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Computer Simulation of EPR Orthorhombic Jahn-Teller Spectra of Cu^{2+}in $Cd_2(NH_4)_2(SO_4)_3$ Single Crystals at Low Magnetic Field Direction (M=-3/2) at Different Temperatures

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Abstract: In this paper, we have carried out computer simulation of Cu^{2+}:$Cd_2(NH_4)_2(SO_4)_3$ in the low magnetic field corresponding to x-direction and M=-3/2 at different temperatures. The normalized intensity decreases with temperature showing a phase transition temperature of about 195 K. The least squares method yields the intensity-temperature relation $I_N = -0.0466T + 10.482$ with correlation coefficient of R^2=0.9789. The activation energy varies withtemperature in a similar pattern as intensity but has lower values than those obtained from intensity and linewidths studies in all directions. The resonance field and linewidths depend on temperature in the form of sum of polynomials and exponential terms confirming earlier findings (Yerimaand De, 2014; De, 1986).

Keywords: Computer simulation, temperature, intensity, activation energy

Introduction

The Langbeinite family of complexes with general chemical formula $(X^+)_2(Y^{2+})_2(SO_4)_3$ was discovered by Jona and Pepinsky (1956) where X^+ is ammonia or monovalent metal and Y^{2+} is a divalent metal. Babu et al (1984) stated that a host of authors have carried out a number of investigations on the microscopic properties of the langbeinite family of crystals. The complex cadmium ammonium sulphate, $Cd_2(NH_4)_2(SO_4)_3$ abbreviated as CAS is isomorphous to potassium magnesium sulphate, $K_2Mg_2(SO_4)_3$ abbreviated as PMS and both are members of the langbeinite family of crystals. The explicit x-ray data on the atomic positions in CAS does not seem to be available in the literature but that of PMS have been reported by Zemann and Zemann (Babu*et al*, 1984). In addition, they stated that some authors have shown that the langbeinite family of complexes in cubic space group $P_{2/3}$ with a=10.35 $\dot{A}$ have four molecules per unit cell. The structure consists of a group of $(SO_4)^{2-}$ tetrahedral and Cd^{2+} metal ions. There are two each crystallographically non-equivalent Cd^{2+} and $(NH_4)^+$sites. Each Cd^{2+} is surrounded by six oxygen atoms which form a slightly distorted octahedron. Yerima (2005, 2007) stated that EPR studies of Misra and Korezak in 1986 using Mn^{2+} as a probe revealed a phase transition at 94.5 K whose mechanism was attributed to the freezing out of the rotation of the $(SO_4)^{2-}$ ion. In addition, he stated that EPR studies of Mouli and Sastry in 1962 using Cu^{2+} probe at room temperature and 77 K yielded eight poorly resolved hyperfine lines in a general direction and a set of four unresolved hyperfine lines in any crystallographic plane. Their computed values of the g-factor showed that $g_{//}>g_{\perp}$ and that the A_{max} is falling along g_{min}. They concluded that Cu^{2+} ions in this system may be in a compressed octahedral position or entered into the system interstitially rather than substitutionally. The shortcomings of the study of Mouli and Sastry include its limitation to 77 K and its failure to focus on JT effect that could be associated with Cu^{2+} in this crystal as earlier hinted by Babu et al in 1984. Raman spectroscopy performed by Rabkin*et al* (1981) provided substantial information on the structural phase transition in this crystal. They observed that CAS exhibits a structural phase transition on lowering the temperature from space group $p_{2/3}$ to p_{21} at about 95 K, the lower the temperature phase being ferroelectric. Babu et al (1984) in their summary stated that Bhat*et al* (1973) EPR spectra of Mn^{2+} in the two phase groups of CAS observed at room temperature and at liquid nitrogen were slightly different, particularly in the magnitudes of their zero-field splitting, as a result of small orthorhombic component in the low temperature phase. The differences in the spectra indicated a phase transition from high temperature phase $p_{2/3}$ to a low temperature phase p_{21}. In another outlook, Yerima (2005) stated that Ng and Calvo in 1975 observed in their EPR studies using Mn^{2+} in the temperature range 300-77 K observed definite change in the spectral pattern from that of room temperature to that of liquid nitrogen temperature due to a phase transition from $p_{2/3}$ to a space group of lower symmetry at low temperature. They did not analyze the spectra nor determine the phase transition temperature due to the complexity of the spectra at liquid nitrogen temperature.

