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Dynamic–Static Jahn–Teller Effects. EPR Spectra of ^{63}Cu(II)-Doped $Rb_2Pb_{1/3}Cd_{5/3}(NO_2)_6$, $Rb_2CdCd(NO_2)_6$, and $Cs_2PbCd(NO_2)_6$

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Experimental EPR spectra of ^{63}Cu(II)-doped $Rb_2Pb_{1/3}Cd_{5/3}(NO_2)_6$, $Cs_2PbCd(NO_2)_6$, and $Rb_2CdCd(NO_2)_6$ at 90 K show both Cu(II) hyperfine structure and nitrogen superhyperfine structure. A good fit of the experimental spectra is obtained with an elongated tetragonal CuN_6 model. Parameters for the $g_\parallel$ single-crystal EPR spectrum of ^{63}Cu(II)-doped $Rb_2CdCd(NO_2)_6$ are as follows: $g_\parallel = 2.281$, $A_{Cu_\parallel} = 159.4 \times 10^{-4}$ cm^{-1}, $A_{N_\parallel} = 13.18 \times 10^{-4}$ cm^{-1}, $LW_\parallel = 4.270$ G.

Introduction

During the past 10 years solid-state studies by several groups have advanced the understanding of the dynamic–static Jahn–Teller effect in copper(II) compounds.[2-15] The $M_2M'Cu(NO_2)_6$ series of compounds, where M is Rb^+, Cs^+, and Tl^+ and M′ is Ca^{2+}, Sr^{2+}, Ba^{2+}, and Pb^{2+}, is particularly well suited for such studies since M influences the transition temperature for the dynamic–static phase change and M′ determines the type of distortion found in the static phase.

The high-temperature cubic α-phase (space group *Fm*3) transforms to an orthorhombic β-phase (space group *Fmmm*) and finally at still lower temperatures to a triclinic γ-phase. Thermal parameters as determined by crystallographic analysis of the cubic α-phase of $K_2PbCu(NO_2)_6$[15] have been interpreted in terms of a three-dimensional dynamic average of elongated tetragonal CuN_6 groups. The orthorhombic β-phase of $M_2M'Cu(NO_2)_6$ compounds shows two types of CuN_6 configurations. $M_2PbCu(NO_2)_6$ compounds have a compressed-tetragonal CuN_6 configuration while $M_2M'Cu(NO_2)_6$ compounds with M′ = Ca, Sr, and Ba have elongated-tetragonal CuN_6 configurations.

Structural data for the orthorhombic phase of both $K_2PbCu(NO_2)_6$ and $Rb_2PbCu(NO_2)_6$ support the hypothesis that the compressed-tetragonal CuN_6 configuration is a two-dimensional average of two elongated-tetragonal CuN_6 groups.[2] The long Cu–N bonds in the compressed-tetragonal CuN_6 groups are approximately equal to the average of one long and one short Cu–N bond in the elongated-tetragonal configuration while the short Cu–N bonds in both compressed- and elongated-tetragonal CuN_6 groups are equal. In addition, the root mean square vibration amplitudes for nitrogen are in agreement with this interpretation.[2]

Mori et al.[11] discovered satellite reflections in the β-phase of $K_2PbCu(NO_2)_6$ which were not present in the α-phase. Since the satellite reflections cannot be indexed with integral indices, the actual structures must be incommensurate. In the γ-phase the satellite reflections are replaced by reflections with half-integral indices. Reinen and Friebel[3] have proposed that the β-phase is a mixture of the two-dimensional dynamic effect with an antiferrodistortive order of static elongated-tetragonal groups. The lower temperature γ-phase is viewed as having only the long-range antiferrodistortive order.

The EPR spectra for pure $M_2PbCu(NO_2)_6$ compounds give values of $g_\parallel = 2.07$ and $g_\perp = 2.15$ in agreement with an antiferrodistortive (af) model where $g_\parallel(\mathrm{af}) = g_\perp(\mathrm{f})$ and $g_\perp(\mathrm{af}) = [g_\parallel(\mathrm{f}) + g_\perp(\mathrm{f})]/2$ with f = ferrodistortive elongated tetragonal.[2,3] Although suitable host compounds have been prepared, very few EPR studies of Cu(II)-doped $M_2M'M''(NO_2)_6$ compounds have been published. Available host compounds include the following: M = K^+, NH_4^+, Cs^+, Tl^+; M′ = Pb^{2+}, Sr^{2+}, Cd^{2+}, Hg^{2+}; M″ = Cd^{2+}, Hg^{2+}.[16,17] The only published reports for Cu(II)-doped compounds of this type are those of Reinen and Friebel for $Cs_2SrCd_{0.98}Cu_{0.02}(NO_2)_6$,[18] an elpasolite host structure, and $TlCd_{1-x}Cu_x(NO_2)_3$,[19-21] a perovskite host structure. The former compound is isotropic at 298 K and becomes anisotropic at 4.2 K. The latter compound gives an isotropic signal at the lowest temperature utilized (4.2 K) when $x > 0.1$, but an anisotropic signal is observed at 4.2 K when $x < 0.1$. Apparently, no hyperfine structure was observed for either compound at 4.2 K. However, Friebel and Reinen[22] have reported the presence of copper hyperfine structure at 4.2 K in the powder spectrum of another doped elpasolite system, $Sr_2Cu_{0.015}Zn_{0.985}WO_6$.

