result is so small, there is no evidence that the healing length is much different from ξ at any temperature.

On the other hand, the result for d obtained in Ref. 2 is

$$d \approx d_0[1 + 10(1-t)] \qquad (22)$$

near $T = T_c$; the two results differ by a factor of 50 in the correction to the Ginzburg-Landau result. The source of the discrepancy is at present unknown and further work is required. It is clear, however, that Eq. (21), rather than Eq. (22), is the correct result for the healing length in "this model."

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Spin-Hamiltonian Parameters and Spin-Orbit Coupling for V^{3+} in ZnO†

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The spin-Hamiltonian parameters for ZnO : V^{3+} have been refined using electron-paramagnetic-resonance (EPR) line position calculations. The principal sources of error are discussed. The accurate spin-Hamiltonian parameters are used to discuss the spin-orbit coupling within the $3d$ manifold of electronic states.

Values for the spin-Hamiltonian parameters of V^{3+} in ZnO have been reported recently by Filipovich, Taylor, and Coffman[1] and by Hausmann and Blaschke.[2] Significant differences between several of the reported parameter values, and the question of the importance and magnitude of the anisotropy of the spin-orbit coupling coefficients, have prompted us to reinvestigate these parameter values using an accurate EPR spectrum calculation. The experimental data were fitted with an axial-symmetry spin Hamiltonian which included the nuclear Zeeman and electric quadrupole interactions:

$$\mathcal{H} = D(S_z^2 - \tfrac{2}{3}) + g_\parallel \mu_B H_z S_z + g_\perp \mu_B (H_x S_x + H_y S_y) + A S_z I_z + B(S_x I_x + S_y I_y) + g_n \mu_N \vec{H}\cdot\vec{I} + Q'(I_z^2 - \tfrac{21}{4}). \qquad (1)$$

The (isotropic) nuclear g value for V^{51} was taken from the Varian NMR tables.[3] The resonance field values and intensities were calculated using the program MAGSPEC,[4] which determined the resonance fields for a given set of parameter values in (1) to within at least ± 0.1-G accuracy (see Table I), and correctly determines the intensities by computing the transition probabilities from the radiation Hamiltonian and the matrix of the eigenvectors of $\mathcal{H}$. The results were compared with the accurate field and frequency measurements of Coffman and Filipovich.[5] Parameter variation after each calculation, so as to decrease the errors $(H^i_{\text{expt}} - H^i_{\text{calc}})$ for all i absorption lines, was done by inspection using previously derived perturbation theory formulas.

The spectrum matching procedure was carried out for two EPR bands: one measured with $\vec{H}_0 \parallel c$, $\nu = 9.30875$ GHz with center at about 4800 G, and the other with $\vec{H}_0 \perp c$, $\nu = 9.51026$ GHz and center at about 6400 G. The value for $g_\parallel$ was assumed from the previous study,[1] since it can be measured independently of all other parameters. The values of D, A, $g_\perp$, B, and Q' were varied until one set of values gave the best agreement with experiment in a least-squares sense with respect to the measured line centers. The values of the parameters so derived (see Table I) led to the calculated line positions which are compared with experiment in

TABLE I. Spin-Hamiltonian parameters for ZnO:V^{3+} with estimated probable errors.

Parameter	Value	Estimated error
D/hc	± 0.74637 cm^{-1}	± 0.0005 cm^{-1}
$g_\parallel$	1.9451	± 0.0005
$g_\perp$	1.9329	± 0.0005
A/hc	$\pm 66.0\times10^{-4}$ cm^{-1}	$\pm 0.5\times10^{-4}$ cm^{-1}
B/hc	$\pm 77.1\times10^{-4}$ cm^{-1}	$\pm 0.5\times10^{-4}$ cm^{-1}
Q'/hc	0.0 cm^{-1}	± 0.00005 cm^{-1}

TABLE II. Experimental and calculated EPR line positions (all values in G).