The study of phase transition in CAS using VO^{2-} as a probe in the temperature range of 573-77 K showed a complex spectrum, in which Babu et al (1984) were unable to identify the phase transition temperature and they suggested that the lower temperature phase stabilizes at temperatures higher than 95 K. This was due to a local stabilization of the low symmetry phase by vandyl ions. They also found that the data of their experiment contained Cu^{2+} ion as contaminant and thus concluded that the complication in their results could have been due to a possible JT effect associated with Cu^{2+} ion in this crystal. Unfortunately, they did not carry out further investigation to establish or rule out the possibility of JT effect due to Cu^{2+} ion in this system.

De (2010) said in order to ascertain JT effect of Cu^{2+} in CAS Oguama carried out detailed EPR study of Cu^{2+} doped in CAS at various temperatures in the range of 300-15 K with angular variations usually at steps of 5^o and 0.5^o near JT extreme points in three mutually perpendicular planes of CAS single crystals. The Cu^{2+}:CAS spectra consists of finely resolved hyperfine lines in the low magnetic field region at all temperatures except 15 K while those in the high magnetic field region are poorly resolved at high temperatures. The insufficient resolved splitting patterns of the spectra constitute a major problem in the extraction of the relevant spectroscopic parameters (resonance frequency, coupling constants, linewidths) from the spectra as starting points in the computer simulation of the spectra. Therefore, a straightforward analysis is not possible in general (neither for the human expert nor for a conceivable computer expert system (kirste, 1992)). It is against this background, several methods (spectrum contraction or elimination hyperfine splitting constants, extraction of hyperfine splitting constants, correlation method, maximum method, significance plots and ‘’roll-up’’ transformation) have been employed in the analysis of high resolution EPR spectra (Kirste, 1992; Wu, 2006). These methods may be more or less useful in providing estimates for the hyperfine coupling constants. On the other hand, the set of relevant spectroscopic parameters extracted from the spectra can be verified by spectrum simulation and comparison with the experimental spectrum which is the method adapted in this paper. We have adapted the spectrum fitting because it is considered an indispensable component in any scheme automated spectrum analysis. In this work, we have considered the computer simulation of Cu^{2+}:$Cd_2(NH_4)_2(SO_4)_3$ spectra for M=-3/2 in the low field or x-direction.

Theory and method of computer simulation of EPR spectrum

In our earlier work (Yerima*et al.*,2014),we have reported that the first derivative line shape function of EPR spectra of Cu^{2+} manifesting static JT effect with orthorhombic g and A tensors in CAS is given by

$$F^{'}(H) = -\{2\alpha f_1\}\left[\frac{H-\frac{h\upsilon}{\beta g_z}+A_z M_I}{\left(\left(H-\frac{h\upsilon}{\beta g_z}+A_z M_I\right)^2+R_1\right)^2}\right] - \{2\alpha f_2\}\left[\frac{H-\frac{h\upsilon}{\beta g_x}+A_x M_I}{\left(\left(H-\frac{h\upsilon}{\beta g_x}+A_x M_I\right)^2+R_2\right)^2}\right] - \{2\alpha f_3\}\left[\frac{H-\frac{h\upsilon}{\beta g_y}+A_y M_I}{\left(\left(H-\frac{h\upsilon}{\beta g_y}+A_y M_I\right)^2+R_3\right)^2}\right]$$

