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Transition Metal Iodates. IV. Crystallographic, Magnetic and Nonlinear Optic Survey of the Copper Iodates

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Three anhydrous polymorphs of cupric iodate, two hydrates, and the basic iodate salesite have been investigated. α-$Cu(IO_3)_2$ is monoclinic, space group $P2_1$, with $a = 5.551 \pm 0.008$, $b = 5.101 \pm 0.004$, $c = 9.226 \pm 0.010$ Å and $\beta = 95°4' \pm 11'$, with two formulas in the unit cell. Below $\Theta_N = 8.5$ K, α-$Cu(IO_3)_2$ is antiferromagnetic and also pyroelectric. β-$Cu(IO_3)_2$ is triclinic, space group $P\bar{1}$, with $a = 11.230 \pm 0.006$, $b = 11.368 \pm 0.009$, $c = 10.630 \pm 0.009$ Å, $\alpha = 99°18.3' \pm 0.3'$, $\beta = 107°0.4' \pm 0.2'$ and $\gamma = 114°23.8' \pm 0.2'$ and eight formulas per unit cell: the crystal is paramagnetic to 1.4 K. γ-$Cu(IO_3)_2$ is monoclinic, space group $P2_1/m$, with $a = 4.977 \pm 0.004$, $b = 6.350 \pm 0.004$, $c = 8.160 \pm 0.004$ Å and $\beta = 92°20' \pm 4'$, with two formulas per unit cell; γ-$Cu(IO_3)_2$ becomes antiferromagnetic below $\Theta_N = 5$ K. $Cu(IO_3)_2 \cdot 2H_2O$ is monoclinic, space group $P2/_1c$, with $a = 6.725 \pm 0.005$, $b = 4.770 \pm 0.007$, $c = 11.131 \pm 0.013$ Å and $\beta = 103°1' \pm 4'$, with two formulas per unit cell; $Cu(IO_3)_2 \cdot 2H_2O$ is paramagnetic to 1.4 K. $Cu(IO_3)_2 \cdot \frac{2}{3}H_2O$ (mineral bellingerite) is triclinic, space group $P\bar{1}$, with $a = 7.197 \pm 0.005$, $b = 7.824 \pm 0.004$, $c = 7.904 \pm 0.004$ Å, $\alpha = 105°2' \pm 2'$, $\beta = 97°7' \pm 2'$ and $\gamma = 92°54' \pm 2'$ with three formulas per unit cell; this crystal is paramagnetic to 1.4 K, with a moderate antiferromagnetic Cu–Cu interaction. $Cu(OH)IO_3$ (mineral salesite) is orthorhombic, with $a = 10.772 \pm 0.004$, $b = 6.702 \pm 0.002$ and $c = 4.769 \pm 0.002$ Å and four formulas per unit cell. The magnetic susceptibility indicates the possibility of antiferromagnetic ordering at 162 K; strong antiferromagnetic interactions give $\Theta_p = -340$ K. The only copper iodate studied that generates second harmonics is α-$Cu(IO_3)_2$. Indexed powder patterns are given for all six compounds.

1. Introduction

Methods of preparation, together with a survey of the crystallographic, magnetic and nonlinear optic properties of all the 3*d*-transition metal (except for Cu) iodates have been previously presented (*1*, *2*). The gel growth and some characterization of six cupric iodates is discussed in the preceding report (*3*) and the corresponding properties are considered in the present report. Later papers will survey the preparation and properties of the 4*f*-iodates, in a continuing investigation of materials with potentially coupled magnetization, dielectric and optic properties.

2. Properties of Anhydrous Alpha-, Beta- and Gamma-Cupric Iodates

a. Crystallographic Properties

Three polymorphic phases of anhydrous cupric iodate, all available as single crystals, are now known (*3*). The lattice constants and space group symmetry were determined from precession and Weissenberg photographs. Refined lattice constants, given in Table I, were obtained by the method of least squares from lattice spacings measured on Debye–Scherrer photographs taken with Cr*K* radiation (see Table II).

α-$Cu(IO_3)_2$, a light yellowish-green material, crystallizes in the monoclinic system with space group $P2_1$ or $P2_1/m$. Observation of second harmonic generation (see Sect. 2c below) determines the correct choice as $P2_1$.

