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Paramagnetic Resonance of Cr^{3+} in the Layer Structure of $NaInS_2$

K. A. Müller and W. Berlinger
IBM Zurich Research Laboratory, 8803 Rüschlikon, Switzerland

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The resonance of a localized paramagnetic impurity in a ternary layer structure is reported for the first time. The Cr^{3+} substitutes for the In^{3+} and shows a resolved hyperfine interaction with the six coplanar next-neighbor indium cations. An in-plane fractional charge transfer of 3.0% on the indium ions or 1.0% per $3d$ electron is deduced. $g=1.983\pm0.001$ and $D=-0.0392\pm0.003$ cm^{-1} at 300°K. The axial D parameter changes linearly with temperature down to 120°K at a high rate of $\partial D/\partial T=-0.86$ G/°K, which is ascribed to the thermal expansion of the lattice. A comparison between the D parameter observed at 4.2°K and the total uniaxial magnetic anisotropy field of $NaCrS_2$ is made, from which it is concluded that about $-\frac{1}{7}$ of the latter quantity results from single-ion ligand field effects.

I. INTRODUCTION

A LARGE amount of electron paramagnetic resonance data has so far been accumulated in single crystals, amorphous solids, and molecules in solution, and also partially on surfaces. In layer structures the electron spin resonance of mobile carriers in graphite[1] and in the alkali-metal graphites[2] C_nMe has been observed. Although in graphite, apart from the alkali metals, over twenty compounds[3] like $FeCl_3$ are known to intercalate between the graphitic layers, no resonance has been reported for these compounds. This is in part due to the difficulty of diluting a special system with a nonmagnetic species and partly because these systems are highly turbostratic. Resonance of a number of paramagnetic ions—V^{2+}, Mn^{2+}, Fe^{2+}, Ni^{2+}, and Cu^{2+}—has been reported in the layer structures of $CdCl_2$ and $MgCl_2$.[4] All these ions are octahedrally surrounded by six Cl ions. In these studies no particular emphasis was put on the layer structure, nor results obtained which are related to it. An exception is the most recent study of Hoeve and Van Ostenburg[5] of Mn^{2+} in $CdCl_2$. Here an appreciable dependence of the spin Hamiltonian parameter D with temperature was found and related to the anisotropic thermal expansion of the layer structure.

In the present paper we summarize a study on $NaInS_2$ micalike single crystals doped with chromium ions.[6] The resonance of the trivalent chromium ions substituted for a trivalent indium ion is analyzed. A large temperature dependence of the axial D parameter is also found and shown to be mainly due to thermal changes of the layer structure parameters. However, the most interesting observation of the present study and directly related to the layer structure is the resolved superhyperfine structure (SHFS) of the Cr^{3+} ion with the six *coplanar* In^{3+} ions. From this SHFS a quantitative analysis of the fractional charge transfer of the three electrons in the $^4A_2$ ground state of the Cr^{3+} ion to its six coplanar next-nearest neighbors could be obtained.[6] The fractional amount of indium $5s$ and $5p$ wave functions admixed is nearly as large as the one resulting from the excited $(3d)$ $^4T_2$ level via spin-orbit coupling. A consequence of this excited indium wave function admixture appears to be a negative contribution to the EPR g shift Δg. The latter is found to be more negative than the shift we estimate theoretically from all the possible excitations excluding those to the indium levels. To this end, the optical properties of the Cr^{3+} ion are relevant. In fact, the present study was initiated because measurements of the optical and magnetic properties of single crystals of the isomorphic magnetic $NaCrS_2$ compound were underway in this laboratory.[7] From them the uniaxial magnetic anisotropy was known. From our data then the ratio of the single-ion crystal-field anisotropy to the sum of exchange and dipolar contribution could be obtained.

Independently of the present effort, and nearly simultaneously with it, Béne and White[8] reported a study of the chromium-doped layer structure BiI_3. The object was also to compare single and pair ion properties in the layer structure with those of the magnetic $Cr^{3+}X_3$ layer compounds. We shall see that their reported D parameter of the single substitutional Cr^{3+} ion in BiI_3 agrees well with the one we find in $NaCrS_2$, and that their g value supports the conclusions we draw from our observation regarding the effects of charge transfer levels on the g shift.

In the diamagnetic $NaInS_2$ and in the magnetic $NaCrS_2$ compound, the mono- and trivalent cations as

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[5] H. G. Hoeve and D. O. Van Ostenburg, Phys. Rev. **167**, 245 (1968).

[6] K. A. Müller, W. Berlinger, R. Meili, and C. Schüler, Helv. Phys. Acta **41**, 392 (1968).

[7] K. W. Blazey and H. Rohrer, Helv. Phys. Acta **41**, 391 (1968).

[8] R. W. Béne and R. L. White, Bull. Am. Phys. Soc. **13**, 435 (1968).

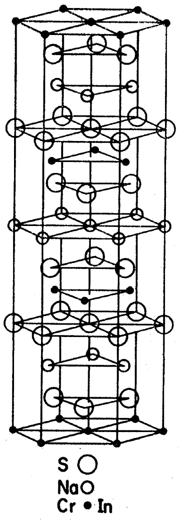

FIG. 1. The crystal lattice of $NaInS_2$ isotype to $NaCrS_2$ after Rüdroff and Stegman (Ref. 10).

well as the sulfur ions form hexagonal layers with the same basis length of 3.80 and 3.53 Å for $NaInS_2$ [9] and $NaCrS_2$,[10] respectively. The stacking along the c axis is $\cdots NaS_{(1)}Me^{3+}S_{(2)} \cdots$, where $S_{(1)}$ and $S_{(2)}$ denote two layers of sulfur rotated around the c axis by 60° [a Me^{3+} is sited at the position (0, 0, 0)]. (See Fig. 1.) Each of these layers follows a cubic close-packed stacking A, B, C along the main axis. The result is that each sodium or Me^{3+} ion is surrounded octahedrally by six sulfur ions; three in layer $S_{(1)}$ and three in $S_{(2)}$. The Me^{3+} and Na^{1+} point symmetry is D_{3d}. The In-S distance is 2.63, whereas in the magnetic compound the Cr-S distance is 2.46 Å.

