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Magnetic Susceptibility of $Co^{4+}(d^5)$ in Octahedral and Tetrahedral Environments

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Measurements of magnetic susceptibility on compounds containing stoichiometric Co^{4+} are reported. The compound Ba_2CoO_4 has the $Co^{4+}(d^5)$ ion at a tetrahedral site and displays a susceptibility of the expected magnitude for $S = 5/2$. The compounds $Ba_3Co_2CO_9$ and $BaCoO_3$ have the Co^{4+} at an octahedral site and show a susceptibility expected for low spin, $S = 1/2$. For the low spin case significant deviations from Kotani's calculated susceptibility were observed. Improvement of the theory was made through incorporation of the effects of distortion from perfect octahedral symmetry and the inclusion of higher electronic configurations above t_2^5 in the $^2T_2$ ground state. A case of low spin Ni in octahedral environment is also reported.

I. Introduction

We report here the results of studies on the Co^{4+} ion in a series of compounds. The only previously known stoichiometric compound of Co^{4+} is $BaCoO_3$, in which the Co ion is at an octahedral site (*1–3*). In the present paper we give results on two new stoichiometric compounds recently prepared, for which structures have been proposed (*2*). These are Ba_2CoO_4, with the cobalt in tetrahedral environment, and $Ba_3Co_2CO_9$, with the cobalt in octahedral environment. In these compounds the cobalt has the d^5 configuration and shows interesting magnetic properties. In tetrahedral environments only the high spin configuration occurs, but in octahedral coordination both low and high spin arrangements are possible. In the cases studied here the cobalt displays high spin in tetrahedral and low spin in the octahedral environment. For the low spin case significant deviation from Kotani's calculated susceptibility (*4*) was observed. Improvement of the theory was made through incorporation of the effects of distortion from perfect octahedral symmetry and the inclusion of higher electron configurations present in the t_2^5 ground state.

II. Experiment

A. Preparation and Structure

The phases Ba_2CoO_4, $BaCoO_3$, $Ba_3Co_2CO_9$ and $Ba_3Ni_2CO_{9-x}$ were prepared in powder form at elevated temperatures in air by methods described by Negas and Roth (*2*). High purity, spectrographic grades of $BaCO_3$, Co_3O_4, and NiO were the starting materials generally used. Detailed chemical analyses, X-ray diffraction data, phase equilibria and structural considerations involving the above phases and other similar compounds have been given in Ref. 2.

1. Ba_2CoO_4

Specimens of Ba_2CoO_4 were prepared for this study by reacting the appropriate amounts of the starting materials at 998°C for 5 days. When exposed to ambient conditions for extended time, the phase slowly decomposes by reacting with CO_2 and/or moisture. For susceptibility and EPR measurements, the material therefore was quenched from 998°C and immediately sealed in quartz ampules. At room temperature, the X-ray diffraction powder pattern of Ba_2CoO_4 was indexed on the basis of a monoclinic cell with $a = 5.909 \pm 0.001$ Å, $b = 7.617 \pm 001$ Å, $c = 10.406 \pm 0.002$ Å, and $\beta = 91°6.8 \pm 1.2'$.

Based on the similarity of X-ray line intensities and cell parameters, Ba_2CoO_4 is isostructural with monoclinic Ba_2TiO_4 (*5*), which is a distorted form of the orthorhombic K_2SO_4 structure type. Indeed, Ba_2CoO_4 transforms to the orthorhombic form near 145°C (*2*). Therefore, in this phase, the Co^{4+} is tetrahedrally coordinated by oxygens. Chemical analyses (*2*) are in accord with the proposed formula.

An orthorhombic form of Ba_2CoO_4 can be retained to room temperature when as little as a few mole % excess BaO is present. The physical nature of this orthorhombic solid solution has not been elucidated (*2*). Recently, Mattausch et al. (*6*) reported the crystal structure of orthorhombic Ba_2CoO_4 from single crystal data. The tetrahedral environment of Co^{4+} was confirmed. Our magnetic measurements were made using the monoclinic modification.

2. *$BaCoO_3$*

This phase was prepared by heating the starting materials at 1000°C for 3 days, followed by annealing at 600°C in air for 6 weeks. The resulting material was also annealed at 300–350°C in oxygen for 1 week to maximize the oxygen content as suggested by Greaves (*1*). The X-ray diffraction powder patterns of both materials were identical and were indexed on the basis of a hexagonal cell with $a = 5.648 \pm 0.001$ Å and $c = 4.756 \pm 0.001$ Å.

Although the X-ray data for $BaCoO_3$ are in excellent agreement with those of Greaves, our evidence does not support a doubling of the *c*-axis. In a recent dissertation, Zanne (*3*) reports a similar, but slightly oxygen deficient, $BaCoO_{2.95}$ phase with $a = 5.640$ Å and $c = 4.753$ Å, also in good accord with our material. Our chemical analysis does not preclude a slight deviation from $BaCoO_3$ stoichiometry similar to the $BaCoO_{2.95}$ reported by Zanne.