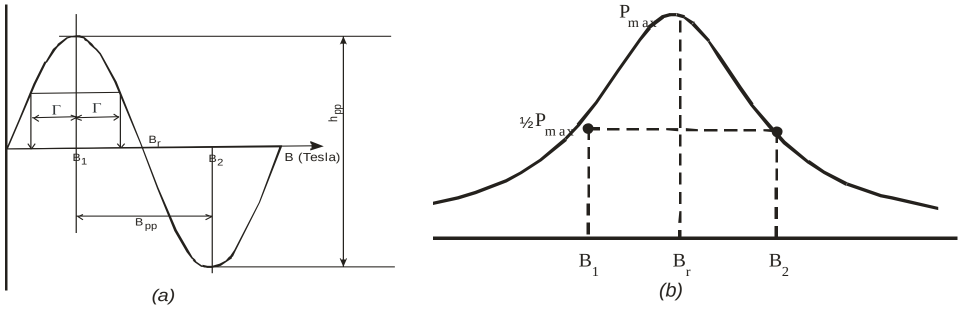
1

where $f_1 = g_z^2\left(g_x^4 - g_y^2\right)\frac{\pi}{2} + \pi g_y^4,\ f_2 = g_x^2\left(g_z^4 - g_y^2\right)\frac{\pi}{2} + \pi g_y^4,\ f_3 = g_y^2\left(g_x^4 - g_z^2\right)\frac{\pi}{2} + \pi g_y^4$, α is the fractional relative abundance of copper isotopes $\alpha(Cu^{63}) = 0.69$ and $\alpha(Cu^{65}) = 0.31$; g_x, g_y, g_z are g-factors along the x-, y-, and z-axes respectively; H is the applied magnetic field; A_x, A_y, A_z are the hyperfine constants in the x-, y-, and z-axes respectively; R_1, R_2, R_3 are the linewidth parameters in the x-, y-, and z-axes respectively; M_I=-3/2, -1/2, 1/2, 3/2 and β is the Bohr magneton. The terms in the curly brackets represent the magnification factor of the line shape while the terms in square brackets determine the shape of the EPR line.

Since computer simulation of the line shape function represented by equation (1) is cumbersome and time consuming because many variables are involved, we search for a simpler line shape function involving less number of variables. One of such functions is the integrated Lorentzian line shape function involving only three variables of theform (Blakemore, 1985)

$$P = \frac{\Gamma^2 P_{max}}{\Gamma^2 + (H - H_r)^2} \qquad 2$$

where P power, Γ is the half linewidth, H is the magnetic field and H_r is the resonance magnetic field. Equation (2) is simpler to simulate since it has only three variables (H, H_r, Γ) as compared to sixvariables (H, α, R_i, A, M, g) in equation (1). In theory, the plot of P versus H gives the expected resonance curve as shown in Fig.1b. In practice, when the resonance curve is broad, it becomes difficult to locate the resonance magnetic field precisely. As a result, the EPR spectrometer machine is designed in such a way that it records the derivative spectrum instead (Fig.1a) from which the resonance field can be located precisely.



(a) (b)

Fig.1 (a) first derivative and (b) integrated EPR spectrum

Now from Fig.1b, it can easily be shown that

$$2\Gamma = \Delta B_{\frac{1}{2}} \qquad 3$$

Taking the first derivative of equation (2) with respect to H, we have

$$\frac{dP}{dH} = \frac{-2\Gamma^2 P_{max}\,(H-H_r)}{\left[\Gamma^2+(H-H_r)^2\right]^2} \qquad 4$$

The ratio $\frac{dP}{dH}$represents the normalized intensity designated by I_N. In practice, the normalized intensity is defined as the ratio of the peak-to-peak height of the spectrum of the sample to that of the standard spectrum. It is also defined as the ratio of power to maximum power which is equal to 1 at maximum absorbance power by the sample in the cavity. At this point resonance occurs and the resonance condition is $h\nu = g\beta H$ where h is the Planck's constant, ν is the frequency of the microwave signal, g is the spectroscopic splitting constant, β is the Bohr magneton and H is the varying magnetic field.

The plot of $I_N$versus H is the EPR spectrum (Fig.1a) that the EPR machine displays. Also, from Fig. 1a we can easily deduce the resonance magnetic field $H_r$as the field corresponding to zero lineshape, that is, $H = H_r$.

Similarly, taking the second derivative of equation (4) with respect to H, gives

$$\frac{d^2P}{dH} = \frac{\Gamma^2+(H-H_r)^2-4(H-H_r)^2}{\left[\Gamma^2+(H-H_r)^2\right]^3} \qquad 5$$

Again we can easily show that at resonance, $\frac{d^2P}{dH^2}=0$, which gives

$$2\Gamma = \sqrt{3}\Delta H_{pp} \qquad 6$$

Therefore, combining equations (3) and (6), we have

$$\Delta H_{\frac{1}{2}} = \sqrt{3}\Delta H_{pp} \qquad 7$$

The ratio $\frac{\Delta H_{\frac{1}{2}}}{\Delta H_{pp}} = \sqrt{3} = 1.7321$from equation (7) gives the condition that the line is Lorentzian.