In Sec. II some experimental details are given, including growth conditions for the $NaInS_2$ crystals. In Sec. III the superhyperfine interaction of the impurity Cr^{3+} with the six coplanar In^{3+} with $I=\frac{9}{2}$ is analyzed in terms of an LCAO wave function including the next-neighbor sulfur ions and the next-nearest-neighbor In^{3+} ions. In Sec. IV the spin Hamiltonian parameters g and D of Cr^{3+} replacing an In^{3+} ion are discussed. The temperature variation and sign of D is assigned and its low-temperature value is compared to the uniaxial anisotropy constant found for $NaCrS_2$.

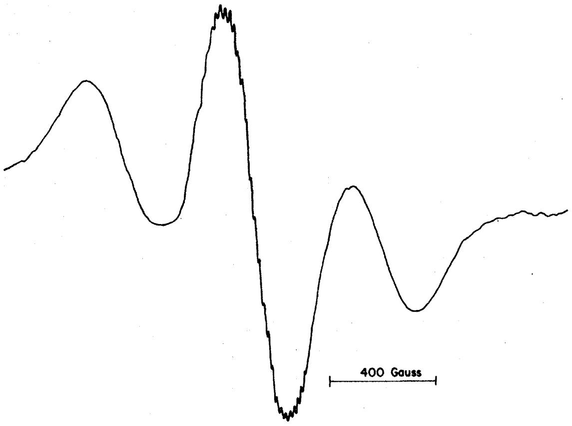

FIG. 2. EPR spectrum of Cr^{3+} in $NaInS_2$ at 19.2 Gc/sec and 77°K for **H** || c.

II. EXPERIMENTAL RESULTS

Single crystals were obtained by a method first described by Schneider.[11] A mixture of six parts sodium carbonate, six parts sulfur and one part indium oxide by weight, plus 0.3% of Cr_2O_3 was heated in a well-covered alumina crucible to 800°C. The melt was then cooled to room temperature within 4–5 h. The yellow micalike single crystals were washed out from the flux cake with water.

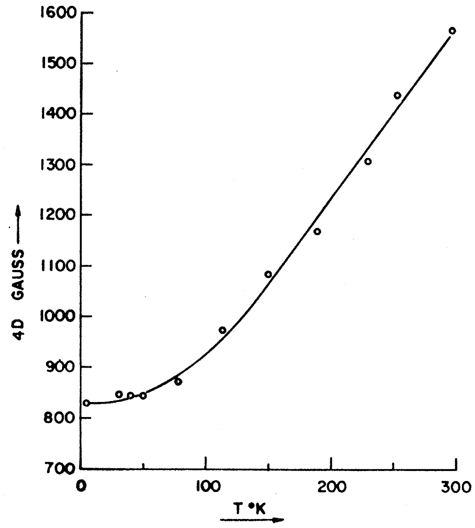

FIG. 3. Temperature dependence of the splitting $4D$ between 4.2 and 300°K.

The resonances were observed for **H** parallel and perpendicular to the c axis with a K-band single-side-band superheterodyne EPR spectrometer. The variable temperature cavity was operated between 4.2 and 300°K. Between 300 and 77°K a spectrum of three lines was observed due to the $\pm\frac{3}{2}\leftrightarrow\pm\frac{1}{2}$ and $+\frac{1}{2}\leftrightarrow-\frac{1}{2}$ transitions of the $^4A_2$ ground state of Cr^{3+} (Fig. 2).

The Cr^{3+} substitute for the In^{3+} ions as expected from their charge state and their similar ionic radii. This is inferred from the superhyperfine structure with the six coplanar In ions to be discussed in Sec. III. This hyperfine interaction also causes the $\pm\frac{1}{2}$ transition to have, at room temperature, an over-all line-width only a factor of 1.07 smaller than the outer

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[9] R. Hoppe, W. Lidecke, and F. C. Frorath, Z. Anorg. Allgem. Chem. **309**, 49 (1961).

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[11] R. Schneider, J. Prakt. Chem.(2) **56**, 401 (1897).

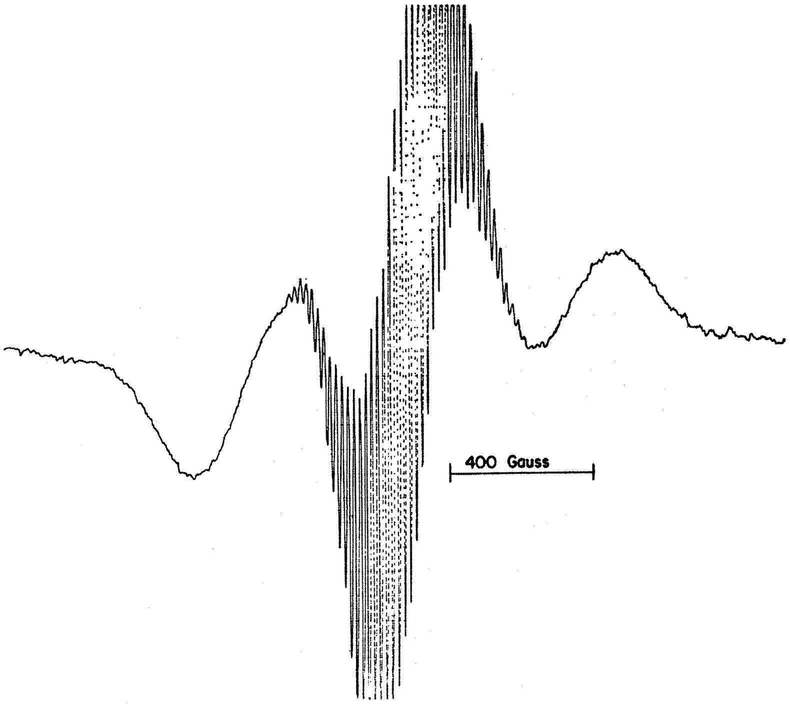

FIG. 4. EPR spectrum of Cr^{3+} in $NaInS_2$ at 4.2°K for $\mathbf{H}\,||\,c$ showing resolved superhyperfine structure of the $+\frac{1}{2}\rightarrow-\frac{1}{2}$ transition.

two lines which have $\Delta H=270$ G. This means that the fraction of the width of the $\pm\frac{3}{2}\leftrightarrow\pm\frac{1}{2}$ lines caused by strains in the crystal is at least one order of magnitude smaller than that due to the hyperfine interaction.