$BaCoO_3$ is isostructural with $BaNiO_3$ and $BaMnO_3$ reported by Lander (*7*, *8*) and Hardy (*9*), respectively. These phases have a two-layer, hexagonal (*2H*) structure. It consists of two hexagonal close-packed BaO_3-layers perpendicular to *c* with infinite strings, parallel to *c*, of face-sharing oxygen octahedra containing the transition metals. A slight oxygen deficiency can be accommodated easily by the reduction of some of the Co^{4+} to Co^{3+} with a corresponding decrease of the coordination number of cobalt from six (octahedron) to probably five (trigonal bipyramid).

3. *$Ba_3Me_2CO_{9-x}$ ($Me = Co$ or Ni) Phases*

Single phase materials were prepared at the $Ba/Me = 1.50$ composition below ~800°C in air. Powder X-ray diffraction data for these phases are similar to the corresponding 2H phases which occur at the $Ba/Me = 1.00$ composition. The phases are hexagonal with $a = 9.688 \pm 0.001$ Å, $c = 4.757 \pm 0.001$ Å (cobalt form), and $a = 9.671 \pm 0.001$ Å, $c = 4.836 \pm 0.002$ Å (nickel form). These unit cells are related to the *2H* structure according to $a_{new} \approx a_{2H}\sqrt{3}$ and $c_{new} \approx c_{2H}$. Electron diffraction data confirmed the *a*-axis multiplicity but also provided evidence suggesting possibly larger periodicities for the *c*-axis (*2*). X-ray precession data using crystals of the nickel form, grown and described by Negas and Roth (*2*), confirmed the indexing of the powder data. A structural analysis using these crystals revealed that the transition metals are in octahedral coordination similar to the *2H* structure.

Chemical analyses of these phases unequivocally established the presence of carbon. Several analyses of the cobalt form yielded stoichiometries with carbon contents ranging from .75 to 1.0 carbons per formula unit. The suggested stoichiometry is nominally $Ba_3Co_2CO_9$. Analysis of the nickel form suggested the formula $Ba_3Ni_2CO_{9-x}$ with $0 < x < 1$. As the average oxidation state of nickel was not established, susceptibility measurements were made to provide a possible solution. Greaves (*1*) and Krischner *et al.* (*10*) reported that Ni^{4+} is diamagnetic in the *2H* $BaNiO_3$ structure. The presence of lower nickel oxidation states, therefore, would be apparent from the susceptibility data.

The chemistry of these phases, including the structural role of carbon which is present in carbonate groups, is discussed in greater detail elsewhere (*2*).

B. Magnetic Measurement

The magnetic susceptibility of the samples was determined in the range 2–350 K by a modified Faraday method. The apparatus has been previously described (*11*). The measurements were performed with the samples in contact with a heat exchange gas (He or N_2). The temperatures above 77 K were measured with a calibrated copper–constantan thermocouple. In the 2–4 K range, the temperature was determined from the vapor pressure of the liquid He used as the coolant. Corrections were always made for the sample container and for the diamagnetism of the materials. The corrections used for the diamagnetism were as follows (*12*):

Ba_2CoO_4	$10^6 \cdot \chi_d = -120$ cm³ mol⁻¹
$BaCoO_3$	$10^6 \cdot \chi_d = -78$ cm³ mol⁻¹
$Ba_3Co_2CO_9$	$10^6 \cdot \chi_d = -220$ cm³ mol⁻¹.

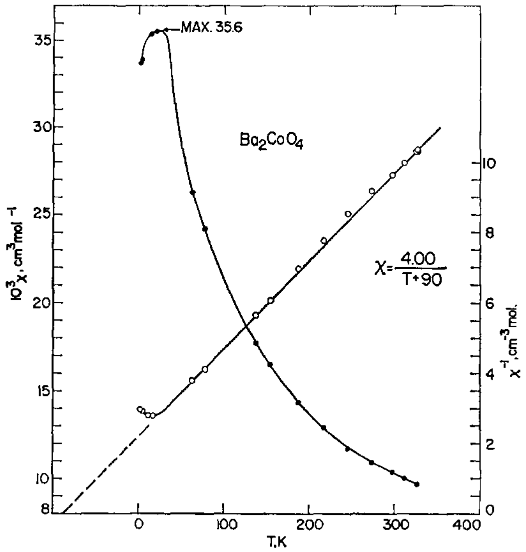

FIG. 1. Magnetic susceptibility (●) and reciprocal susceptibility (○) vs temperature for Co^{4+} in a tetrahedral site in Ba_2CoO_4.

We report all susceptibilities per mol of cobalt and plot the experimental data in Figs. 1–3.

C. Electron Paramagnetic Resonance (EPR)

Room temperature and liquid nitrogen temperature spectra above the Néel point were observed for powdered samples of Ba_2CoO_4. The signal-to-noise ratio and resolution were very low due to the broadness of the lines. Approximately seven very broad absorptions were observed but not clearly resolved. One absorption peak occurred at a g-value corresponding to 2 and all other lines correspond to g-values greater than 2, that is, all on the low field side. The EPR results were not in contradiction with the interpretation deduced from the magnetic susceptibility measurements (cf. below). However, as mentioned, the spectra were of low signal-to-noise ratio and resolution.