β-$Cu(IO_3)_2$ forms light green triclinic crystals. The large unit cell contains eight formulas, with a density appreciably lower than that of either α- or γ-$Cu(IO_3)_2$. Lack of second harmonic generation (Sect. 2c) eliminates the polar choice of space group between $P1$ and $P\bar{1}$.

γ-$Cu(IO_3)_2$ is dark yellow and crystallizes in the monoclinic system, with space group $P2_1$ or

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TABLE I

Physical Constants of Anhydrous α-, β- and γ-$Cu(IO_3)_2$[a]

	α-$Cu(IO_3)_2$	β-$Cu(IO_3)_2$	γ-$Cu(IO_3)_2$
a(Å)	5.551 ± 8	11.230 ± 6	4.977 ± 4
b	5.101 ± 4	11.368 ± 9	6.350 ± 4
c	9.226 ± 10	10.630 ± 9	8.160 ± 4
α	(90°)	99°18.3 ± 0.3′	(90°)
β	95°4′ ± 11′	107°0.4 ± 0.2′	92°20′ ± 4′
γ	(90°)	114°23.8 ± 0.2′	(90°)
Vol. (Å^3)	260.24	1117.97	257.66
Space group	$P2_1$	$P\bar{1}$	$P2_1/m$
Z	2	8	2
D_x(g cm^{-3})	5.275	4.911	5.328
D_m(g cm^{-3})			5.33 ± 10
Θ_N(K)	8.5	—	5.0
Θ_p(K)	6.0	0	17.0
C_m(cm^3 K/mole)	0.422	0.168	0.522
p_{eff}(obs) (μ_B)	1.84	1.75	2.05
p_{eff}(theor) (μ_B)	1.73	1.73	1.73
SHG	10^{-1}	0	0

[a] The abbreviations $a, b, c, \alpha, \beta, \gamma$ 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 tempertures, C_m the Curie–Weiss constant, p_{eff}(obs) and p_{eff}(theor) the observed and theoretical spin-only paramagnetic moment and SHG is the ratio of second harmonic generation at 1.06 μm of the powdered sample to that of powdered quartz.

TABLE II

Observed and Calculated d-Spacings of α-, β- and γ-$Cu(IO_3)_2$

α-$Cu(IO_3)_2$				β-$Cu(IO_3)_2$				γ-$Cu(IO_3)_2$			
$h\,k\,l$	d_{obs}	d_{calc}	I_{obs}	$h\,k\,l$	d_{obs}	d_{calc}	I_{obs}	$h\,k\,l$	d_{obs}	d_{calc}	I_{obs}
0 1 1	4.46	4.44	$\frac{1}{2}$	1 $\bar{2}$ 1	5.15	5.15	4	1 0 0	4.97	4.97	1
1 1 0	3.73	3.75	1	$\bar{1}$ 1 2	4.45	4.45	2	0 0 2	4.06	4.08	2
$\bar{1}$ 1 1	3.55	3.55	8	$\bar{2}$ $\bar{1}$ 1	3.97	3.97	2	1 1 0	3.92	3.92	1
1 1 1	3.41	3.40	8	0 1 2	3.85	3.85	3	$\bar{1}$ 1 1	3.57	3.57	4
1 0 2	3.39	3.39	8	$\bar{1}$ $\bar{2}$ 2	3.72	3.72	3	1 1 1	3.49	3.49	8
0 0 3	3.00	3.06	2	2 1 0	3.60	3.60	8	0 1 2	3.42	3.43	$\frac{1}{2}$
$\bar{1}$ 0 3	2.80	2.79	4	2 $\bar{3}$ 1	3.46	3.46	6	$\bar{1}$ 0 2	3.22	3.22	2
2 0 0	2.76	2.76	4	2 $\bar{2}$ 2	3.23	3.23	1	0 2 0	3.18	3.18	$\frac{1}{2}$
0 1 3	2.63	2.63	$\frac{1}{2}$	$\bar{3}$ 2 2	3.20	3.20	2	1 0 2	3.09	3.09	$\frac{1}{2}$
1 0 3	2.57	2.58	4	3 $\bar{2}$ 1	3.10	3.10	6	0 2 1	2.96	2.96	$\frac{1}{2}$
0 2 0	2.55	2.55	1	3 $\bar{1}$ 1	3.00	2.99	6	$\bar{1}$ 1 2	2.87	2.87	2
0 2 1	2.46	2.46	$\frac{1}{2}$					0 0 3	2.72	2.72	2
$\bar{1}$ 2 1	2.27	2.27	$\frac{1}{2}$					$\bar{1}$ 2 1	2.56	2.56	1
								0 1 3	2.50	2.50	4
								2 0 1	2.35	2.35	3