In our previous works (Yerima 2014; Yerima and De 2014), we have studied the linewidth, intensity, relaxation times and computer simulation of the spectra of Cu^{2+} in CAS at various temperatures using equation (1) involving six variables which made the simulation tedious and time consuming (Yerima*et al.*, 2014). In all these studies, we have reported that the orthorhombicity of the spectra is attributed to the non-equivalency of the three JT potential wells of Cu^{2+} in this system. Therefore, it is expected that the potential would vary with temperature. However, in our earlier study of linewidth and intensity as functions of temperature it was only possible for us to determine the average potential. It is against this background that we investigated the variation of energy with temperature by simulating the spectra in the lower magnetic field or x-direction for M=-3/2 using equation (4) which is simpler involving only two variables instead of that of Yerimaand De (2014) involving six variables.In the computer simulation process, first, the resonance magnetic field H_r, estimated value of peak-to-peak linewidthΔH_{pp} from the observed spectrum (Fig. 1a) and the calculated value of Γ from equation (6) were used as starting points. Second, these values of H_r, Γ and ΔH_{pp} were substituted in equation (4) and the resulting line shape was compared or matched with observed EPR line. Third, the value of H_r was kept constant since it can be measured accurately from the spectrum while thevalues of Γ and ΔH_{pp} were varied by small amounts in the ranges ±0.005-0.01 and ±5-10 G respectively around the initial values until the line that best fits the observed EPR line was obtained. Fourth, the effective values ofH_r,Γ and ΔH_{pp} corresponding to the simulated EPR lines of Cu^{2+} in CAS at a particular temperature was recorded. Fifth, the effective values of H, Γ and ΔH_{pp} were substituted into equation (2) to obtain the type of integrated spectrum (Fig. 1b) from which $\Delta H_{\frac{1}{2}}$ was measured. Sixth, other EPR parameters of interest were either measured from the type of spectra in Fig. 1 and others calculated from relevant equations. Finally, these procedures were repeated for Cu^{2+}:CAS spectra at different temperatures.

Results and discussion

Table 1 Intensity and potential energy of CAS at various temperatures

T (K)	I_N	ΔH_{pp}(Tesla)	Γ (Tesla)	H_r (Tesla)	E(cm^{-1})
80	7.14	0.00121	0.00104	0.2634	59.7
110	5.83	0.00329	0.00285	0.2522	58.9
120	5.41	0.00241	0.00209	0.2684	57.6
130	5.20	0.00263	0.00228	0.2660	56.0
140	4.45	0.00219	0.00190	0.2680	51.4
180	1.89	0.00351	0.00304	0.2618	23.9
190	1.79	0.00482	0.00418	0.2737	23.8
200	0.91	0.00307	0.00266	0.2765	12.2
210	0.85	0.00406	0.00351	0.2794	11.9

220	0.60	0.00329	0.00285	0.2779	8.7
230	0.50	0.00351	0.00304	0.2787	7.5
240	0.30	0.00318	0.00275	0.2772	4.7

The peak to peak height of the spectra of Cu^{2+}:CAS and that of the standard were measured at various temperatures. The ratio of the peak to peak height of Cu^{2+}:CAS spectrum to that of the standard gives the normalized intensity $I_N$of this system.