III. Theory and Discussion

A. Co^{4+} in Tetrahedral Environment

The compound Ba_2CoO_4 is to our knowledge the only reported case of an oxide with stoichiometric Co^{4+} at a tetrahedral site. The measured susceptibility of sample No. 1, corrected for diamagnetism, is plotted in Fig. 1; it can be expressed by

$$\chi = 4.00/(T + 90) \qquad (cm^3/mol). \qquad (1)$$

The susceptibility of a substance which follows a Curie–Weiss law is given by

$$\chi = N\beta^2 g^2 S(S+1)/3k(T+\theta) = C/(T+\theta), \quad (2)$$

according to the molecular field analysis (*13*), where N is Avogadro's number, β is the Bohr magneton, k the Boltzmann constant, and g the spectroscopic splitting factor. For the high spin value of Co^{4+} we have $S = 5/2$, $g = 2$, and

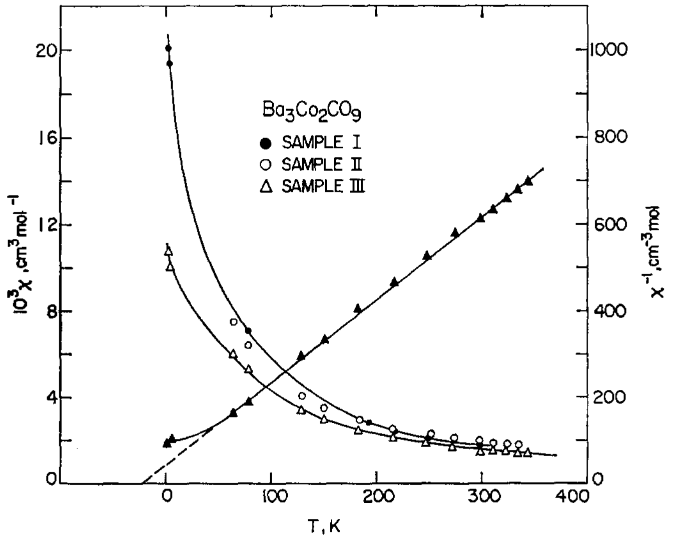

FIG. 2. Magnetic susceptibility and reciprocal susceptibility (▲) vs temperature for Co^{4+} in an octahedral site in $Ba_3Co_2CO_9$.

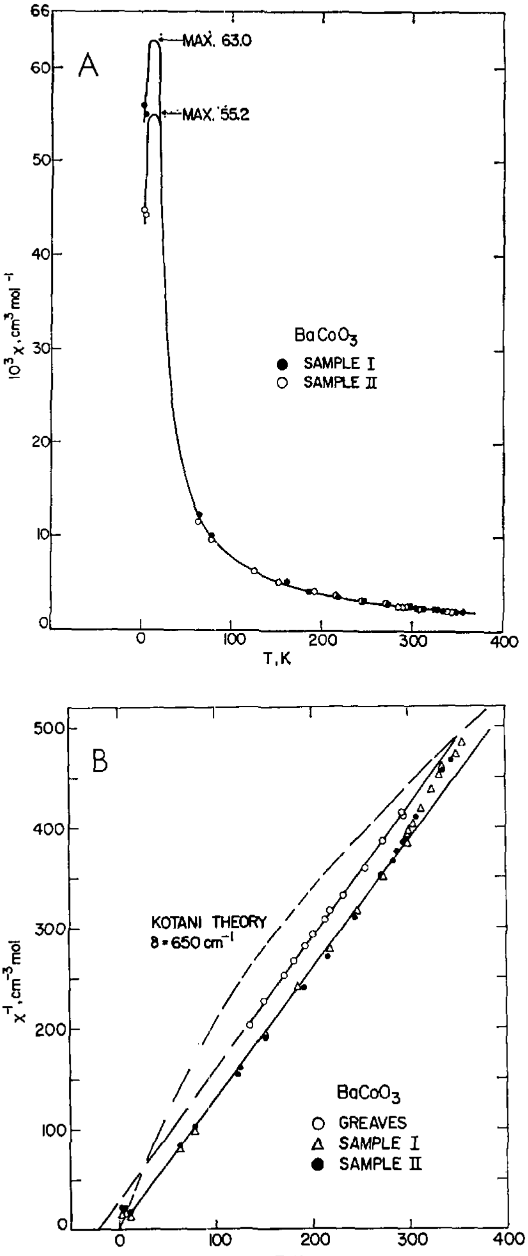

FIG. 3. Co^{4+} in an octahedral site in $BaCoO_3$ a) Magnetic susceptibility vs temperature b) Reciprocal of susceptibility vs temperature. Open circles are after Greaves (*1*).

$C = 4.38$ cm^3 K/mol. Therefore the measurements agree with this model within 10%.

In tetrahedral environments, $3d^5$ ions experimentally exhibit the high spin value, $S = 5/2$. In contrast, in octahedral fields both low and high spins have been observed.