$P2_1/m$. The point group $2/m$ is indicated by the absence of second harmonic generation (Sect. 2c). The unit cell has nearly the same volume as that of α-$Cu(IO_3)_2$, but apart from the space group choice and comparable lengths of one axis [*b*- in α-$Cu(IO_3)_2$ and *a*- in γ-$Cu(IO_3)_2$] no other striking similarities are found.

b. *Magnetic Properties*

The magnetic susceptibility of α-$Cu(IO_3)_2$ was measured over the temperature interval 1.4 to 300 K, β-$Cu(IO_3)_2$ was measured from 1.4 to 20.8 K and γ-$Cu(IO_3)_2$ from 1.4 to 169 K, each with applied fields varying between 0 and 15.3 kOe. The specific magnetization of each anhydrous cupric iodate, as a function of temperature, is given in Fig. 1.

α-$Cu(IO_3)_2$ is antiferromagnetic with a Néel ordering temperature of 8.5 K, Table I. The inverse susceptibility follows Curie–Weiss behavior at higher temperatures, corresponding to a paramagnetic moment for Cu^{2+} of 1.84 μ_B: the spin-only value for Cu^{2+} is 1.73 μ_B. The susceptibility as a function of magnetic field is linear with zero intercept: heat treatment in a field produces no change.

β-$Cu(IO_3)_2$ is paramagnetic above 1.4 K, see Fig. 1. Sensitivity was lost, for the small sample used, above 20.8 K. A second sample, measured by F. J. DiSalvo on a more sensitive magnetometer, had room temperature susceptibility $\chi_g = 3.1 \times 10^{-6}$ emu g^{-1} corresponding to a paramagnetic moment of 1.75 μ_B for Cu^{2+}. At 1.5 K, the specific magnetization tends to saturate as the field reaches 15.3 kOe.

γ-$Cu(IO_3)_2$ is antiferromagnetic, with a Néel temperature of 5 K. The susceptibility maximum appears masked by a paramagnetic impurity, and is shown on Fig. 1 by an inflection. The Curie–Weiss constant above 5 K corresponds to a paramagnetic moment of 2.05 μ_B, within the normal range experimentally found for Cu^{2+}. The susceptibility varies linearly with magnetic field, and has zero intercept.

The paramagnetic Curie temperatures for both α-$Cu(IO_3)_2$ and γ-$Cu(IO_3)_2$ are positive, indicating ferromagnetic Cu–Cu interactions in these antiferromagnetic materials.

c. *Nonlinear Optical Properties*

Second harmonic generation, originating in a nonlinear response of the electronic polarizability in acentric crystals, was detected only in α-$Cu(IO_3)_2$, see Table I. The β- and γ-polymorphs failed to generate and hence were assigned to centrosymmetric point groups.

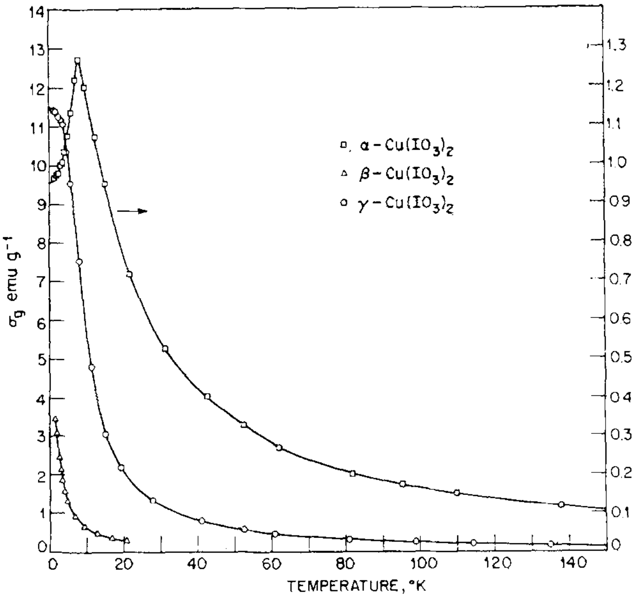

FIG. 1. Magnetic susceptibility of anhydrous α-, β- and γ-$Cu(IO_3)_2$ between 1.5 and 150 K. The ordinate for α-$Cu(IO_3)_2$ is at right, for β- and γ-$Cu(IO_3)_2$ at left.

