triclinic unit cell, but whereas we followed the convention $c < a < b$, Elemans and Verschoor used $b < c < a$. The two sets of magnetization results agree that α-$Co(IO_3)_2 \cdot 2H_2O$ and $Co(IO_3)_2 \cdot 4H_2O$ do not order magnetically in the liquid helium temperature range: however, Elemans and Verschoor do not report the antiferromagnetic ordering of $Ni(IO_3)_2 \cdot 4H_2O$ shown in Fig. 2. It is entirely possible that our $Ni(IO_3)_2 \cdot 4H_2O$ sample contained some $Ni(IO_3)_2 \cdot 2H_2O$ as an impurity, since the tetrahydrate converts slowly to the dihydrate even in the solid state. The very small zero-field susceptibility of the tetrahydrate sample suggests an upper limit for this impurity of about 5%, too small an amount to give the observed dip in susceptibility below 3K.

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References

1. J. G. Bergman, G. D. Boyd, A. Ashkin, and S. K. Kurtz, *J. Appl. Phys.* **40**, 2860 (1969).
2. E. T. Keve, S. C. Abrahams, and J. L. Bernstein, *J. Chem. Phys.* **54**, 2556 (1971).
3. S. C. Abrahams, *Mater. Res. Bull.* **6**, 881 (1971).
4. K. Nassau, J. W. Shiever, and B. E. Prescott, *J. Solid State Chem.* **7**, 186 (1973).
5. S. C. Abrahams, J. L. Bernstein, J. B. A. A. Elemans, and G. C. Verschoor, *J. Chem. Phys.* In press.
6. J. B. A. A. Elemans, B. Van Laar, and B. O. Loopstra, *Physica (Utrecht)* **57**, 215 (1972).
7. K. Nassau, *J. Cryst. Growth* **15**, 171 (1972).
8. J. C. Burgiel, V. Jaccarino, and A. L. Schawlow, *Phys. Rev.* **122**, 429 (1961).
9. H. J. Williams and R. C. Sherwood, unpublished data, quoted in Ref. (*8*).
10. H. C. Meijer, L. M. W. A. Pimmelaar, and J. Van Den Handel, *Physica (Utrecht)* **44**, 626 (1969).