A second sample was prepared and yielded a susceptibility 5% lower. We conclude that the 10% discrepancy between the experimental susceptibility on the first sample and that calculated from theory (see Fig. 1) is most likely due to the presence of an additional phase with a lower susceptibility.

B. Co^{4+} in Octahedral Environment

In the compounds $Ba_3Co_2CO_9$ and $BaCoO_3$ the Co^{4+} is at an octahedral site. A d^5 ion in an octahedral field can exhibit either high or low spin moment, depending on the crystal field strength (*14*). The experimental susceptibility of the above two compounds corresponds to the low spin case ($S = 1/2$). The spin-only value of the Curie constant is

$$\chi(T + \theta) = C = N\beta^2 g^2 S(S+1)/3k$$
$$= .375 \text{ cm}^3 \text{ K/mol.} \qquad (3)$$

Experimentally the Curie constants are .55 ± .05 and .77 ± .02 cm^3 K/mol respectively for $Ba_3Co_2CO_9$ and $BaCoO_3$.

The low-spin ground state of Co^{4+}, $^2T_2(t_2^5)$, is complementary to t_2^1, and may be viewed as one t_2 hole (*15*). This orbital triplet may be considered to be equivalent to a fictitious orbital angular momentum $\tilde{L} = 1$ with an orbital g factor $\gamma = -1$, as described by Griffith (*16*) and Abragam and Bleaney (*17*). Under spin-orbit coupling this $^2T_2$ splits into a ground level with fictitious spin $\tilde{J} = 1/2$ and a higher quartet $\tilde{J} = 3/2$. We assume that the octahedral crystal field splitting is large with respect to the spin-orbit coupling, i.e., the e states and other states lying above t_2 may be omitted.

The susceptibility of this ion, and other transition ions, has been calculated under these assumptions by Kotani (*4*). The susceptibility may be put into the form

$$\chi = \frac{\Sigma_J(2J+1)\chi_J e^{-\zeta J(J+1)/2kT}}{\Sigma_J(2J+1)e^{-\zeta J(J+1)/2kT}} \qquad (4)$$

with

$$\chi_J = \frac{N\beta^2}{3kT}\left[A + B\frac{kT}{\zeta}\right] \qquad (5)$$

and

$$A = g^2 J(J+1)$$
$$B = 2(g-\gamma)(g-2).$$

The spin-orbit parameter is ζ. The above expression may be viewed as displaying the susceptibility as arising from a set of spin-orbit split levels; each level is labeled by effective spin J, each with its Curie and temperature independent

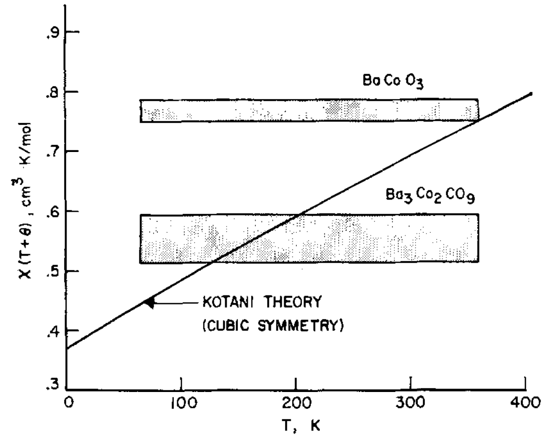

FIG. 4. Comparison of Kotani theory with experiment. χT vs T is plotted for the Kotani theory of the ${}^2T_2$, t_2^5 configuration in pure cubic symmetry. The experimental values of $\chi(T+\theta)$ vs T are shown as the shaded areas, indicating variation over several samples.

susceptibility (TIP), and each populated according to a Boltzmann distribution. The energy levels are given by $\zeta J(J+1)/2$. For the case of Co^{4+} in cubic symmetry, the ground level is a doublet ($J=1/2$), and the excited state is a quartet ($J=3/2$); $\gamma=-1$ for both. The spin-orbit parameter is given by ζ/k ($\zeta=650$ cm^{-1} (*18*)).

In Fig. 4 we show the results of the Kotani theory for low spin Co^{4+}, t_2^5. It is seen that the theoretical value of χT has a much stronger temperature dependence than the approximately constant values obtained experimentally. Also the low temperature theoretical limit, $\chi T \rightarrow N\beta^2 g^2/4k = .375$ cm^3 K/mol (equal to the spin-only value) is low relative to the experimental value of $\chi(T+\theta)$.

In an attempt to find the causes of this discrepancy and to understand the susceptibility, we have considered the role of a number of contributions not included in the cubic crystal field model. The additional effects considered are exchange coupling between Co^{4+} ions, trigonal crystalline field, configuration mixing, and lower coordination. These are now considered successively.