The distance of the outer lines equidistant to the pure magnetic $\pm\frac{1}{2}$ transition was for $\mathbf{H}\perp c$ approximately one half that for $\mathbf{H}\,||\,c$. Because the width of the three lines is comparable to their splitting, $D(3\cos\theta^2-1)$, they partially overlap. The derivatives of the lines were computer-simulated with intensities in the ratio 3:4:3. Gaussian line shapes had to be assumed to obtain a good fit. This is in agreement with the line shape being principally determined by the hyperfine splitting. From the best-fitting simulation (including the line shape) the values of D and g were obtained using the conventional spin Hamiltonian:

$$\mathcal{H}=g_{\perp}\beta(S_xH_x+S_yH_y)+g_{||}\beta S_zH_z+D[S_z^2-\tfrac{1}{3}S(S+1)],$$

$$g_{\perp}\simeq g_{||}=1.983\pm0.001,$$

and

$$|D|=0.0362\pm0.0030\ \text{cm}^{-1}$$

at 300°K. The axial D parameter was then measured as a function of temperature, and a large 47% change was found on cooling down to 4.2°K. Figure 3 shows the analyzed peak-to-peak distance $4\,|\,D\,|$ of the two outer fine-structure lines of the spectrum as a function of temperature. The change in D is linear, $(\partial\,|\,D\,|/\partial T)=0.86$ G/°K, down to 120°K, where a gradual change to zero slope occurs. The trace taken at 4.2°K (Fig. 4) shows that the low-field line has a larger intensity than the high-field line. This became more pronounced by pumping on the helium, and at 1.7°K the high-field line was barely visible. This indicates that the $-\frac{3}{2}\rightarrow-\frac{1}{2}$ line lies at $H_0-2\,|\,D\,|/g\beta$ and thus D is negative. Therefore the near-constant low-temperature value of $D(T)$ (see Fig. 3) amounts to

$$D(0)=-(208\pm20)\ \text{G},$$

a result we shall refer to in Sec. IV; further, $\partial D(T)/\partial T<0$.

In certain samples a line at $g=2.05\pm0.02$ was visible. This may be due to the $\pm\frac{1}{2}$ transition of Cr^{1+} at a Na^{1+} site. In covalent crystals, a positive g shift has been calculated for a $3d^5$ configuration by Watanabe[12] and has also been observed experimentally.[13] No fine structure was observable; probably the $\pm\frac{1}{2}\leftrightarrow\pm\frac{3}{2}$ and $\pm\frac{3}{2}\leftrightarrow\pm\frac{5}{2}$ lines were too broad or the fine-structure constants too small. Their detection would have allowed an unambiguous assignment of this line.

III. CATION-SUPERHYPERFINE STRUCTURE

A hyperfine pattern near $g=2$, barely visible at room temperature, became more distinct on cooling to low temperatures if care was taken not to overmodulate. At 4.2°K for $\mathbf{H}\,||\,c$, over 50 equidistant hyperfine lines were detected, as shown in Figs. 4 and 5.

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[12] H. Watanabe, J. Phys. Chem. Solids **25**, 1471 (1964).

[13] K. Morigaki and T. Hoshina, Phys. Letters **17**, 85 (1965).

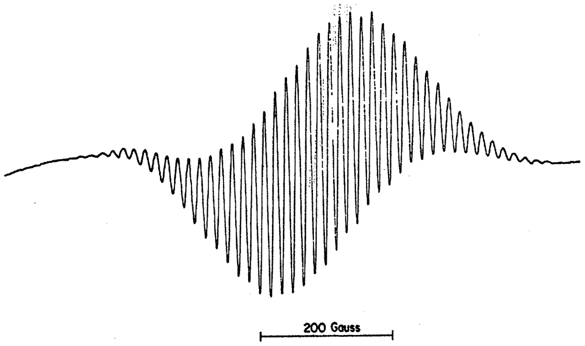

FIG. 5. An expanded record of the $+\frac{1}{2}\rightarrow-\frac{1}{2}$ transition at 4.2°K with over 50 resolved superhyperfine lines due to the interaction of the Cr^{3+} with its six coplanar next-nearest-neighbor In^{3+} cations.

The lines could also be resolved for $\mathbf{H}\perp c$, but not for other angles of the magnetic field with the c axis. Apparently for the nonpreferred directions the lines are broader. At first it was thought that this pattern resulted from an F center. However, a missing S^{2-} ion, which has trapped an electron, would have three sodium and three indium nearest neighbors. The odd isotopes of these cations have different nuclear spins, and an irregular spacing of the hyperfine lines would result. Further, a very accurate g-value determination of the electronic spin which gives rise to the hyperfine structure was made for $\mathbf{H}\parallel c$. The resulting $g_{\parallel}$ value coincided within the experimental accuracy with that of the $\pm\frac{1}{2}$ transition of Cr^{3+} at 300°K: $g_{\parallel}=1.983$. Thus the lines must result from the superhyperfine interaction of the unpaired d^3 spins of the transition-metal ion with its six coplanar next-nearest-neighbor In^{3+} ions. There exist two indium isotopes with spin $\frac{9}{2}$, In^{113} and In^{115}, with magnetic moments of $5.507\mu_N$ and $5.496\mu_N$, and natural abundancies of 95.84% and 4.16%, respectively. For our purposes we can then assume that 100% of the indium atoms have a spin of $I=\frac{9}{2}$ and a magnetic moment of $5.50\mu_N$. Therefore a 55-line pattern should result. The relative intensities of these lines can be calculated as follows.

At each of the six sites the indium nuclear spins have ten possibilities to orient themselves with respect to the external applied field. Thus the intensity problem is equivalent to counting in how many numbers from 000 000 to 999 999 the sum of the digits is 0, 1, $\cdots$, 54. This yields once each the sums 0 and 54, six times each the sums 1 and 53, etc. The result of a computer calculation performed on an IBM 360/40 is given in Table I in the second column.[14] In the third column the relative intensities to the central line $m=\sum_{iI}m_I{}^i=0$ with an assumed intensity of 1 are listed. In Fig. 6 these relative theoretical intensities for $|m|$ values are plotted together with the measured relative amplitudes of the $M_s=\pm\frac{1}{2}$ transitions. The latter were taken to be proportional to the relative intensities of the $\frac{1}{2}$, $|m|$ lines assuming a negligible dependence of the width of the single line as a function of $|m|$ value (no such a dependence was detectable within our experimental limits). A comparison between the experimental and theoretical intensities is quite good in spite of this assumption except in the region of $|m|=14$. Here the results fell somewhat short of their expectations. However, the over-all agreement is such that it further supports our assignment of the origin of the superhyperfine structure.