This paper presents EPR spectra for ^{63}Cu(II)-doped $M_2M'Cd(NO_2)_6$ systems which show both copper hyperfine and nitrogen superhyperfine structure at 90 K.

Experimental Section

EPR spectra were obtained with a Varian E-3 X-band EPR spectrometer, which has a fixed modulation frequency of 100 kHz. The microwave frequency was between 9.090 and 9.095 GHz. A Varian E-4557-9 variable-temperature accessory was used to cool the EPR cavity to 90 K. A Varian E-229 goniometer was used for orientation of single crystals of Cu(II)-doped $Rb_2CdCd(NO_2)_6$.

Powders of $Rb_2CdCd(NO_2)_6$ (**1**) and $Cs_2PbCd(NO_2)_6$ (**2**) doped with ^{63}Cu(II) were prepared by following published methods for

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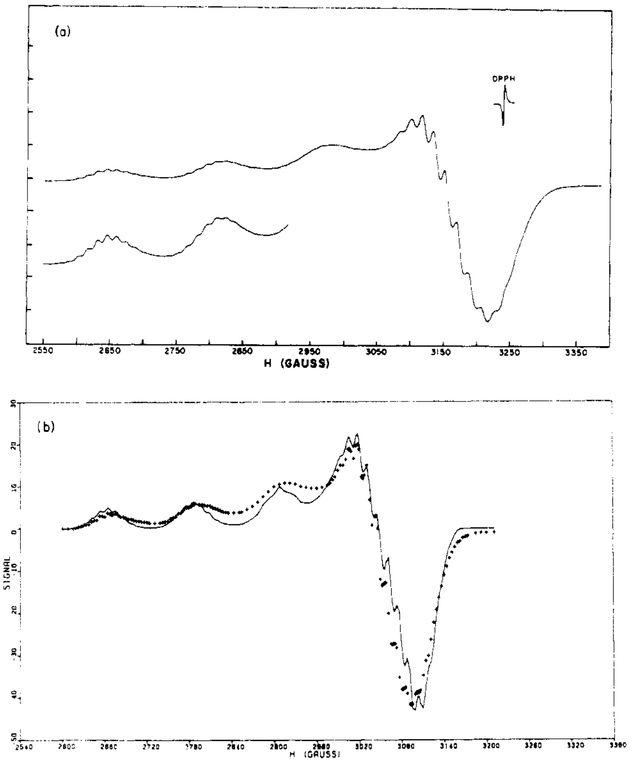

Figure 1. (a) EPR powder spectrum of Cu(II)-doped $Rb_2Pb_{1/3}Cd_{5/3}(NO_2)_6$ at 90 K. (b) Computer-simulated spectrum (—) of 149 points (+) from (a).

$M_2M'M''(NO_2)_6$ compounds[16,19,23] with the addition of 3–6 mg of $^{63}Cu(NO_3)_2$ to the $Cd(NO_3)_2$ solution. The same procedure was followed in an attempt to prepare other elpasolite host structures such as $Rb_2PbCd(NO_2)_6$ (**3**) and $Rb_2SrCd(NO_2)_6$ (**4**) doped with $^{63}Cu(II)$. However, only partial substitution of Cd^{2+} by Pb^{2+} or Sr^{2+} took place as shown by elemental analysis. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN, and include determination of the level of copper doping. ^{63}CuO with 99.89% ^{63}Cu was purchased from Oak Ridge National Laboratory. Anal. Calcd for $RbCd(NO_2)_3$ (**1**): Rb, 25.4; Cd, 33.5; N, 12.5. Found: Rb, 24.4; Cd, 33.8; N, 12.0; Cu, 0.018. Calcd for $Cs_2PbCd(NO_2)_6$ (**2**): Pb, 24.1; Cd, 13.0; N, 9.75. Found: Pb, 25.2; Cd, 12.3; N, 10.3; Cu, 0.035. Calcd for $Rb_2Pb_{1/3}Cd_{5/3}(NO_2)_6$ (**3**): Rb, 24.3; Pb, 9.73; Cd, 26.7; N, 11.95. Found: Rb, 23.6; Pb, 9.77; Cd, 26.6; N, 11.4; Cu, 0.012. Calcd for $Rb_2Sr_{0.05}Cd_{1.95}(NO_2)_6$ (**4**): Sr, 0.65; Cd, 32.7; N, 12.5. Found: Sr, 0.43; Cd, 32.6; N, 11.5; Cu, 0.02.