1. Exchange Coupling

To estimate the effect of antiferromagnetic exchange coupling on the susceptibility above the Néel point we have considered a single pair of Co^{4+} ions coupled according to

$$H' = AS_1 \cdot S_2. \qquad (6)$$

Van Vleck has pointed out (*19*) that by application of the Wigner–Eckart theorem this interaction will have the same matrix elements as

$$A(g_{J_1}-1)(g_{J_2}-1)J_1 \cdot J_2. \qquad (7)$$

This interaction couples the populated ground level doublets of Co^{4+} with the excited quartets and contributes to the temperature independent part of the susceptibility. We calculate a susceptibility contribution from this effect of the order of $2N\beta^2 A/k\zeta^2$ in the paramagnetic range. Using $A \lesssim \theta$ (=100 K) to relate the pair problem to the Curie–Weiss behavior of the antiferromagnetic compound (*13*) we obtain a change in Van Vleck TIP susceptibility of 2×10^{-4} cm^3 mol^{-1}. This contribution is not adequate to explain the deviation from the Kotani theory. Also, this interaction does not add to the expected low-temperature value of χT.

2. Trigonal Crystalline Field

The low spin ${}^2T_2(t_2^5)$ configuration, is complementary (*15*) to t_2^1. The t_2^1 ion in a trigonal crystalline field has been treated in detail by Abragam and Bleaney (*17*).

In this case of the cubic field much larger than the trigonal field or spin-orbit coupling, the ${}^2T_2$ splits into three Kramers doublets specified in the following notation:

$$\begin{aligned} A^+ &= \cos\delta\,|+\tilde{1}^- > - \sin\delta\,|\tilde{0}^+ > \\ B^+ &= \sin\delta\,|+\tilde{1}^- > + \cos\delta\,|\tilde{0}^+ > \\ C^+ &= |+\tilde{1}^+ >, \end{aligned} \qquad (8)$$

and the Kramers conjugates of these. In the above $+\tilde{1}$, $\tilde{0}$, $-\tilde{1}$ refer to the z-component of the fictitious orbital angular momentum and the superscripted + and − signs refer to the z-component of the spin. The parameter δ, which describes the mixing of states by the spin-orbit coupling, depends upon Δ, the trigonal field splitting, and ζ, the spin-orbit parameter. From these wave functions and the corresponding eigenvalues (*17*) E_A, E_B, E_C, with δ as an arbitrary parameter, we have calculated the magnetic susceptibility in the form

$$\chi = N\frac{\Sigma \chi_i e^{-E_i/kT}}{\Sigma e^{-E_i/kT}} \; (i = A, B, C). \qquad (9)$$

The energy levels relative to the ground level are shown in Fig. 5. The susceptibility of each level i is given by

$$\chi_i = \frac{\beta^2}{kT}[A_i + (kT/\zeta)B_i]. \qquad (10)$$

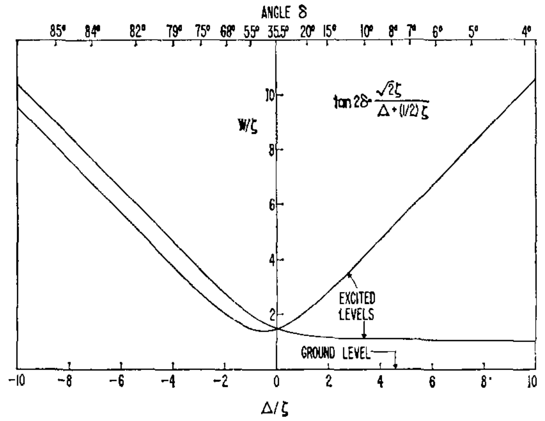

FIG. 5. Energy level diagram of t_2^5 configuration in cubic and trigonal fields. Reduced energy levels W/ζ are plotted against reduced trigonal field strength Δ/ζ, where ζ is the spin orbit coupling constant. After Abragam and Bleaney (*15*).

The values of A_i and B_i have been determined numerically for the full range of δ, i.e. for arbitrary trigonal field strength, with the only restrictions that the low spin configuration (t_2^5) be the ground state and that the higher configurations be neglected. In the range of kT/ζ pertinent to this discussion, the expression for χ, eq. 9, is dominated by the lowest lying Kramers doublet. The results for various representative values of δ are given in Fig. 6.

Note that for $\delta = 35.5°$ the trigonal splitting vanishes and the Kotani result is recovered. It is seen that at $\delta = 71°$, which corresponds to trigonal splitting $\Delta = 2.5\ \zeta = 1630\ \text{cm}^{-1}$, the low temperature limit of χT is a maximum, but not quite large enough to agree with the experimental value. Also the slope of χT is reduced, tending toward a better fit at higher temperatures.

3. *Configuration Mixing*

The presence of higher configurations, above t_2^5, in the $^2T_2$ ground state of the Co^{4+} can have significant effect on the susceptibility. This has been studied by de Lisle and Golding (*20*) and Golding (*21*), and also by Harris (*22*), primarily for the ferric ion.

The Racah parameters for the Co^{4+} free ion have been obtained for us by Dr. Jack Sugar of the National Bureau of Standards; the values are $B = 1250\ \text{cm}^{-1}$ and $C = 4750\ \text{cm}^{-1}$. These values were estimated by extrapolation from spectra of neighboring ions (*23*, *24*, *25*). The estimated maximum error is approximately $\pm 100\ \text{cm}^{-1}$. For the application which follows, no modification of the coefficients is made for the effect of chemical binding. It is found that variations in B of the order of 20% will produce insignificant changes in the susceptibility.

