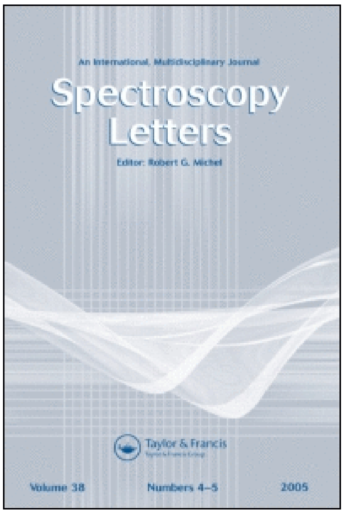

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A Computer Program to Help Resolution of Complex and Poorly Resolved Cu^{2+} and VO^{2+} Ions Doped Single Crystals Electron Paramagnetic Resonance Spectra

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ABSTRACT Complex and poorly resolved Cu^{2+} and VO^{2+} doped single-crystal electron paramagnetic resonance (EPR) spectra are some of the serious problems that exist in this area. In order to help the resolution of this sort of spectra, and for easily resolvable spectra as well, a versatile computer program known as EPR RESolution, or EPRES, is presented. All detectable line positions in the single-crystal spectra taken in three mutually perpendicular planes are given as input. The program plots these line positions. The user then manually determines the lines by selecting the true data points on the plot and fitting them to a well-known variation function. If selection is not suitable, the process is canceled and renewed. By this process, as many resolvable lines as in the spectra can be resolved and determined. The user then groups the resolved lines according to the paramagnetic center to which they belong. This includes the attribution of correct nuclear spin I and M_I to correct lines. After this step, hyperfine and $\mathbf{g}$ tensor elements can be found, constructed, and diagonalized.

[Supplemental materials are available for this article. Go to the publisher's online edition of *Spectroscopy Letters* for the following free supplemental resource: a copy of the EPRES computer program.]

KEYWORDS Cu^{2+} and VO^{2+} ions doped, electron paramagnetic resonance, EPR RESolution (EPRES), poorly resolved spectra, resolution of spectra, single-crystal

INTRODUCTION

Resolution of complex and poorly resolved Cu^{2+} and VO^{2+} doped single-crystal EPR spectra consisting of a relatively large number of overlapping lines is a serious difficulty. When liquid, powder, polycrystalline, or glassy samples give nonresolvable spectra, there is not enough variety for correct resolution and further processes. On the other hand, single-crystal spectra, when available, either gives the most detailed information or presents a number of different spectra for different crystal orientations and, therefore, presents a great chance for resolution.

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If single-crystal spectra taken for different orientations are clear enough to identify all or most of the lines, or if the lines are traceable in most of the orientations, there will be no need for any helpful procedures for resolution. But, when the spectra are irresolvable because of large numbers of overlapping lines, the spectroscopist may need auxiliary techniques for correct resolution, that is, for tracing almost all lines in almost all orientations to identify them. EPR parameters can be determined in usual ways after identification of the lines.[1,2]

In order to resolve such complex and poorly resolved EPR spectra consisting of overlapping broader lines, or consisting of a large number of lines accumulated in a limited spectral range, certain technological advances and numerical techniques have been utilized. Spectrometers running from L band (1.5 GHz) up to far infrared (THz) frequencies equipped with pulse and Fourier transform (FT) capabilities are in use.[2–4] Various spectroscopic techniques are also applied together with EPR spectroscopy to resolve and to get necessary information from spectra. Acoustic paramagnetic resonance (APR), optically detected magnetic resonance (ODMR), electric field EPR, zero field resonance (ZFR), electron-nuclear double resonance (ENDOR), and thermally detected EPR are some examples of composite techniques.[2,3] 2D-EPR spectroscopy is also in rapid progress. Famous 2D-nuclear magnetic resonance (NMR) experiments, such as correlation spectroscopy (COSY), spin echo correlation spectroscopy (SECSY), and 2D exchange spectroscopy (EXSY), could be transferred to EPR spectroscopy, presenting new and powerful techniques for resolution and opening fields of applications.[5,6]

Although the technological progresses are continuously improving the characteristics and power of spectrometers, the resolution problem will always exist because of the line widths that cannot be made narrower than a limiting value. Therefore, certain reasonable auxiliary techniques built on basic spectroscopic laws will always be in need.