From the equidistant spacings of the hyperfine lines for $\mathbf{H}\parallel c$ and $\mathbf{H}\perp c$ we find the interaction constants to be

$$A_{\parallel}=16.5\pm0.2\ \text{G},$$

$$A_{\perp}=17.2=0.2\ \text{G},$$

$$\Delta H_{\parallel}=\Delta H_{\perp}=8\ \text{G}.$$

It is not surprising that for single $(\frac{1}{2}, m)$ lines the width is broader for orientation angles of $\mathbf{H}$ different from 0° and 90°. This also applies for the impossibility to resolve the hyperfine structure in the non-purely-magnetic $\pm\frac{3}{2}\leftrightarrow\pm\frac{1}{2}$ lines. In both cases the lines are usually broader due to strain effects in conventional crystals. In addition to these effects, irregularities in the stacking of the layers and turbostratic regions are also present in our not particularly well-grown layer crystals. These latter effects were at first estimated to be so large that we regard it as an unexpected success to have been able to resolve the cation-superhyperfine structure.

No hyperfine structure of the nearest-neighbor sul-

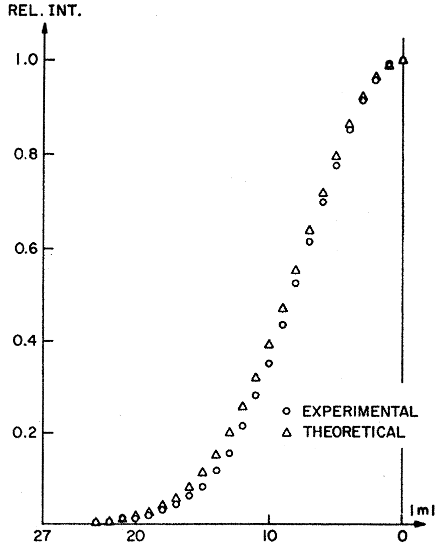

FIG. 6. A comparison between the theoretical intensities and experimental amplitudes of the Cr^{3+}-In^{3+} superhyperfine interaction.

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[14] We are indebted to Dr. E. O. Schulz-DuBois for the computer-adapted formulation of the problem and to I. Csajka for helping us to program it.

fur ions is observable, as only the isotope S^{33} with spin $I=\frac{3}{2}$ and a natural abundance of 0.7% can yield such an interaction.

The In superhyperfine interaction may be represented by a term in the spin Hamiltonian of the form

$$\mathcal{H}_{\mathrm{SHF}}=\sum_{i=1}^{6} a\mathbf{S}\cdot\mathbf{I}_i+b(3S_zI_{zi}-\mathbf{S}\cdot\mathbf{I}_i), \qquad I_i=\tfrac{9}{2},\ z\parallel c$$

where i denotes the six coplanar In^{3+} neighbors, and within our experimental accuracy a and b do not depend on i, i.e., the directions of all the axial terms are parallel to the c direction. We have with

$$a=\tfrac{1}{3}(A_{\parallel}+2A_{\perp}), \qquad b=\tfrac{1}{2}(A_{\parallel}-a),$$

$$|a|=47.1\pm0.4\ \mathrm{Mc/sec},$$

$$|b|=0.8\pm0.4\ \mathrm{Mc/sec}, \qquad \mathrm{sign}\ b=-\mathrm{sign}\ a.$$

$A_{\perp}$ and $A_{\parallel}$ are not temperature-dependent between 4.2 and 300°K within our experimental accuracy. Thus a and b do not show any explicit vibrational or other thermal effects.[15]

We analyze our data in terms of a three-electron wave function whose components are linear combinations of atomic orbitals of the central Cr^{3+} ion, the six nearest-neighbor sulfur ions, and next-nearest-neighbor coplanar indium ions.

TABLE I. Computed absolute and relative intensities of the $(\frac{1}{2}, m)\leftrightarrow(-\frac{1}{2}, m)$ superhyperfine transitions.

$\|m\|$	Intensities	Relative intensities
27	1	0.000018
26	6	0.000109
25	21	0.000380
24	56	0.001014
23	126	0.002280
22	252	0.004561
21	462	0.008362
20	792	0.014334
19	1 287	0.023293
18	2 002	0.036234
17	2 997	0.054242
16	4 332	0.078404
15	6 062	0.109715
14	8 232	0.148990
13	10 872	0.196771
12	13 992	0.253240
11	17 577	0.318124
10	21 582	0.390610
9	25 927	0.469250
8	30 492	0.551871
7	35 127	0.635760
6	39 662	0.717838
5	43 917	0.794849
4	47 712	0.863534
3	50 877	0.920817
2	53 262	0.963983
1	54 747	0.990860
0	55 252	1.000000

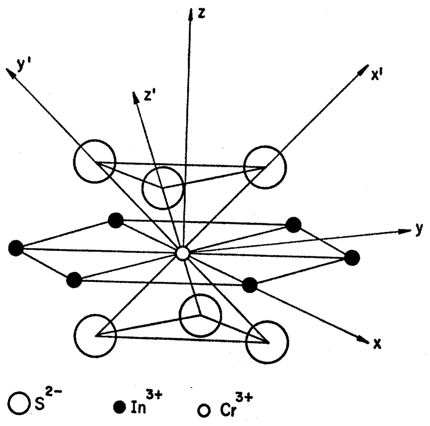

FIG. 7. A graph of the nearest six S^{2-} anions and next-nearest six In^{3+} cation neighbors of a Cr^{3+} impurity in NaInS$_2$. Assuming the sulfur ions form a regular octahedron, the x, y, and z axes are shown as chosen in the text for the zero-order approximation of the employed wave functions. Those of the x', y', z' axes used in the first-order approximation for D_{3d} symmetry are also shown.