Using these values, we may solve the secular equations for the d^5 crystal field problem (*15*,

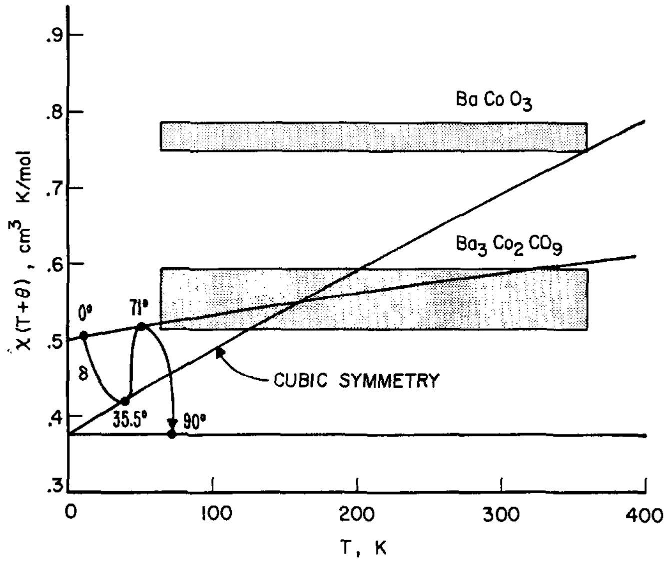

FIG. 6. Comparison of experiment with calculated susceptibility of the $^2T_2$, t_2^5 configuration in cubic symmetry with the addition of a trigonal crystal field. Theoretical values are plotted as χT vs T; experimental data shown as $\chi(T+\theta)$ vs T. Angle δ is determined by the ratio of the strength of the trigonal field to the spin orbit interaction. For $\delta = 35.5°$ the trigonal distortion vanishes, reproducing the Kotani result.

21). We approximate the ground state in the low spin domain by

$$\Psi(^2T_2) = a|t_2^5> + b|t_2^4(^3T_1)e> + c|t_2^4(^1T_2)e> + d|t_2^3(^2T_2)e^2(^1A_1 + \ldots\ldots \quad (11)$$

Higher terms do not make a signficant contribution to the susceptibility. The numerical results are similar to those of Mn^{2+} and Fe^{3+}. The crossover to low spin occurs at a ratio of crystal field strength to Racah parameter of Dq/B = 2.5. The low spin wave-function eq. (11) is not very sensitive to Dq/B. We give the values of the wave function parameters for three values of Dq/B.

Dq/B	a	b	c	d
2.5	.974	−.182	−.041	−.126
3.0	.979	−.163	−.039	−.114
4.0	.986	−.135	−.1035	−.096

Since there is no indication of a competition between low and high spin (*22*), we present the calculated susceptibilities in the low spin at the value of Dq/B = 3.0. Golding (*21*) and de Lisle and Golding (*20*) have shown how one may incorporate the effects of configuration mixing into the calculation of the ground state susceptibility in a simple way. This is accomplished by considering the $^2T_2$ to be an orbital triplet with g-factor and spin-orbit coupling parameter having respectively the values γ and ν, where γ and ν are determined from

$$\gamma = -1 + \frac{3}{2}b^2 + \frac{1}{2}c^2 + \frac{\sqrt{6}}{2}(b-c)(2a-d)$$

$$\nu = \left[a^2 - \frac{1}{3}b^2 - bc - \frac{1}{\sqrt{6}}(2a+d)(b+3c)\right]\zeta. \quad (12)$$

In the absence of configuration mixing, $\gamma = -1$, corresponding to the g-factor of the effective orbital triplet of a t_2 hole; ν is then the usual spin-orbit parameter ζ. The values obtained and the ground state g-factor for cubic symmetry are:

Dq/B	γ	ν	g(cubic)
2.5	−1.308	1.157	−2.41
3.0	−1.274	1.154	−2.37
4.0	−1.225	1.145	−2.30

With a g-factor of 2.4 in the ground level we obtained the low temperature limit $\chi T \rightarrow 0.54$ K/mol, in very good agreement with the results for the 3:2 compound $Ba_3Co_2CO_9$. Using this modification to account for the configuration mixing, we have repeated the calculation of the susceptibility in the presence of a trigonal field. The plots of χT vs T are shown in Fig. 7 for several values of δ corresponding to varied trigonal splittings. It is seen that the configuration mixing does raise the moment significantly. The effect of the trigonal splitting spreads the orbital levels apart, and thereby reduces the TIP of the ground level and gives a smaller slope in the χT vs T plot. The slight curvature seen in Figs. 4, 6, and 7 is due to a small thermally excited population above the lowest Kramers doublet.