Single crystals of ^{63}Cu-doped $Rb_2CdCd(NO_2)_6$ were grown by cooling a 50 °C solution of the reaction mixture at the rate of 6 °C/day. A crystal with dimensions of 2.5 × 2.3 × 1.25 mm was used for EPR studies. The crystal was mounted on a notched quartz rod with the *c* axis of the predominant domain perpendicular to the magnetic field.

Computer simulations of powder and single-crystal spectra were carried out on a DEC 1099 computer. The computer program of Venable[24] was modified to include superhyperfine parameters.

Results and Discussion

Powder EPR Spectra of ^{63}Cu(II)-Doped $M_2M'Cd(NO_2)_6$ at 90 K. The EPR spectra for $^{63}Cu(II)$-doped $M_2M'Cd(NO_2)_6$ compounds show broad copper hyperfine structure at 298 K. As the temperature is lowered, nitrogen superhyperfine structure begins to appear at 200 K and is well resolved at 150 K. Experimental spectra shown in Figures 1–3 illustrate the excellent resolution obtained at 90 K. The excellent resolution of fine structure seen here at 90 K compared to the lack of resolution in EPR spectra of $Cs_2SrCd_{0.98}Cu_{0.02}(NO_2)_6$[18] and

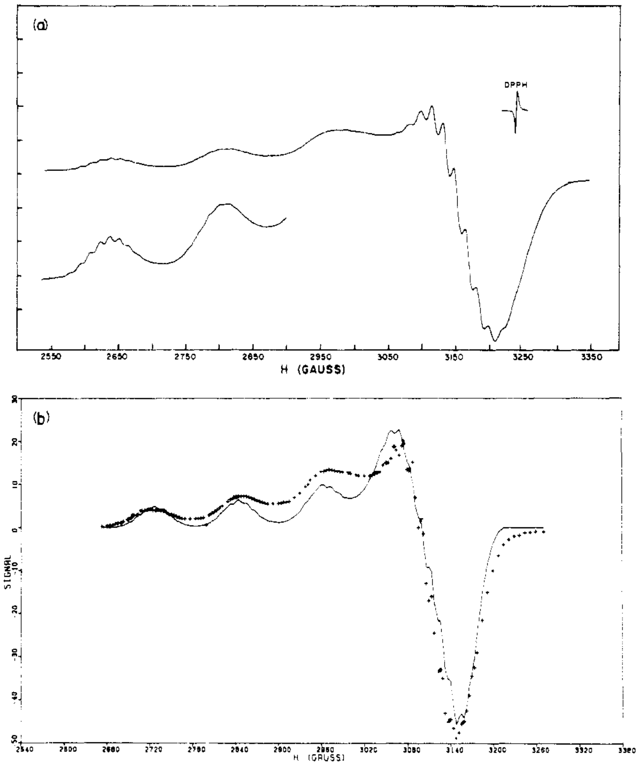

Figure 2. (a) EPR powder spectrum of Cu(II)-doped $Cs_2PbCd(NO_2)_6$ at 90 K. (b) Computer-simulated spectrum (—) of 155 points (+) from (a).