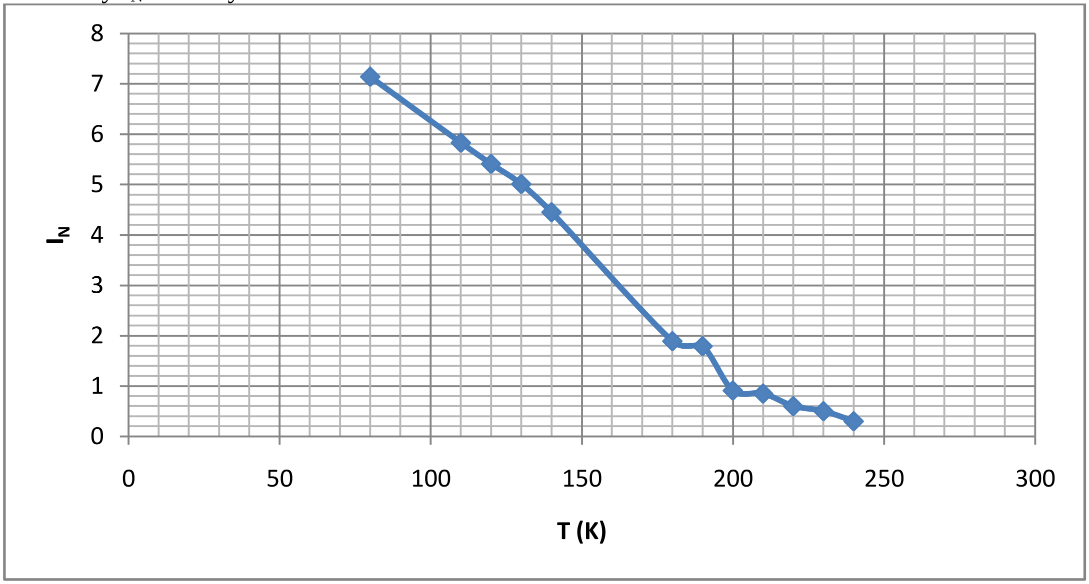
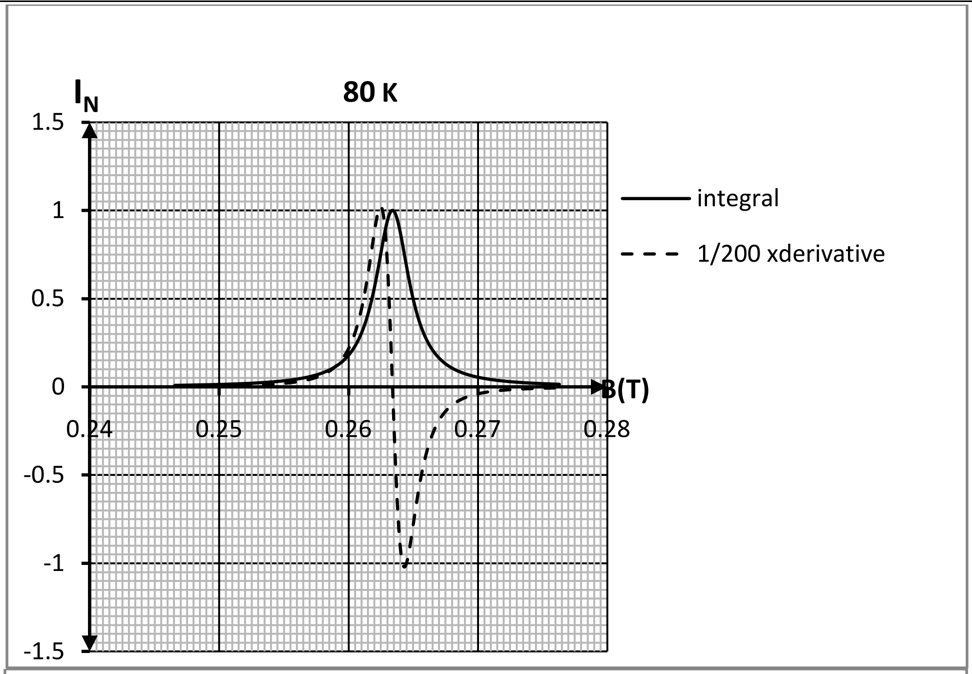
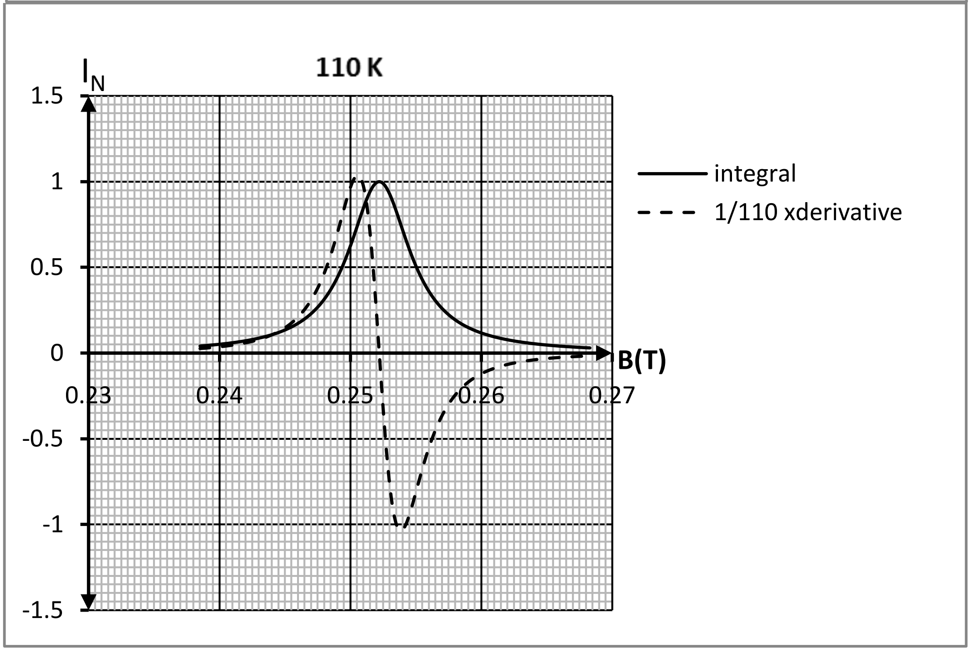