The best fits, as seen in Fig. 7, occur for angle δ in the region $64° < \delta < 76°$, corresponding to $-1.8 > \Delta/\zeta > -3.3$. It is possible to show that the negative sign of Δ is in agreement with simple considerations of the crystal structure. In $BaCoO_3$ the six oxygen ligands nearest the Co^{4+} ion lie in almost perfect octahedral symmetry ideally at a distance of 2.02 Å. The angle O–Co–trigonal axis is 53.9°, within one degree of the perfect octahedral value of 54.7°. Thus, it is unlikely that the nearest neighbors are responsible for a trigonal splitting greater than the spin orbit splitting. However, the nearest Co^{4+} neighbors lie along the trigonal axis, each 2.38 Å from the central one. (The next nearest Co^{4+} ions are 5.65 Å away, belonging to oxygen octahedra unshared by the central Co^{4+}.) The axial electrostatic field of the nearest Co^{4+} ions is expected to produce a negative splitting of the states of the one t_2 hole of the Co^{4+}, thus causing the orbital triplet to split into a doublet and singlet with the singlet lying lower. It is a characteristic of the theoretical model that positive values of Δ $(0° < \delta < 35.5°)$ would correspond to much steeper slopes in the plot of χT vs T, and are thereby rejected. In the compound $Ba_3Co_2CO_9$ similar considerations apply.

4. *Lower Coordination*

In both of these compounds a small fraction of the Co^{4+} may be reduced to Co^{3+} with a corresponding oxygen deficiency. If the Co^{3+} is at an octahedral site, then most likely $S = 0$, and only a slight reduction in the susceptibility occurs. However, if the Co^{3+} is five-fold coordinated, as is more likely, the high spin value,

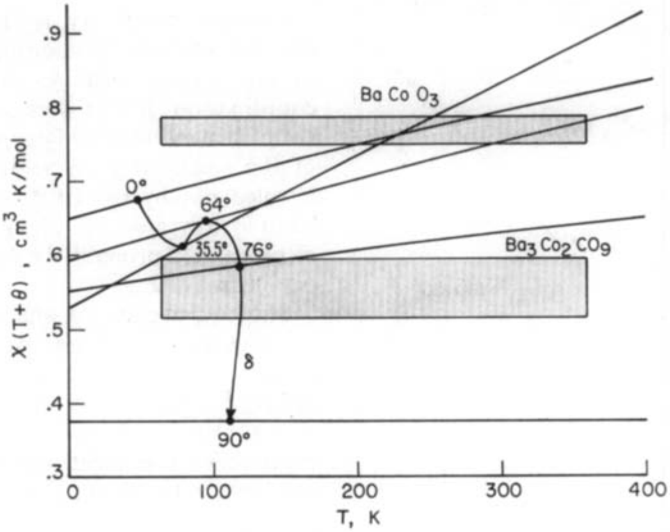

FIG. 7. Comparison of experiment with calculated susceptibility of the $^2T_2$, with t_2^5 and higher configurations in cubic symmetry with the addition of a trigonal crystal field. Theoretical values are plotted as χT vs T; experimental data shown as $\chi(T+\theta)$ vs T. Angle δ is determined by the ratio of the strength of the trigonal field to the spin-orbit interaction. For $\delta = 35.5°$ the trigonal field vanishes.

$S = 2$, may result. This would increase the value of χT, but would not remove the curvature of χT vs T predicted by the Kotani theory. However, if this additional contribution of Co^{3+} is taken into account, along with configuration mixing and distortion for the Co^{4+}, then a better fit between theory and experiment would be possible, especially for the compound $BaCoO_3$.

C. Ni in Octahedral Environment

Susceptibility and EPR measurements were made on the compound $Ba_3Ni_2CO_{9-x}$. The EPR measurements were performed at X-band (9.30 gHz) on powdered samples at both room and liquid nitrogen temperatures. One strong absorption line was observed at .310 T (1 Tesla = 10,000 Gauss); the full widths between inflection points of the absorption were .040 T and .010 T respectively at the two temperatures. No other absorption peaks were observed between zero field and approximately .6 T. It is most likely that this line arises from one Kramers doublet corresponding to $g = 2.15$. This is in close agreement with g-values obtained in other compounds containing octahedrally coordinated Ni^{3+} in lower spin configuration (*26*). The experimental results cannot be interpreted as arising from high spin Ni^{3+} ($S = 3/2$) or Ni^{2+} ($S = 1$). In these cases either very broad lines or additional lines would have been expected.

If it is assumed that the Ni is in the 3+ and 4+ oxidation states, the formula may be written $Ba_3Ni_n^{3+}Ni_{2-n}^{4+}CO_{9-n/2}$. Then, if we assume that both Ni ions are at octahedral sites, the low spin description provides satisfactory agreement with the experimental susceptibility. The estimate of the susceptibility is based on the following: For Ni^{4+} low spin (d^6, $S = 0$), Griffith (*16*) gives the temperature independent paramagnetic (TIP) susceptibility as

$$\chi_{d^6} = 16N\beta^2/\bar{E}, \tag{13}$$

where $\bar{E}$ is an average energy denominator associated with non-vanishing matrix elements of the angular momentum operator. For Ni^{3+} low spin (d^7, $S = 1/2$), we have Curie and TIP contributions,

$$\chi_{d^7} = N\beta^2\left[\frac{g^2}{4kT} + \frac{12}{\bar{E}}\right]. \tag{14}$$

The measured susceptibility per mole of Ni was fitted to the equation

$$\chi = \frac{A}{T+\theta} + B, \tag{15}$$

the best fit being obtained for $\theta = 1$ K, $A = .125$ cm³ K/mol, and $B = 100 \times 10^{-6}$ cm³/mol; see Fig. 8. The calculated value of the Curie constant of Ni^{3+} ($S = 1/2$, $g = 2.15$) is 0.433 cm³ K/mol.