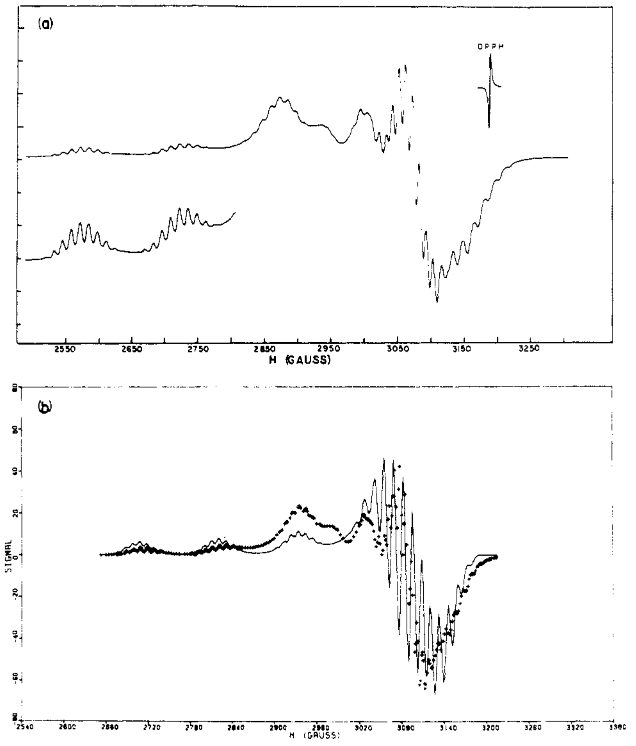

Figure 3. (a) EPR powder spectrum of Cu(II)-doped $Rb_2CdCd(NO_2)_6$ at 90 K. (b) Computer-simulated spectrum (—) of 200 points (+) from (a).

$TlCd_{1-x}Cu_x(NO_2)_3$ systems[19-21] is probably a result of the much lower level of doping in the present study. Our level of doping ranges from 0.01% to 0.035%, which is 10–50 times more dilute than in previously studied systems. When we increased the amount of $^{63}Cu(NO_3)_2$ added during the synthesis to 15–20 mg (see Experimental Section), the resulting samples did not have resolved nitrogen superhyperfine structure

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Table I. Parameters for Computer-Simulated Spectra in Figures 1–4

compd doped with ^{63}Cu(II)	scale factor	$g_\parallel$	$10^4 A_{\mathrm{Cu}\parallel}$, cm^{-1}	$10^4 A_{\mathrm{N}\parallel}$, cm^{-1}	LW$_\parallel$, G	LW$_\perp$, G	$g_\perp$	$10^4 A_{\mathrm{Cu}\perp}$, cm^{-1}	$10^4 A_{\mathrm{N}\perp}$, cm^{-1}
$Rb_2Pb_{1/3}Cd_{5/3}(NO_2)_6$ powder	−455	2.247	170	15.0	6.0	9.0	2.060	16.5	17.0
$Cs_2PbCd(NO_2)_6$ powder	−473	2.251	165	15.5	6.65	9.5	2.066	16.5	17.0
$Rb_2CdCd(NO_2)_6$ powder	−450	2.277	160	13.5	4.75	6.5	2.077	19.0	17.5
$Rb_2CdCd(NO_2)_6$ cryst ($g_\parallel$ spectrum)	−42.1	2.281	159.4	13.18	4.270				

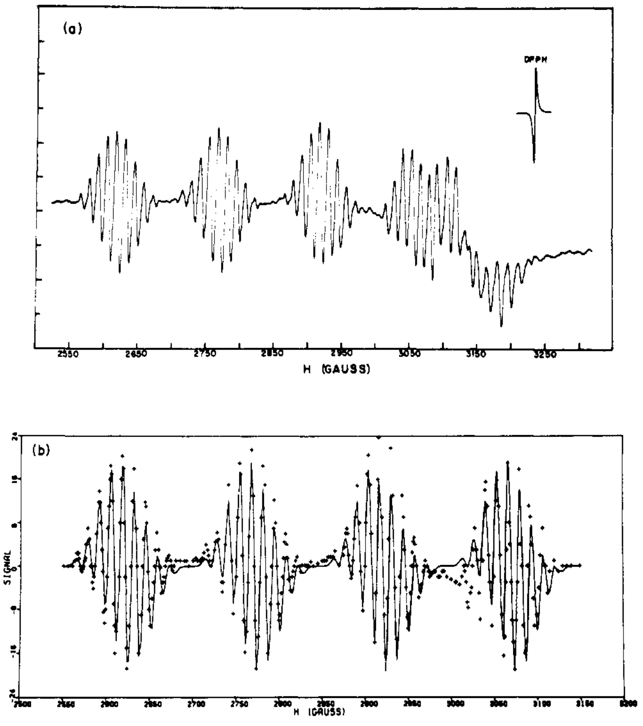

Figure 4. (a) Single-crystal $g_\parallel$ EPR spectrum for Cu(II)-doped $Rb_2CdCd(NO_2)_6$ at 90 K. (b) Computer-simulated spectrum (—) of 316 points (+) from (a).

at 90 K, but the copper hyperfine structure was still present.