3. Properties of Hydrated and Basic Cupric Iodates

a. Crystallographic Properties

Hydrated cupric iodate $Cu(IO_3)_2 \cdot \frac{2}{3}H_2O$ and basic cupric iodate $Cu(OH)IO_3$ are well known minerals named, respectively, bellingerite and salesite. A second hydrate, $Cu(IO_3)_2 \cdot 2H_2O$, is new. The preparation of crystals of these three materials is given in the preceding report (*3*). The crystallographic properties of all three iodates are presented here for completeness.

$Cu(IO_3)_2 \cdot \frac{2}{3}H_2O$ forms light greenish-blue triclinic crystals, The lattice constants of gel-grown material (*3*) were refined by the method of least squares from the observed *d*-spacings of Table IV and are given in Table III. These values may be compared with previous reports on mineral specimens of $a = 7.228$, $b = 7.829$, $c = 7.940$ Å, $\alpha = 105.039°$, $\beta = 96.985°$ and $\gamma = 92.942°$ (*4*), and $a = 7.250 \pm 9$, $b = 7.886 \pm 9$, $c = 7.966 \pm 5$ Å, $\alpha = 105°6'$, $\beta = 96°57.5'$ and $\gamma = 92°55'$ (*5*). The structure of bellingerite has been reported by Kaplan (*5*), who used equi-inclination diffractometer data and obtained a final *R*-factor of 0.089. The iodine atoms in bellingerite, as is generally found in iodates (*6*, *7*), form highly distorted octahedra with characteristic short (1.81 Å) and long (2.84 Å) I–O distances.

$Cu(OH)IO_3$ forms deep bluish-green orthorhombic crystals. The lattice constants have previously been reported as $a = 10.80$, $b = 6.71$, $c = 4.79$ Å (*8*): the values in Table III are obtained by least-squares refinement of the Debye–Scherrer *d*-spacings given in Table IV. The structure has been determined by Ghose (*8*), using photographic techniques, with final *R*-factor of 0.098. The average short I–O distance is 1.81 Å, the average long distance is 2.63 Å.

$Cu(IO_3)_2 \cdot 2H_2O$ forms light greenish-blue monoclinic crystals, in point group $2/m$. The unit cell volume and two of the lattice constants bear a striking resemblance to the corresponding salesite values, despite the smaller number of copper atoms present per unit cell. The 6.7 Å lattice repeat distance in $Cu(IO_3)_2 \cdot 2H_2O$ and in salesite is also found in the di- and tetrahydrates of the Ni and Co iodates (*2*).

The lattice spacings and X-ray powder intensities of bellingerite, salesite and $Cu(IO_3)_2 \cdot 2H_2O$ are given in Table IV.

b. Magnetic Properties

The magnetic susceptibility of bellingerite (Fig. 2) is consistent with paramagnetic behavior, although the inverse susceptibility shows a change

TABLE III

PHYSICAL CONSTANTS OF $Cu(IO_3)_2 \cdot \frac{2}{3}H_2O$, $Cu(OH)IO_3$ AND $Cu(IO_3)_2 \cdot 2H_2O$[a]

	$Cu(IO_3)_2 \cdot \frac{2}{3}H_2O$	$Cu(OH)IO_3$	$Cu(IO_3)_2 \cdot 2H_2O$
a(Å)	7.197 ± 5	10.772 ± 4	6.725 ± 5
b	7.824 ± 4	6.702 ± 2	4.770 ± 7
c	7.904 ± 4	4.769 ± 2	11.131 ± 13
α	105°2′ ± 2′	(90°)	(90°)
β	97°7′ ± 2′	(90°)	103°1′ ± 4′
γ	92°54′ ± 2′	(90°)	(90°)
Vol (Å^3)	424.99	344.31	347.92
Space group	$P\bar{1}$	$Pnma$	$P2_1/c$
Z	3	4	2
D_x(g cm^{-3})	4.985	4.928	4.289
D_m(g cm^{-3})	4.89 ± 1	4.77[b]	
Θ_N(K)	—	(162)[c]	—
Θ_p(K)	−55	−340	0
C_m(cm^3 K/mole)	0.59	0.62	0.37
p_{eff}(obs) (μ_B)	2.17	2.23	1.72
p_{eff}(theor) (μ_B)	1.73	1.73	1.73
SHG	0	0	0

[a] See footnote to Table I.