We start out with the zero-order ground-state Slater determinant of the $3d^3$, t^3 configuration $|a^+b^+c^+\rangle$. Here abc represent d^3 wave functions transforming as $x'y'$, $x'z'$, $z'x'$, and sited at the center of a regular sulfur octahedron with the S^{-2} at the coordinates $x'=+a$, $y'=0$, $z'=0$ and cyclic permutations thereof (see Fig. 7). We further assume that each of these three antibonding orbitals is already hybridized with those of the sulfur orbitals including overlap; following Lacroix[16] we have

$$|a\rangle=\beta\,|a_0\rangle-(1-\beta^2)^{1/2}\,|a_0'\rangle, \qquad |b\rangle=\cdots\ |c\rangle=\cdots,$$

where $1-\beta^2$ represents the π bonding parameter τ_π of the orthonormalized chromium $3d$ and sulfur $3p$ functions

$$|a_0\rangle=\xi'\,|da\rangle+\eta'\,|p\pi a\rangle,$$

$$|a_0'\rangle=\eta'\,|da\rangle+\xi'\,|p\pi a\rangle,$$

$$\xi'=\frac{1}{2}\left(\frac{1}{(1-\Sigma_\pi)^{1/2}}+\frac{1}{(1+\Sigma_\pi)^{1/2}}\right),$$

$$\eta'=-\frac{1}{2}\left(\frac{1}{(1-\Sigma_\pi)^{1/2}}-\frac{1}{(1+\Sigma_\pi)^{1/2}}\right),$$

and $\Sigma_\pi=\sqrt{3}S(dt, p\pi)$ is the π overlap integral of the $3d$ and $3p$ functions.

The t_2 functions so far given reflect pure O_h symmetry, while our center has D_{3d} symmetry with the threefold rotation axis parallel to the [111] axis of the octahedron. Thus we transform our zero-order

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[15] W. M. Walsh, Jr., J. Jeener, and N. Bloembergen, Phys. Rev. **139**, A1338 (1965).

[16] R. Lacroix and G. Emch, Helv. Phys. Acta **35**, 592 (1962).

functions to obtain appropriate basis functions for the D_{3d} point group:

Wave function	D_{3d} representation
$\lvert o\rangle = (1/\sqrt{3})(\lvert a\rangle + \lvert b\rangle + \lvert c\rangle)$,	Γ_1
$\lvert p\rangle = (1/\sqrt{6})(2\lvert a\rangle - \lvert b\rangle - \lvert c\rangle)$, $\lvert q\rangle = (1/\sqrt{2})(\lvert b\rangle - \lvert c\rangle)$,	Γ_3

$$\lvert a^+, b^+, c^+\rangle \equiv \lvert o^+, p^+, q^+\rangle.$$

The $\lvert o\rangle$ function can form σ bonds with the $5s$ and in-plane $5p$ indium orbitals. Indeed, six of their twelve lobes are in plane with the six In^{3+} ions and point in their direction (see Fig. 7). The lowest Γ_1-type function of the latter which can be obtained with the method of linear combination of atomic orbitals (LACO) from $5s$ indium orbitals is

$$\lvert o_{\mathrm{In}}\rangle = (1/\sqrt{6}) \sum_{i=1}^{6} \lvert 5s_i^{\mathrm{In}}\rangle.$$

An analog function can be set up for the in-plane $5p$ indium functions pointing toward the Cr^{3+} ion. $\lvert o_{\mathrm{In}}\rangle$ corresponds to the lowest filled bonding $2s$ orbital of a benzene ring.

If we neglect overlap in the normalization, which is justified by the actual admixture described below, then the first-order $\lvert o'\rangle$ function is

$$\lvert o'\rangle = (1-\rho^2)^{1/2} \lvert o\rangle + \rho \lvert o_{\mathrm{In}}\rangle.$$

Here ρ^2 represents the amount of in-plane σ bonding of the antibonding electrons. To the above, mainly $3d$ antibonding wave functions, two others can be put aside: one bonding, with mainly sulfur character, and an antibonding with mainly indium character. The latter is of no further interest for the following; however, we shall also omit the bonding orbital. In doing so we neglect the transfer of electron charge via the sulfur orbitals to those of indium. A justification of this approach is given below.

Using the matrix elements of the Fermi contact interaction term which is responsible for the isotropic part a of the hyperfine interaction

$$\mathcal{H}_{\mathrm{HF}} = -(8\pi/3)(\mu_e\mu_n/I_n)\delta(r),$$

for a we obtain

$$a = \langle o' \lvert \mathcal{H}_{\mathrm{HF}} \rvert o'\rangle,$$

$$a = (8\pi/3)(I_n)^{-1}\mu_e\mu_n(\rho^2) \lvert \psi_{5s}^{\mathrm{In}}(0) \rvert^2,$$

which can be equated to the measured value previously given.

Räuber and Schneider[17] have recently observed by EPR experiments the hyperfine interaction of two-valent indium In^{2+} in ZnS with configuration $5s^1$ to be $a = 9.362 \pm 0.005$ Gc/sec. This corresponds to $\lvert \psi_{5s}^{In^{2+}}(0) \rvert^2 = 64.0 \times 10^{-24}$ cm^{-1} as compared to the isoelectric Ag^0 for which, for the same wave function, atomic beam resonance experiments yielded $\lvert \psi_{5s}^{Ag^0}(0) \rvert^2 = 63.9 \times 10^{-24}$ cm^{-1}.[17] Thus we can be confident that the value reported by Räuber and Schneider is an adequate measure for the probability of the $5s$ In^{2+} wave function at the nucleus. With this we obtain

$$\rho^2 = 3.0\%,$$

a remarkably large value for in-planar cation-cation bonding. We have to restrict this remark because ρ^2 corresponds to the factor of the $\lvert o\rangle$ function electronic transfer. However, in the Slater determinant $\lvert o^+, p^+, q^+\rangle$ all three $3d$ functions are equivalent. Thus we conclude that from the totally present three $3d$ wave functions, only a third of ρ^2 or 1.0% per electron is transferred to the six coplanar indium ions.

So far we have omitted the discussion of the b term. First we remark that in the previous discussion we have implicitly assumed that a is positive as $a(In^{2+})$ must be, because the In^{115} and In^{113} nuclear magnetic moments are positive. Because b has the opposite sign of a, $b<0$.