Fig. 2 Variation of normalized intensity of Cu^{2+}:CAS with temperature

In Fig. 2, the normalized intensity of Cu^{2+}:CAS spectra in the lower magnetic field (M=-3/2) decreases with temperature. The intensityshows abrupt change between 190 K and 200 K which may be attributed to phase transition temperature at about 195 K. The decrease in the intensity of this system depends on the way the population of the lower energy level changes on heating i.e. the population of the lower energy state or intensity is higher than that of the excited state.This is in agreement with earlier findings that the three Jahn-Teller (JT) potential wells are non-equivalent i.e. the separation of the potential wells in this direction varies with temperature. To calculate the potential energy of the wells in this direction, we employed to first approximation the least squares method and we obtained the intensity-temperature relation$I_N = -0.0466T + 10.842$ with correlation coefficient R^2=0.9789. The coefficient -0.0466 K^{-1} of T in this relation represents the rate of the decrease of the intensity with temperature and the intercept represents the intensity I_o=10.842as the temperature tends to absolute zero. The activation or potential energy $E = -kTln\left(1 - \frac{I_N}{I_o}\right)$ is calculated for each measured I_N at temperature T where k is the Boltzmann constant and recorded in Table 1. The variation of E with temperature is similar to that of intensity with temperature. However, the values of E obtained in this work in the x-direction or low magnetic field lie in the range 4.7-59.7 cm^{-1}as opposed to average range 393.5-417.2 cm^{-1} obtained for intensity and linewidth studies of this system in all directions (Yerima and De, 2014).

On the other hand, the resonance field H_r, linewidthsΓandΔH_{pp}were obtained from the simulated spectra (Fig. 3) and recorded in Table 1. These quantities fluctuate with temperature in the form of polynomial (Table 1). This agrees with earlier findings that bothrelaxation time and linewidthdepend on temperaturein the form of sum of polynomials and exponential terms (Yerima, 2014; De, 1986).


I_N
80 K
1.5
1
0.5
0
-0.5
-1
-1.5
0.24
0.25
0.26
0.27
0.28
B(T)
integral
1/200 xderivative