[b] From Ref. (*8*).

[c] Antiferromagnetic ordering may be indicated, see text.

TABLE IV

OBSERVED AND CALCULATED *d*-SPACINGS OF $Cu(IO_3)_2 \cdot \frac{2}{3}H_2O$, $Cu(OH)IO_3$ AND $Cu(IO_3)_2 \cdot 2H_2O$

$Cu(IO_3)_2 \cdot \frac{2}{3}H_2O$				$Cu(OH)IO_3$				$Cu(IO_3)_2 \cdot 2H_2O$			
h k l	d_{obs}	d_{calc}	I_{obs}	*h k l*	d_{obs}	d_{calc}	I_{obs}	*h k l*	d_{obs}	d_{calc}	I_{obs}
1 0 1	4.85	4.85	2	0 0 2	5.39	5.39	1	0 0 2	5.38	5.42	3
0 1 1	4.71	4.74	2	0 1 1	4.35	4.36	4	0 1 1	4.37	4.37	1
$0\,\bar{1}\,\bar{2}$	3.80	3.81	4	1 1 1	3.65	3.66	8	1 1 0	3.86	3.86	8
1 1 1	3.70	3.71	8	2 0 2	2.84	2.85	4	$\bar{1}\,1\,1$	3.80	3.80	$\frac{1}{2}$
$\bar{1}\,0\,2$	3.55	3.55	4	0 0 4	2.69	2.69	3	1 1 1	3.49	3.49	8
$\bar{1}\,\bar{1}\,2$	3.51	3.51	$\frac{1}{2}$	1 1 3	2.63	2.64	4	$\bar{2}\,0\,1$	3.36	3.35	8
$\bar{1}\,2\,0$	3.45	3.45	$\frac{1}{2}$	2 1 2	2.45	2.44	$\frac{1}{2}$	2 0 0	3.26	3.28	3
$\bar{2}\,0\,1$	3.41	3.41	1	0 2 0	2.39	2.38	3	$\bar{2}\,0\,2$	3.13	3.13	4
$1\,\bar{2}\,1$	3.37	3.37	1	2 1 3	2.18	2.18	2	1 1 2	2.96	2.96	4
$\bar{1}\,\bar{2}\,1$	3.33	3.33	4	2 0 4	2.10	2.10	$\frac{1}{2}$	$\bar{1}\,1\,3$	2.84	2.83	4
$1\,\bar{1}\,2$	3.23	3.23	4	3 1 1	1.99	1.99	2	$\bar{2}\,1\,1$	2.74	2.74	$\frac{1}{2}$
1 0 2	3.16	3.16	4	0 1 5	1.97	1.96	1	2 1 0	2.71	2.70	1
2 1 0	3.12	3.12	4	2 2 0	1.94	1.94	$\frac{1}{2}$	$\bar{2}\,1\,2$	2.62	2.62	$\frac{1}{2}$
0 2 1	3.06	3.06	4	1 1 5	1.88	1.88	2	2 0 2	2.55	2.56	2
$\bar{1}\,2\,1$	2.95	2.95	3	2 2 2	1.83	1.83	6	1 1 3	2.48	2.48	$\frac{1}{2}$
$\bar{1}\,\bar{2}\,2$	2.91	2.90	2	0 2 4	1.79	1.79	4	$\bar{2}\,1\,3$	2.39	2.39	1
				3 1 3	1.76	1.76	1	$\bar{2}\,0\,4$	2.37	2.37	1
				4 0 0	1.68	1.68	1	0 1 4	2.34	2.36	2
								2 0 3	2.20	2.19	$\frac{1}{2}$
								1 1 4	2.09	2.09	$\frac{1}{2}$
								$\bar{3}\,1\,1$	2.03	2.03	4
								$\bar{3}\,1\,2$	2.00	2.00	4

in slope at 34 K with the lower temperature inverse susceptibility passing through zero. Extrapolation of the higher temperature paramagnetic inverse susceptibility gives a Curie temperature of −55 K (Table III), suggesting some antiferromagnetic Cu–Cu interaction, with