A single, fully occupied $5p_\xi$ orbital yields an anisotropy constant

$$b_\xi = \tfrac{2}{5}(1/I_n)\mu_e\mu_n\langle 1/r^3\rangle 5p_\xi$$

from the dipolar matrix elements of the o', p', and q' functions. As discussed above, $b = b_z$ is negative. To obtain such a result, the in-plane contribution of the function on the In^{3+} must be larger than the p_z one. Further, $b_x = b_y$, if the nonisotropic part is exactly axial along z, i.e., the p contribution of the ith In^{3+} ion pointing towards the Cr^{3+} must be as large as that of the p function, being tangential to this direction and in-plane. The former would form σ bonds with the Cr^{3+}, as does the $\lvert o_{\mathrm{In}}^{5s}\rangle$ function, and is expected to be larger than π bonding. The second forms σ bonds with the $5p$ function of the $(i-1)$th and $(i+1)$th In^{3+} in the ring, and π bonds with the central wave function. When these two contributions differ, an in-plane anisotropic hyperfine interaction should be observable. Furthermore, if π bonding of the $5p_z$ functions with the p and q orbitals is present, then the former contributions are enhanced, because in measuring $b_z = b$ only their difference is known.

From the analysis of F centers, it is known[18] that if the b term is approximately an order of magnitude smaller than the a term, the fractional percentage of the s and p characters of the single ith-ion wave function is comparable. Thus from the two orders of magnitude smaller b value we conclude that in our case the p character is an order of magnitude smaller. In view of this small amount, the near 50% uncertainty, and the intricacy of its assignment discussed

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[17] A. Räuber and J. Schneider, Phys. Status Solidi **18**, 125 (1966).

[18] J. J. Markham, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1966), Suppl. 8.

above, we do not attempt a quantitative interpretation of the b parameter.

Resolved cation superhyperfine interaction was first observed for Mn^{2+} in CdS by Dorain[19] a decade ago. Subsequent experiments in CdSe and CdTe indicated that the fractional transfer to the twelve next-nearest-neighbor indium atoms (Cd^{111} and Cd^{113}) is the same within the experimental accuracy, namely, 0.24%, and equals the one found for Mn^{2+} in ZnS on the twelve Zn^{67} atoms.[20,21] A value of 0.51%, or twice as large, was obtained for Cr^{1+} in CdTe.[20] Chen *et al.*[21] discuss the possibility that part of the observed values is due to indirect transfer. More recently, Estle and Holton[22] published a remarkable study on the zinc chalcogenides. They showed that from the superhyperfine structure resulting from nearest-neighbor anions, only a small fraction of a few percent of unpaired spin density was found on these four nearest neighbors. From their results an induced transfer mechanism over the anions to the cation does not seem very probable in II-VI compounds.[23]

In another study Chen *et al.*[24] showed that cation-superhyperfine structure (SHFS) of V^{4+}, Cr^{3+}, and Mn^{4+} observed in SnO_2 on Sn^{115} and Sn^{117} nuclei was due to direct overlap. These authors computed the overlap of the transition-metal ions with the next- and second-next-nearest tin $5s$ functions lying at 3.19 Å (Sn 1) and 3.70 Å (Sn 2) from the Me ion. Although they did not estimate the fractional transfer, they showed that the SHFS is directly proportional to the overlap, as the covalency coefficients should be for direct interaction. They also estimated the indirect interaction by computing anion-cation overlaps, and concluded that the indirect mechanism gives an opposite spin density and is an order of magnitude smaller.[25]

In our case the In^{3+} ions are located at 3.8 Å from the Cr^{3+}, i.e., at the same distance as the Sn 2 ions in SnO_2 are separated from the Cr^{3+}; thus the direct interaction must be dominant in $NaInS_2$, too. Furthermore, the In^{3+} lie directly along the $|o'\rangle$ σ orbitals (as the Sn 1 ions do in SnO_2). One may wonder whether the indirect interaction is not enhanced owing to the sulfur anions which usually show larger covalency effects than the oxygens. We do not think that the enhancement over the result of Chen *et al.*[24] is appreciable, especially in view of the conclusions drawn from the work of Estle and Holton on the II-VI chalcogenides and the larger anion-cation distances in $NaInS_2$.

IV. DISCUSSION OF THE g AND D PARAMETERS

A. g Shift

The g shift is similar to that found for Cr^{3+} in many oxide compounds, and it may be concluded that the covalency is not enhanced in this sulfur compound. This shift results from two opposing mechanisms: Excitation to nonoccupied antibonding orbitals yields a negative shift, and excitation from occupied bonding states to the $^4A_2$ ground state yields a positive shift. The importance of the second mechanism was recognized by Lacroix[16] in analyzing the Cr^{3+} and isoelectronic Mn^{4+} g shifts in $SrTiO_3$.[26] Here, mainly three states contribute—the $(\bar{\delta}\bar{\epsilon}_a{}^2)$, the $(\bar{\gamma}_l\bar{\epsilon}_a{}^2)$, and the $(\bar{\epsilon}_l\bar{\epsilon}_a{}^2)$ ones—whereas for the antibonding ones only the $(\epsilon_a{}^2\gamma_a)$ state $10Dq$ above the $\epsilon_a{}^3$ contributes.[16] Here γ, ϵ, and δ denote a certain type of subshell. The nomenclature a and b distinguishes between antibonding or bonding ones, and the bar refers to holes in a particular subshell. If, for a given Dq parameter and given term separation between the $^4A_2$ and the bonding states, the influence of the covalency parameters α and β for σ and π bonding of the Cr^{3+} ion with its ligands is considered, the following is recognized from Lacroix's[16] work. For increased covalency, i.e., reduced α and β parameters, the ***negative g shift*** due to the electron excitation to the antibonding $(\epsilon_a{}^2\gamma_a)$ level is ***reduced***, and the ***positive*** shift due to hole excitation to the bonding states is ***enhanced***. Therefore, assuming that the covalency in octahedral sulfur coordination is not lower than in oxygen coordination, and using the results in Ref. 16 for the $CrO_6{}^{-3}$ complex, an upper limit of the total negative g shift can be estimated if the excitation energies are known. Using preliminary optical work in $NaCrS_2$,[27] this is done in the Appendix. The result of the tentative estimate is $-\Delta g^{\mathrm{th}} < 0.013$, which may be compared to the observed value of $-\Delta g^{\mathrm{expt}} = 0.017$. Thus the conclusion is that either the covalency in the sulfur environment is smaller than that in the oxygen coordination, which seems somewhat unlikely, or else one must seek an additional excitation mechanism to antibonding states to account for the negative g shift contribution (no further excitation from bonding states can be conceived).