Scientists have developed and used various auxiliary techniques to resolve poorly resolved EPR spectra. Applications of these techniques go back to the 1960s and basically need the use of computers for massive calculations. For example, a program was developed to analyze EPR spectra by means of line-shape analysis.[7] Another technique was using resolution enhancement procedures depending on FT analysis;[8] this technique, however, is normally used in modern pulse and FT instruments. Another technique has used an algorithm, called reduced spectra, where the effects of some hyperfine splitting constants are removed from spectra with some numerical processes to simplify them.[9–11] Numerical hyperfine extraction or decoupling analyses were other techniques employed for the same purpose;[12,13] in fact, the decoupling technique is one of the basic functions of modern pulse and FT instruments.[3] Another technique is the nonlinear least squares fitting, which tries to fit a presumed spectrum to an experimental one.[14,15] The success of this technique is highly dependent on the initial values and the number of lines in the spectrum.

The most widely used technique for resolution is the spectrum simulation, which produces numerical spectra using presumed EPR parameters and line-shape functions. This simulation procedure was sometimes used together with nonlinear least squares fitting process for better results. If the procedure is used suitably with correct parameters and line-shape functions, it gives mostly reasonable results.[16–20] Currently, highly developed and powerful simulation programs for personal computers can be found in referenced websites.[21]

When the transition metal ions are doped in a diamagnetic host lattice as an impurity, they form paramagnetic centers from which structures of the local symmetry can be obtained with EPR spectroscopy. In particular, Cu^{2+} and VO^{2+} ions have extensively been used as a probe to obtain structural properties. These ions mostly replace a divalent and monovalent cation in the host by compensating the charge deficiency with some other nuclei. Cu^{2+} and VO^{2+} ions have the nuclear spin $I = 3/2$ and $I = 7/2$ and give the 4- and 8-EPR line, respectively, so it is very easy to resolve the EPR spectrums. But when the number of magnetically or chemically distinct metal ion complexes in a single host crystal is large, then many EPR lines, and in some cases spacing of the lines, may change rapidly; linewidths may change slightly with orientation, and the lines may overlap frequently so it is impossible to trace and identify the lines visually. In these situation, the resolution of the spectra is not so easy, and therefore, some techniques for resolution must be utilized. Another technique that has been used for the beginning of EPR spectroscopy is plotting all of the line positions against rotation angles (or mapping all line positions). The whole picture can be observed on this plot; that is, the variations of all or some of the lines may become traceable and resolvable.[22,23] Depending on this assumption, a series of programs were written, each of which was making a different calculation. Some were in Basic and some were in Pascal languages. Each program in the series was using the outputs of the previous one. Some poorly resolvable single-crystal spectra have been resolved by means of these programs and have been published.[24–31] Because of the separate modular structure, they were not advantageous for use in all situations; therefore, all programs were reviewed and rewritten in the visual environment, in Delphi. The interface is designed for easy use. Although the goal is mainly resolution of complex spectra, programs can be utilized for evaluation of clearly resolvable spectra as well.

THEORETICAL BACKGROUNDS

Most of the EPR spectra, including those of chemical radicals and transition metal ion complexes, are explained with the Hamiltonian including electron Zeeman, nuclear Zeeman, and hyperfine interactions[1,2]

$$\mathcal{H} = \beta \mathbf{H}\cdot\mathbf{g}\cdot\mathbf{S} + g_N\beta_N \mathbf{H}\cdot\mathbf{S} + \mathbf{I}\cdot\mathbf{A}\cdot\mathbf{S}, \tag{1}$$

where **g** and **A** are spectroscopic splitting and hyperfine tensors, respectively. Since nuclear Zeeman interaction is negligibly small for most applications, it cannot be considered further. For $S=1/2$ and nuclear spin I, the solution of this Hamiltonian gives the expression for line positions correct to second-order term:

$$H_{M1} = H_0 + A\cdot M_1 + B[I(I+1) - M_1^2] + \cdots, \tag{2}$$

where $H_0 = h\nu/g\beta$ and B is the coefficient of the second-order correction term. For chemical radicals, it is defined as $B = -A^2/2H_0$. For metal complexes in uniaxial symmetry, it is defined as $B = -A_\perp^2/2H_{//}(0)$ or $B = -(A_{//}^2 + A_\perp^2)/4H_\perp(0)$, according to the orientation of parallel and perpendicular components in the magnetic field.[32,33] $H_{//}(0)$ and $H_\perp(0)$ are the magnetic field values corresponding to the $g_{//}$ and $g_\perp$ values, respectively. Magnetic quantum number M_I takes the values between $-I$ and I. When hyperfine is small compared to H_0, the second-order correction term B is negligible. Therefore, the importance of this term basically depends on the hyperfine and H_0 values.[1,2,33,34]