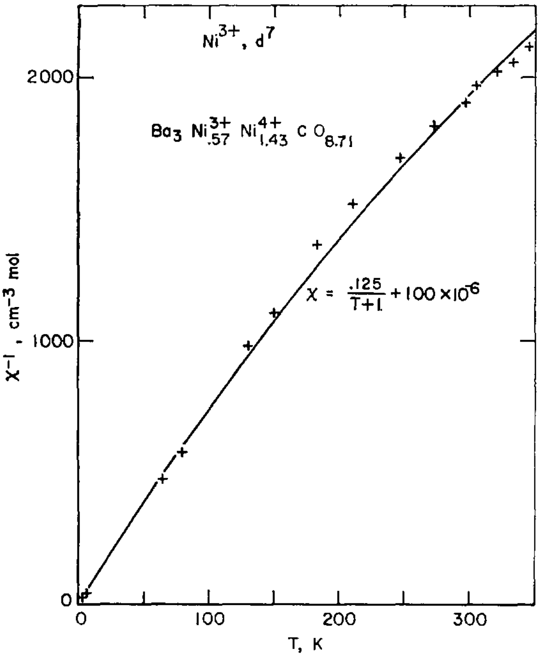

FIG. 8. Measured susceptibility of $Ba_3Ni_n^{3+}Ni_{2-n}^{4+}CO_{9-n/2}$ designated by +. Solid line, described by equation, is fitted to experimental points. Best fit of this form leads to $n = .57$; see text.

Therefore, the mole fraction of Ni^{3+} is 0.29 and the chemical formula is $Ba_3Ni_{.57}^{3+}Ni_{1.43}^{4+}CO_{8.71}$. Having fixed the concentration to match the temperature dependent part of the susceptibility, we can calculate the expected TIP susceptibility. The theoretical estimate of the total susceptibility is

$$\chi_{\text{theor.}} = .29N\beta^2\left[\frac{g^2}{T}+\frac{12}{\bar{E}}\right]_{\mathrm{Ni}^{3+}} + .71N\beta^2\left[\frac{16}{\bar{E}}\right]_{\mathrm{Ni}^{4+}} \tag{16}$$

Using reasonable value of the $\bar{E}$'s (28,000 cm^{-1} and 30,000 cm^{-1} for Ni^{3+} and Ni^{4+}, respectively (*15*)) we obtain the prediction

$$\chi_{\text{theor.}} = .29\left[\frac{.433}{T}+107\times10^{-6}\right]+.71\,[137\times10^{-6}]$$
$$= \frac{.125}{T}+130\times10^{-6}\ \mathrm{cm^3/mol}. \tag{17}$$

Had we used slightly larger values for the $\bar{E}$'s and/or reasonable orbital reduction factors for the TIP matrix elements, then the agreement of the calculated TIP with the experiment would have been even better.

Another possibility is that the Ni^{3+} is not six-fold octahedrally coordinated, but is adjacent to an oxygen vacancy, thus having five-fold coordination. If this were so it is probable that the Ni^{3+} would have high spin ($S = 3/2$) because of the weaker ligand field. However this spin is ruled out by the EPR results. On the other hand if low spin ($S = 1/2$) occurred, the EPR results would probably be similar to those of the octahedral case.

Subsequent chemical analyses were performed[1] to measure the average oxidation state of the nickel. Samples were dissolved in a slightly acidified KI solution and the liberated iodine was titrated with thiosulphate. The analyses, expressed as percent oxygen (active oxygen) available in the starting material when all nickel is reduced to the 2+ state, yielded an average of 4.18% oxygen. This corresponds to the formula $Ba_3Ni_{0.44}^{3+}Ni_{1.56}^{4+}CO_{8.78\pm0.05}$ which is in reasonable agreement (4.02%) with that derived from the magnetic data.

IV. Conclusion

In the compound with tetrahedral environment, Ba_2CoO_4, the susceptibility is explained satisfactorily on the basis of the high spin configuration of the Co^{4+}. In the case of octahedral environments of the Co^{4+}, i.e., for the compounds $Ba_3Co_2CO_9$ and $BaCoO_3$, the low spin configuration is clearly the proper description. However, the *g*-factors observed from susceptibility data are significantly higher than the Kotani prediction, and the temperature independent contribution to the susceptibility is much smaller than the theoretical value. This disagreement is reduced when one considers the effects of the presence of higher configurations (above t_2^5) and departures from perfect octahedral symmetry, compatible with expectations for the crystal structures involved. An additional case of Ni^{3+} in a similar octahedral structure has been discussed and analyzed; EPR and susceptibility results indicate the low spin configuration.

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[1] Performed by a company independent of the National Bureau of Standards.

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