In this conjunction it has been pointed out to us by Lacroix[28] that excitation to the low-lying antibonding $5s$ and $5p$ orbitals of the indium cations may be important. In Sec. III we deduced from the superhyperfine interaction with the indium cations that 1.0% of the unpaired spin density is sited on In $5s$—

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[19] P. B. Dorain, Phys. Rev. **112**, 1058 (1958).

[20] For a review see the article by R. S. Title, in *Physics and Chemistry of II-VI Compounds*, edited by M. Aven and J. S. Prener (North-Holland Publishing Co., Amsterdam, 1967), p.265.

[21] I. Chen, C. Kikuchi, and H. Watanabe, J. Chem. Phys. **42**, 189 (1965).

[22] T. L. Estle and W. C. Holton, Phys. Rev. **150**, 159 (1966).

[23] Cation SHFS has also been reported for V^{3+}, Cr^{2+}, and Co^{2+} (see Ref. 25).

[24] I. Chen, C. Kikuchi, and H. Watanabe, J. Chem. Phys. **42**, 186 (1965).

[25] Cation SHFS in TiO_2 was also reported for Mn^{4+}, V^{4+}, Mo^{5+}, and W^{5+} but analyzed in less detail. A table summarizing the results of the last three ions is found in the paper of Te-Tse Chang, Phys. Rev. **147**, 264 (1966).

[26] K. A. Müller, Phys. Rev. Letters **2**, 341 (1959).

[27] K. W. Blazey (private communication).

[28] R. Lacroix (private communication).

and roughly an order of magnitude less on In $5p$ orbitals. These numbers may be compared to the fractional admixture (via spin-orbit coupling) of the excited $^4T_2$ level within the $3d$ configuration into the $^4A_2$ ground state, which amounts to approximately $(2\sqrt{2}\lambda/10Dq)\sqrt{K}\simeq 1.4\%$ (see the Appendix). Thus we conclude that excitations from the localized $3d^3$ ground state to the lowest antibonding indium levels may indeed contribute to the observed g shift. This possibility seems to be further supported by the g value of $g=2.058$ found for Cr^{3+} in the layer structure of BiI_3.[8] Here the shift is definitely positive. Thus, the contribution due to charge transfer obviously dominates. This result, obtained for a chromium ion octahedrally coordinated by iodine, supports our view that for a sulfur coordination this process must also be important.

B. D Parameter

Unexpectedly, for a layer structure, D is small, namely, 5.2 times smaller than that of Cr^{3+} in ruby,[29] the signs of D being the same. In both, the point symmetry of the impurity ion is trigonal. One may at first assume that this finding reflects the contribution of covalency and nearest-neighbor anion position on D which, for the sulfur ions in the layer structure, are more regular and show inversion symmetry, in contrast to the oxygen anions in ruby.

In $NaInS_2$ [9] and $NaCrS_2$,[10] the distance of two next-layer sulfur triangles is smaller by -11.7% than the in-layer sulfur distance would require to form a regular octahedron around a Me^{3+} ion. In Al_2O_3 this distance is correct to $+1.2\%$ of the average in-layer oxygen distance, but the sides of the two equilateral oxygen triangles differ by 16%,[30] which appears to induce a larger axial ligand effect. Indeed, Artman and Murphy[31] first pointed out that the odd terms in the crystal field contribute appreciably to the D splitting. However, in the magnesium and zinc aluminum spinels, a large value of $|D|$ of about 0.9 cm^{-1} has been reported.[32] In both lattices the Cr^{3+} is octahedrally coordinated; the point symmetry is trigonal and shows inversion. In $MgAl_2O_4$ the octahedron is elongated along one of the trigonal axes by an amount of $+14.9\%$. Its absolute amount of distortion is thus comparable to the one reported for the sulfur octahedron in the layer compound, but the $|D|$ value in the spinels is much larger than that found in $NaInS_2$. Thus in the latter, D cannot be solely a result of the presence of inversion symmetry and nearest-neighbor anion position. Some compensation due to the six in-layer next-nearest In^{3+} cations seems to be important, too. Considerations of the sign dependence of D on distortion also favor such a possibility.

First we note that the negative sign of D is in good agreement with the systematics found for chromium centers with inversion symmetry, where a compressional distortion of an octahedron along a cubic $\langle 111\rangle$ direction yields a negative D. We mention here the positive D value reported for Cr^{3+} in MgO by Watkins and Feher[33] for a uniaxial elongation of the crystal along a $\langle 111\rangle$ direction. In sign and qualitative agreement with this finding is the optical fluorescence work of Burns[34] on Cr^{3+} ground state in the garnets, which also show inversion symmetry. Now equivalent to an elongation of an anion octahedron is the presence of a cation ring in a $\{111\}$ plane, as is the case in the layer structure. Thus the effect of compression of the S^{-2} octahedron yielding a negative D is partially compensated by the presence of the In^{3+} "benzene" ring.

In this connection we note that a small and negative value of $D=-500$ G has been reported for Cr^{3+} in the layer structure of BiI_3.[8] This value is in good agreement with our result. Neither was the finding of a small D expected by Béne and White, who made this investigation.

Starting with zero slope at low temperature, the D parameter becomes gradually more negative and its change is linear above 120°K, amounting to $\partial D/\partial t=-0.86$ G/°K. Such a large linear behavior has not been previously reported for centers in nonlayer structures. Near-linear changes in D at higher temperatures but of only 0.12 G/°K, with zero slope in the helium range, have been discussed by Walsh *et al.*[15] for the Cr^{3+}–O–$V_{Mg^{2+}}$ complex in MgO (where V means a vacancy). These authors showed that for nearly cubic symmetry the total change in D is due to the thermal change in lattice parameter, and the "explicit" vibrational effects cancel to zero.[15] Since we are not aware of any x-ray analysis as a function of temperature on $NaInS_2$, we are not able to tell whether "explicit" effects are present here. However, the axial D in $NaInS_2$ at 4.2°K is smaller than that of the Cr^{3+}–O–$V_{Mg^{2+}}$ complex. Therefore, in the present case, the effective local symmetry approaches the cubic one better than the charge-compensated complex does. Thus we can assume that the results of Walsh *et al.* are applicable in our case too, and nearly 100% of $(\partial D/\partial T)$ is due to changes in interionic spacing probably along the c direction. This is even better justified by the seven

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[29] J. W. Orton, Rept. Progr. Phys. **22**, 204 (1959).