In both of the first- and second-order spectra, the angular variations of g^2 and A^2 values are sinusoidal in any crystalline planes (or around a crystalline axis) and given as

$$\left.\begin{aligned} g_k^2(\theta) &= g_{ii}^2\cos^2\theta + g_{jj}^2\sin^2\theta \\ &\quad + 2g_{ij}^2\cos\theta\sin\theta \\ A_k^2(\theta) &= A_{ii}^2\cos^2\theta + A_{jj}^2\sin^2\theta \\ &\quad + 2A_{ij}^2\cos\theta\sin\theta \end{aligned}\right. \quad (i,j,k = x,y,z), \tag{3}$$

where θ is the angle of rotation of the single crystal with respect to the magnetic field direction.[2] The single index k represents rotation axes x, y, and z, while double indices ii, jj, and ij represent the elements of symmetric **g** and **A** tensors; $g_{xx}^2, g_{yy}^2, g_{zz}^2, g_{xy}^2, g_{xz}^2$ and g_{yz}^2 and $A_{xx}^2, A_{yy}^2, A_{zz}^2, A_{xy}^2, A_{xz}^2$ and A_{yz}^2.

Referring to these variations, the angular variations of any single line for both first- and second-order spectra with the function can also be represented:

$$G_k^{(n)}(\theta) = P_k^{(n)}\cos^2\theta + Q_k^{(n)}\sin^2\theta + 2R_k^{(n)} \cos\theta\sin\theta (k = x,y,z), \tag{4}$$

where the superscript "(n)" represents the number of lines for the rotation around the k axis. The coefficients $P_k^{(n)}, Q_k^{(n)}$, and $R_k^{(n)}$ represent the nth line for rotation around axis k.

Consider an anisotropic paramagnetic center in a single crystal, and take as many spectra as possible in three mutually perpendicular planes by rotating it with certain intervals in each plane. Then plot the positions of all detectable lines taken against rotation angles in three planes separately. It will be seen that the variation of each line in each plane will be sinusoidal, as in Eq. (4). If some of the points belonging to a certain line can be selected carefully and fitted to Eq. (4) by the linear least squares method, the coefficients P, Q, and R will be obtained. These coefficients define each line and pass through all other points belonging to the line. With the aid of this process, all detectable lines in three mutually perpendicular planes can be determined, and each line will be represented by the different *P, Q*, and *R* value sets defined in Eq. (4).

ANALYZE THE EPR SPECTRUMS

The spectra in each plane may consist of lines belonging to different paramagnetic centers, or sites, or different nuclei and nuclear groups. The spectroscopist must be very careful in identifying and grouping the lines. In fact, the lines belonging to the same paramagnetic center will show a sort of parallelism, and lines can also be grouped referring to this behavior.

Each line in a particular group is characterized with nuclear spin I and magnetic quantum number M_I, and these values must be attributed correctly to all of the resolved lines. Of course all lines cannot be resolved at all the times, but spectroscopist's experience and insight in certain applications must be able to compensate for this deficiency.

Determination of Hyperfine and *g* Variations

The hyperfine and g variations can be calculated on this plot, provided that the correct I and M_I values are attributed to the correct lines. The values can be calculated from *P, Q*, and *R* values as well as they can be measured directly on the plot. But instead of time-consuming point-by-point measurement on the plot, and since the calculations are performed by a computer, it is more practical to calculate them from the *P, Q*, and *R* values, as explained below.

If first-order spectra are considered, the magnetic field values of only two hyperfine lines belonging to the same paramagnetic center at any orientation are calculated via Eq. (4) and equated to Eq. (2) to obtain the set below:

$$\begin{aligned} H_{M1} &= \frac{hv}{\beta\sqrt{G_k^{n1}}} = H_0 + A\cdot M_1 \\ H_{M2} &= \frac{hv}{\beta\sqrt{G_k^{n2}}} = H_0 + A\cdot M_2 \end{aligned} \quad (k = x, y, z). \quad (5)$$

The A and $g = hv/\beta H_0$ values for each orientation are calculated from the set, and the angular variations of A and g are obtained. Similarly, if second-order spectra are considered, Eq. (5) must be rewritten using three lines of the same center, as follows:

$$\begin{aligned} H_{M1} &= \frac{hv}{\beta\sqrt{G_k^{n1}}} = H_0 + A\cdot M_1 \\ &\quad + B[I(I+1) - M_1^2] \\ H_{M2} &= \frac{hv}{\beta\sqrt{G_k^{n2}}} = H_0 + A\cdot M_2 \\ &\quad + B[I(I+1) - M_2^2] \\ H_{M3} &= \frac{hv}{\beta\sqrt{G_k^{n3}}} = H_0 + A\cdot M_3 \\ &\quad + B[I(I+1) - M_3^2] \end{aligned} \quad (k = x, y, z). \quad (6)$$

The simultaneous solution will give *g, A*, and *B* values. Since B is a second-order correction term coefficient and contains only A and H_0, as given in Eq. (2), it does not need to be considered further.

These calculations must be performed for each paramagnetic center in all three mutually perpendicular crystalline planes to be able to determine tensor elements. These elements are obtained from the angular variations of g and A, which are calculated using Eqs. (5) or (6), and then fitting these variations to the corresponding expressions given in Eq. (3).