The computer-simulated spectra shown in Figures 1–3 are calculated on the basis of a static elongated-tetragonal CuN_6 configuration, and a good fit is obtained for all but one spectrum. The parameters used for these computer-simulated spectra are given in Table I. The simulated spectra are extremely sensitive to small changes in the parameters which characterize them. Because of the nonlinear simulation model and the existence of a small region in the spectra that is not explained by the model, calculation of the usual error limits for the parameters in Table I would not be meaningful. It is worth noting, however, that a change of one or two parts in the least significant figure reported for each parameter in the table results in a substantial deterioration of agreement between the experimental and simulated spectra.

The EPR spectrum of ^{63}Cu(II)-doped $Rb_2CdCd(NO_2)_6$ has additional absorbance near the third and fourth copper(II) hyperfine peaks which cannot be explained by the axial elongated tetragonal model. This spectrum is reproducible and has been obtained for several different ^{63}Cu(II)-doped samples of $Rb_2CdCd(NO_2)_6$ as well as for doped samples of $Rb_2HgHg(NO_2)_6$. Although the host lattice has been described in terms of an ABX_3 perovskite structure,[3,17] with X = NO_2^-, two types of coordination environments exist for B—either nitrogen atoms or oxygen atoms of six NO_2^- ions. Therefore, the expanded $A_2BB'X_6$ elpasolite structure with $B'N_6$ and BO_{12} coordination sites is a better representation. When B = B′ = Cd(II), the doped Cu(II) ions would still be expected to occupy $B'N_6$ sites. However, the presence of Cd(II) in both B and B′ sites of the host lattice might result in a small portion of the ^{63}Cu(II) ions either entering BO_{12} sites or being surrounded by disordered NO_2^- ions. Values of **g** tensors calculated for extra EPR peaks in figure 3a can be explained by this interpretation. The extra peak at $g = 2.22$ is the same as the isotropic **g** tensor observed at 77 K for $Sr_2Zn_{0.095}Cu_{0.005}WO_6$,[22] an elpasolite host structure with a CuO_6 environment. The other extra peak at $g = 2.12$ is the same as the isotropic **g** tensor for $Cu(NO_2)_6^{4-}$ in a dynamic Jahn–Teller state.[2,3] The disappearance of the extra peaks when Cd(II) at B is partially or fully replaced (Figures 1a and 2a) support this interpretation.

The spectral pattern in Figures 1a and 2a is that expected for elongated-tetragonal CuN_6 coordination. Even partial replacement of Cd(II) in the B site by $^1/_3$ Pb(II) gives the expected pattern as shown in Figure 1a. We have also observed a spectrum identical with that in Figure 1a for ^{63}Cu(II)-doped $Rb_2Sr_{0.05}Cd_{1.95}(NO_2)_6$, which suggests that only a small fraction of Cd(II) ions in B sites need to be replaced to give a classic elongated-tetragonal pattern.

Single-Crystal EPR Spectrum of ^{63}Cu(II)-Doped $Rb_2CdCd(NO_2)_6$ at 90 K. Figure 4 illustrates the single-crystal EPR spectrum for Cu(II)-doped $Rb_2CdCd(NO_2)_6$ with the *c* axis aligned perpendicular to the magnetic field. Since crystals of $M_2M'M''(NO_2)_6$ compounds have a tendency to twin with a common (110) boundary,[25] some absorbance is seen in the $g_\perp$ region from another lattice. As a result, the computer simulation of the experimental spectrum (Figure 4b) is based on using the same pattern for the fourth Cu(II) hyperfine peak as those exhibited in the first three Cu(II) hyperfine peaks. The parameters for the computer-simulated spectrum are given in Table I. The nine superhyperfine peaks superimposed on each Cu(II) hyperfine peak and the excellent agreement between the calculated and experimental curves is further support for the presence of the static elongated-tetragonal CuN_6 configuration in ^{63}Cu(II)-doped $M_2M'M''(NO_2)_6$ compounds.

In conclusion, the EPR spectra presented here are the first examples of high-resolution spectra for Cu(II)-doped $M_2M'M''(NO_2)_6$ systems. Both hyperfine and superhyperfine structure are present in a pattern expected for an elongated-tetragonal CuN_6 configuration. The results also support the previous observation of Reinen and Friebel, who stated in their review "in all cases in which Cu(II) is isomorphously substituted into a host lattice site of regular octahedral symmetry, the Jahn–Teller effect induces a tetragonal elongation—sometimes with an orthorhombic component superimposed".[3]

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Registry No. 1, 85565-57-7; 2, 85565-56-6; 3, 85565-55-5; ^{63}Cu, 14191-84-5.

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