[30] R. W. G. Wyckoff, *Crystal Structure* (Interscience Publishers, Inc., New York, 1964), Vol. 2, pp. 7–8.

[31] J. O. Artmann and J. C. Murphy, in *Proceedings of the First International Conference on Paramagnetic Resonance* (Academic Press Inc., New York, 1963), p. 634; J. Chem. Phys. **38**, 1544 (1963); Phys. Rev. **135**, A1622 (1964).

[32] V. A. Atsarkin, Zh. Eksperim. i Teor. Fiz. **43**, 839 (1962) [English transl.: Soviet Phys.—JETP **16**, 593 (1963)]; J. E. Drumheller, K. Locher, and F. Waldner, Helv. Phys. Acta **37**, 626 (1964).

[33] G. Watkins and E. Feher, Bull. Am. Phys. Soc. **7**, 29 (1962).

[34] G. Burns, E. A. Giess, B. A. Jenkins, and M. L. Nathan, Phys. Rev. **139**, A1687 (1965).

times larger ($\partial|D|/\partial T$) value for Cr^{3+} in the layer compound.

Our assignment on the origin of the variation of $D(T)$ conforms with the one obtained independently for Mn^{2+} in $CdCl_2$.[5] In this layer structure the coordination of the Mn^{2+} is also octahedral, the point symmetry is also D_{3d}, and the nearest-neighbor (Cl) cation and next-nearest-neighbor (Cd^{2+}) anion position is the same as that shown for Cr^{3+} in Fig. 6 for $NaInS_2$. The axial splitting parameter of Mn^{2+} in powder samples of $CdCl_2$ was found to vary appreciably with temperatures from $D=14.8\times10^{-4}$ cm^{-1} at 20°K to -34×10^{-4} cm^{-1} at 710°K, changing sign near room temperature. This finding was assigned to the anisotropic lattice expansion of the $CdCl_2$ lattice which was confirmed by an x-ray analysis.[5]

Blazey and Rohrer, of this laboratory,[7] recently obtained from magnetic differential susceptibility measurements in $NaCrS_2$ the total uniaxial anisotropy field to be $+1.44\times10^3$ G at 4.2°K. This is due to dipolar, exchange, and single-ion ligand field terms. The latter contribution may be estimated from the low-temperature D value in the nonmagnetic compound. The lattice constants of the magnetic and nonmagnetic compounds do not exactly coincide, due to the 0.12-Å larger ionic radius of In^{3+} over that of Cr^{3+}. However, the trigonal distortion of the sulfur octahedron at 300°K as obtained from the x-ray analysis is within experimental accuracy the same for both compounds. Thus we can assume that the D value of 0.208×10^3 G we found in $NaInS_2$ is, to a certain extent, also representative for Cr^{3+} in $NaCrS_2$. Because a negative D was inferred from the low-temperature data, and the anisotropy field is positive, we conclude that in $NaCrS_2$ the sum of the dipolar and exchange terms is 1.65 kG, and roughly $-\frac{1}{7}$ of the observed uniaxial anisotropy field is due to the ligand field effect of the single ion.

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APPENDIX: ESTIMATE OF AN UPPER LIMIT OF THE g SHIFT

We assume that the covalency in octahedral sulfur environment is not lower than in that of oxygen. Therefore the covalency coefficients α and β for σ and π bonding must be smaller than in Lacroix's calculations, i.e., we assume $\alpha<0.84$ and $\beta<0.93$ (see Ref. 16).

An optical band in $NaCrS_2$ at 14 700 cm^{-1} has been observed; further, a strong absorption sets in at 18 600 cm^{-1}.[27] If the localized $^4A_2$ chromium levels lie between the $3s$-$3p$ sulfur valence band and the $2s$ sodium conduction band, then the first relatively narrow band can be ascribed tentatively to $3d\,^4A_2$-$^4T_2$ splitting.

The stronger absorption which sets in at 18 600 cm^{-1} may then be assigned to charge transfer between the (sulfur) valence band and the localized chromium $3d\,^4A_2$ ground states. The transition to the $2s$ sodium conduction band should lie appreciably higher.

If these assignments are correct, we can assume a $10Dq$ parameter in $NaInS_2$ of the same order for Cr^{3+} as in $NaCrS_2$,[35] and obtain

$$-\Delta g(^4T_2)<K\Delta g_{\text{ionic}}=K8\lambda/10Dq=0.023,$$

with $\lambda=91.5$ cm^{-1}, and

$$K=\tfrac{1}{4}[2\alpha\beta-R(1-\alpha^2)^{1/2}(1-\beta^2)^{1/2}]\times[2\alpha\beta-(1-\alpha^2)^{1/2}(1-\beta^2)^{1/2}]=0.51$$

and $R=0.31$ from Ref. 16.[36]

For Cr^{3+} in $NaInS_2$ the charge transfer band between the highest occupied (sulfur-type) bonding to the lowest ($3d$-type) antibonding orbitals should not occur at appreciably shorter wavelength than in $NaCrS_2$. We can scale accordingly Lacroix's result for Cr^{3+} in oxygen environment, who found with a first charge transfer band at 45 000 cm^{-1} and $10Dq=18\,000$ cm^{-1}, $\Delta g^c=-0.11\Delta g_{\text{ionic}}$, i.e., we assume

$$E(\gamma_a)-E(\epsilon_a)=14\,700\text{ cm}^{-1},$$
$$E(\epsilon_a)-E(\delta)=18\,600\text{ cm}^{-1},$$
$$E(\epsilon_a)-E(\gamma_l)=25\,000\text{ cm}^{-1},$$
$$E(\epsilon_a)-E(\epsilon_l)=29\,000\text{ cm}^{-1},$$

and obtain $\Delta g^c>-0.22\Delta g_{\text{ionic}}$.

Thus from our estimate the total negative shift $-\Delta g^{\text{th}}<(0.51-0.22)\Delta g_{\text{ionic}}=0.013$.

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[35] If $10Dq>14\,700$ cm^{-1}, our estimated upper limit of Δg is still valid.

[36] R is the ratio of the single-electron spin-orbit coupling of oxygen $2p$ and chromium $3d$ functions. In our case R will be larger, thus lowering K further.