Construction of Tensors

In order to construct the **g** and **A** tensors, the lines belonging to the same paramagnetic center in three perpendicular crystalline planes must be correctly determined and identified by matching. This is possible primarily if the crystal planes are chosen by taking care of some specific relations. Of course each spectroscopist develops his/her own crystal orientation order and technique in this context. Here, as an example, a cyclic relation is presented, as given in Eq. (7), referring to the expressions given in reference 2 for **g** tensor elements.[2] It is assumed that in each plane, the crystal is rotated between 0° and 180° with definite steps.

Crystal plane (or axis)	Initial orientation	**g** tensor elements		
xy (Axis 1)	**x**//**H**	g_{xx}^2	g_{yy}^2	g_{xy}^2
zx (Axis 2)	**z**//**H**	g_{zz}^2	g_{xx}^2	g_{xz}^2
yz (Axis 3)	**y**//**H**	g_{yy}^2	g_{zz}^2	g_{yz}^2

(7)

It is clearly seen that diagonal elements appear twice, while off-diagonal elements appear only once. If orientations are precise enough, each diagonal pair must have almost the same value within reasonable experimental error. Similar relations must be observed for hyperfine splitting constants as well. This property is one of the main criteria when matching the lines of the same paramagnetic center in all three planes and when constructing the tensors.

The symmetric **A** and **g** tensors, then, are easily constructed by taking the averages of the diagonal pairs; in fact, averaging is a good idea for reducing experimental error. The tensors are then diagonalized to obtain principal elements and direction cosines. The rest is, of course, the structural evaluations of the paramagnetic center.

The Program

The computer program EPR RESolution (EPRES), written to make all intense calculations discussed so far, works according to the following algorithm. The processes mainly depend on some trial-and-error procedures; therefore, all calculations and steps must be renewable. That is, any operation can be repeated and renewed.

1. Corrected microwave frequencies in three axes, magnetic field set, scan range, recorder paper width, and positions of all lines at each orientation in three planes are given as inputs.
2. All of the line positions against rotation angles for three planes are plotted (or mapped). In order to be convenient with Eq. (3), the plots are drawn as $G_k^{(n)}$ (which corresponds to g^2) for each line, Eq. (4). But $\sqrt{G_k^{(n)}}$ (which corresponds to g) and magnetic field value options are also possible to visualize the variations of lines in different units.
3. The plots will be seen as a collection of dots in the first sight; a closer look, however, will show that certain points vary sinusoidally according to Eq. (4). These points, as many as detected, are selected manually and fitted to Eq. (4). If the selected points are correct, fitting will be good enough. The goodness can be controlled visually on the plot or by the regression coefficient. The user accepts fitting if it is good enough and rejects it otherwise. By this *renewable* procedure, all detectable lines can be resolved, and each resolved line is then represented by the *P, Q,* and *R* value set. This step is probably the most time-consuming and care-requiring one.
4. In the next step, correct I and M_I values must be attributed to all lines to complete the identification of the lines. This step also requires care and time, but when this step is complete, the resolution, as well, is almost complete.
5. After identifying all lines, Eq. (5) or (6) is employed to calculate angular variations of both A^2 and g^2. The **A** and **g** tensor elements of all resolvable paramagnetic centers are obtained in each plane by fitting these variations to the corresponding expressions in Eq. (3).
6. In the last step, symmetric **A** and **g** tensors of each center are constructed and diagonalized to obtain principal elements and direction cosines.

EPRES, running according to the algorithm above, is written to help for the resolution of complex and poorly resolved single-crystal EPR spectra. Some poorly resolvable Cu^{2+} and VO^{2+} doped single-crystal spectra have been resolved by means of the EPRES program and then published.[35,36] The program can also be used for easily resolved spectra.[37] EPRES runs only on the Windows operating system. The interface is designed for easy use. Necessary explanations and information are given in the help file. A zipped pack, containing the program, some examples, and a user manual (in a pdf file) can be obtained on request via e-mail from the authors.

CONCLUSION

A newly developed computer program, EPRES, to help for the resolution of poorly resolved complex Cu^{2+} and VO^{2+} ions doped single-crystal EPR spectra, is presented. The program makes use of the plot of angular variations of spectral lines in three mutually perpendicular planes. The lines are determined and resolved by applying the least squares fitting procedure to the selected points, which are supposed to belong to a line on the plot. The fitting process, as well as other steps of the program, can be renewed until correct lines are determined. After determining all detectable lines, they are grouped and identified according to the nuclei to which they belong. The hyperfine **A** and **g** tensors are constructed and diagonalized to obtain principal hyperfine and g values, as well as the direction cosines.

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