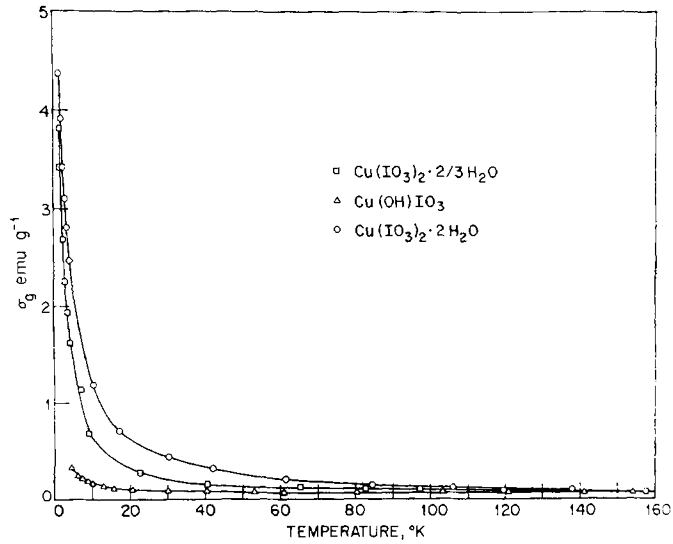

FIG. 2. Magnetic susceptibility of $Cu(IO_3)_2 \cdot \frac{2}{3}H_2O$, $Cu(OH)IO_3$ and $Cu(IO_3)_2 \cdot 2H_2O$ between 1.5 and 150 K

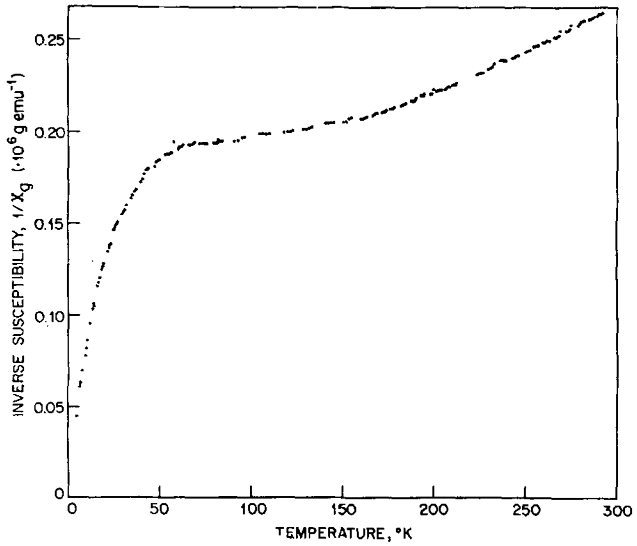

FIG. 3. Inverse susceptibility of $Cu(OH)IO_3$ between 1.5 and 300 K.

the Curie constant corresponding to a paramagnetic moment of 2.17 μ_B. A simple paramagnetic impurity in the $Cu(IO_3)_2 \cdot \frac{2}{3}H_2O$ sample could account for this behavior. The field dependence of the susceptibility shows some saturation at the highest fields used, 15 kOe.

The magnetic susceptibility of salesite below 160 K is also shown in Fig. 2, and the inverse susceptibility below 300 K is given in Fig. 3. The inflection at 162 K in $1/\chi_g$ may indicate antiferromagnetic ordering. The high temperature paramagnetism, with Curie constant of 0.62 cm^3 K $mole^{-1}$, corresponds to a moment of 2.23 μ_B. Extrapolation gives a Curie temperature of −340 K, corresponding to very strong antiferromagnetic Cu–Cu interactions.

$Cu(IO_3)_2 \cdot 2H_2O$ is a simple paramagnetic crystal, see Fig. 2. The Curie constant (Table III) gives a paramagnetic moment of 1.72 μ_B, exactly that predicted for spin-only Cu^{2+}, with a linear field dependence of susceptibility to 15 kOe.

c. *Nonlinear Optical Properties*

Neither $Cu(IO_3)_2 \cdot \frac{2}{3}H_2O$, $Cu(OH)IO_3$ nor $Cu(IO_3)_2 \cdot 2H_2O$ generate second harmonics; all three crystals hence belong to centrosymmetric point groups as indicated by Table III.

Summary

Four new cupric iodates have been prepared and characterized in the search for new nonlinear optic, dielectric and magnetic materials. Of these, only α-$Cu(IO_3)_2$ is acentric; this crystal is pyroelectric and, below 8.5 K, is also antiferromagnetic, with the possibility of cross coupling of properties still to be determined.

Acknowledgment

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