	$\vec{H}_0 \parallel c$, $\nu = 9.30875$ GHz		$\vec{H}_0 \perp c$, $\nu = 9.51026$ GHz	
No.	Expt	Calc[a]	Expt[b]	Calc[c]
1	4552.5	4552.4	6133.5(*R*)	6133.5
2	4638.6	4639.6	6209.9(*R*)	6209.9
3	4721.6	4722.0	6289.0(*R*)	6288.9
4	4799.8	4799.8	6370.5(*R*)	6270.6
5	4872.8	4872.8	6455.1(*R*)	6455.0
6	4941.0	4941.0	6541.5(*A*)	6542.7
7	5004.2	5004.4	6633.1(*A*)	6634.3
8	5063.2	5063.2	6728.7(*A*)	6729.1
	$\langle\Delta H\rangle_{\mathrm{hfs}} = 73.0$	73.0	85.0	85.1

[a] $\langle\Delta H\rangle = \langle H_{\mathrm{expt}} - H_{\mathrm{calc}}\rangle = 0.0$ G, $\Delta H_{\mathrm{rms}} = \pm 0.1$ G, omitting lines 2 and 3.

[b] The resonance line centers marked *R* were resolved in the experimental spectrum. Lines marked *A*, which were too close together to be resolved, were calculated as the weighted means of the calculated line centers, using the calculated intensities as the weighting coefficients.

[c] $\langle\Delta H\rangle = -0.05$ G, $\Delta H_{\mathrm{rms}} = \pm 0.2$ G, omitting lines 6 and 7.

Table II. Lines 2 and 3 for $\vec{H}_0 \parallel c$ and 6 and 7 for $\vec{H}_0 \perp c$ were assigned lower confidence levels during parameter variation.[6] The spin-Hamiltonian parameter values found in this way accurately match the measured line centers, as demonstrated in Table II.

The sign of D was chosen positive, and A and B were assumed negative in the calculations for reasons outlined in our earlier study.[7] The precision of A and B, with respect to these arbitrary signs, is $\pm 0.1 \times 10^{-4}$ cm^{-1}. Changing the sign of D effects a change in hfs separation greater than or equal to the hfs linewidth, which produced an uncertainty in the hfs coefficient of $\pm 0.5 \times 10^{-4}$ cm^{-1}. The details of the calculated hyperfine structure measured for the $\vec{H}_0 \perp c$ band were found to be particularly sensitive to the value of the electric quadrupole interaction coefficient Q'. This spectrum was found to consist of about 23 detectable lines, due to the strong mixing of nuclear energy levels within the $M_S = 0$ states. Thus, letting Q' be 0.0001 cm^{-1} or larger (with either sign) gave spectra in definite disagreement with experiment. Letting $Q' = 0.0$ cm^{-1} gave a stick diagram which accurately matched the experimental spectrum. A line-shape reconstruction using a Lorentzian line shape confirmed the match for this value of Q' (see Fig. 1). The general validity of this small value of Q' was demonstrated by calculating the "stick" spectrum for the angle $\theta = 67°$. The calculated spectrum exhibited the same general pattern of multiplets as observed experimentally,[1] with intensity reduced over-all by about a factor of $\frac{1}{10}$ when compared with the intensity for H_0 along a principal crystallographic direction. The precision of the experimental measurements is estimated to be ± 0.1 G, in accord with the calculations. The most likely source of systematic error is the diamagnetic shielding of the cavity itself, which we have neglected. The quoted error limits therefore reflect this error source as well as the contribution due to the sign uncertainty of D, A, and B.

The numerical value of D is related to $g_\parallel$ and $g_\perp$ by the spin-orbit coupling. It follows for $3d^2$, $S = 1$, and Hagston[8] has shown for $3d^3$, $S = \frac{3}{2}$ that

$$2D = -\lambda_\parallel \Delta g_\parallel + \lambda_\perp \Delta g_\perp\,, \tag{2}$$

where $\Delta g_\parallel = -(g_\parallel - g_e)$, etc. Equation (2) is a perturbation theory approximation. If $\lambda_\parallel = \lambda_\perp = \lambda$, then $\lambda = 2D/(g_\parallel - g_\perp)$, yielding a value for the "isotropic" spin-orbit coupling coefficient. On the other hand, if an average value

$$\bar{\lambda} = \tfrac{1}{3}(\lambda_\parallel + 2\lambda_\perp) \tag{3}$$

were known, then (2) and (3) may be solved for $\lambda_\parallel$ and $\lambda_\perp$. Consider ZnO:V^{3+} first. From Table I, we find $2D/(g_\parallel - g_\perp) = 122$ cm^{-1}, which is larger than the free-ion value of 104 cm^{-1}. If however, we assume $\bar{\lambda} = 95 \pm 5$ cm^{-1} as found by Brumage, Quade, and Lin[9] for Al$_2$O$_3$:V^{3+}, then solving (2) and (3) yields $\lambda_\parallel = 91$ cm^{-1} and $\lambda_\perp = 97$ cm^{-1}, which are reasonable values of the spin-orbit coupling coefficients with a small anisotropy of about 6 cm^{-1}. As a check on this procedure, we consider Al$_2$O$_3$:Cr^{3+}, for which the optical studies by Rimmer and Johnston[10] on the origin of the trigonal field in ruby yielded $\bar{\lambda}$

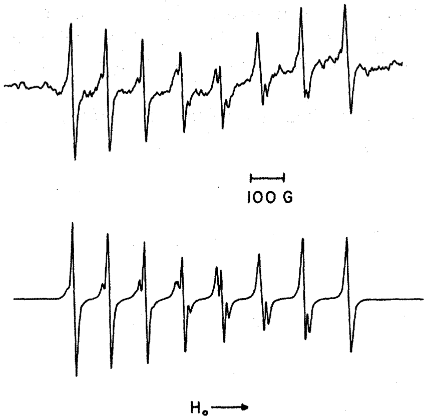

FIG. 1. Experimental and calculated line shapes for the hfs band of transitions with H_0 perpendicular to the crystallographic c axis, corresponding to the numerical data of Table II. Upper tracing, experimental; lower tracing, calculated using a Lorentzian line shape with 6-G half-width. The calculated stick diagram consisted of 23 lines of varying intensity, which occurred in 8 hyperfine "bands." The agreement is quantitative, apart from minor linewidth differences.

$= \frac{1}{3}\,\bar{\zeta} = 60\ \mathrm{cm}^{-1}$. The spin-Hamiltonian parameters of Schulz-duBois,[11] derived from EPR measurements at six different microwave frequencies, gave $2D/(g_{\parallel} - g_{\perp}) = 142\ \mathrm{cm}^{-1}$, which is greater than $\lambda_0 = 87\ \mathrm{cm}^{-1}$ for the free ion. Solving (2) and (3) again with values of D, $\Delta g_{\parallel}$, and $\Delta g_{\perp}$ for $\mathrm{Al_2O_3{:}Cr^{3+}}$ yields $\lambda_{\parallel} = 69\ \mathrm{cm}^{-1}$ and $\lambda_{\perp} = 56\ \mathrm{cm}^{-1}$. These are nearly the same values found by Sugano and Tanabe[12] by analysis of the g values alone. Thus, for each system, the use of the perturbation theory relation (2) leads to a small spin-orbit coupling anisotropy. Now, this anisotropy may be real or it may be an artifact of the use of perturbation theory. Although anisotropy in $\mathcal{H}_{so}$ is permitted by group theory,[13] this method of evaluating it is open to question in light of the observation by Macfarlane[14] that, in the case of ruby, there probably does not exist a *simple* analytical expression for D in terms of the crystal-field and spin-orbit parameters, which is generally necessary for (2) to hold true. This, rather than anisotropy in the spin-orbit coupling, may be the fundamental difficulty we experienced earlier[1] in fitting the $\mathrm{ZnO{:}V^{3+}}$ data to the crystal-field model.

Exact values of $\lambda_{\parallel}$ and $\lambda_{\perp}$ could be extracted from the $\mathrm{ZnO{:}V^{3+}}$ $(3d)^2$ system in the crystal-field approximation if the question of the signs of the spin-Hamiltonian parameters were resolved and if an optical spectrum were available. The magnetic properties could then be readily related to the optical properties, since exact solution for the entire $(3d)^2$ set of states requires diagonalization of only a 45×45 matrix, while for $\mathrm{Cr^{3+}}$ $(3d)^3$, the problem formally requires solution to a Hamiltonian matrix of 120×120 dimension. Obtaining the optical spectrum may prove to be difficult, however, since $\mathrm{V^{3+}}$ is not a stable oxidation state of vanadium and ZnO is definitely a nonstoichiometric solid.

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[7] We have so far been unable to determine the absolute sign of D, and the relative sign of D with respect to both A and B, primarily for experimental reasons. The signs chosen for the calculations are a reasonable choice, consistent with previous assignments and measurements for similar paramagnetic systems.

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