I_N
110 K
1.5
1
0.5
0
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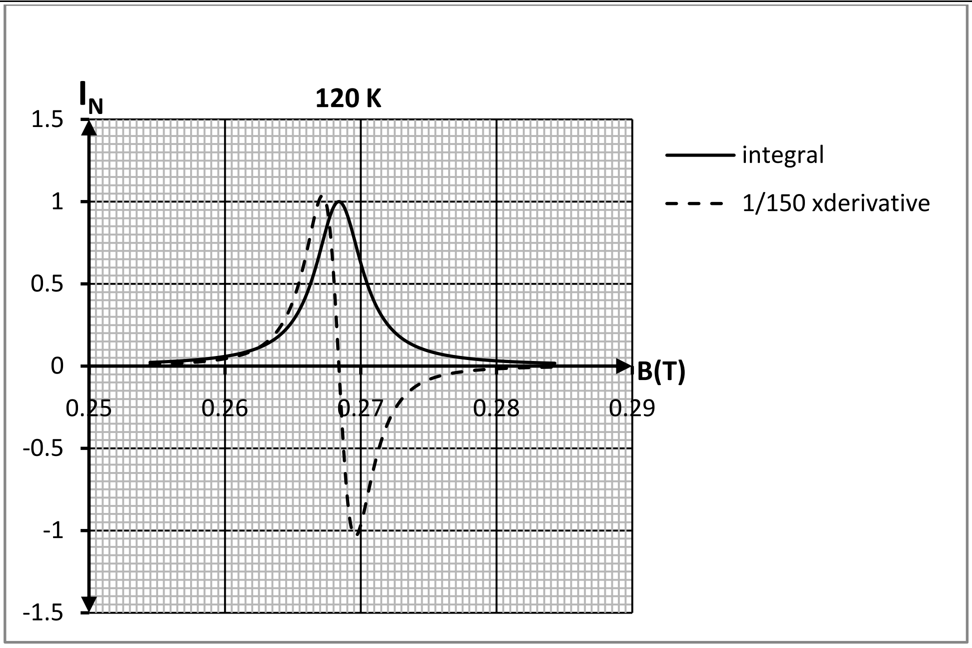
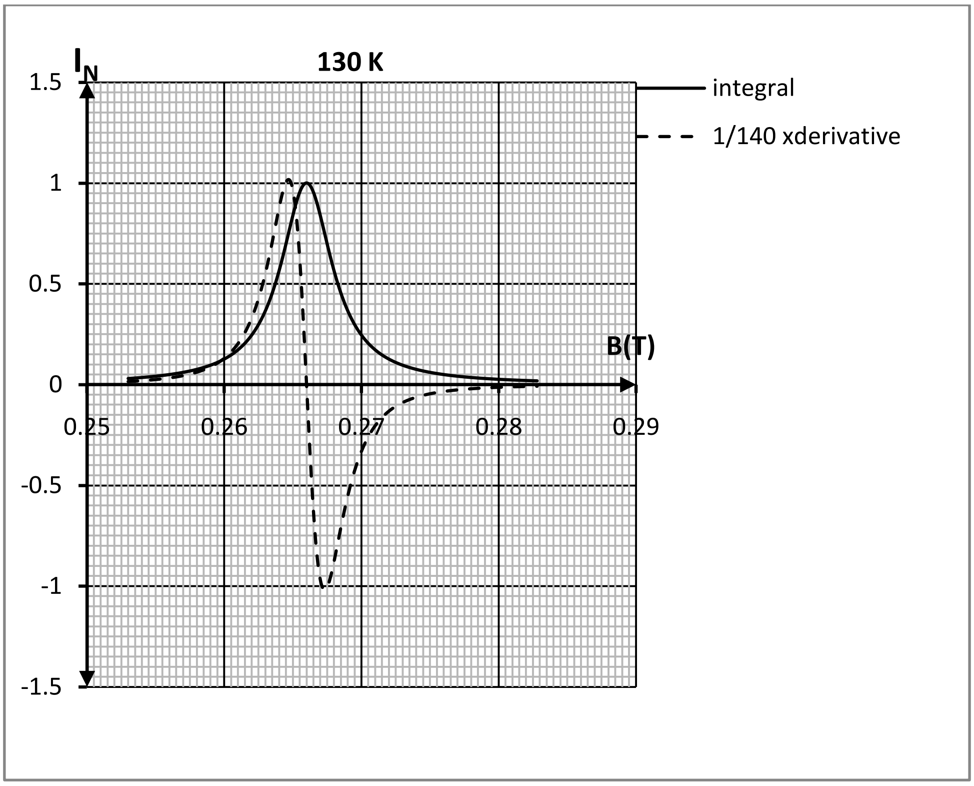
-1
-1.5
0.23
0.24
0.25
0.26
0.27
B(T)
integral
1/110 xderivative


I_N
120 K
1.5
1
0.5
0
-0.5
-1
-1.5
0.25
0.26
0.27
0.28
0.29
B(T)
integral
1/150 xderivative


I_N
130 K
1.5
1
0.5
0
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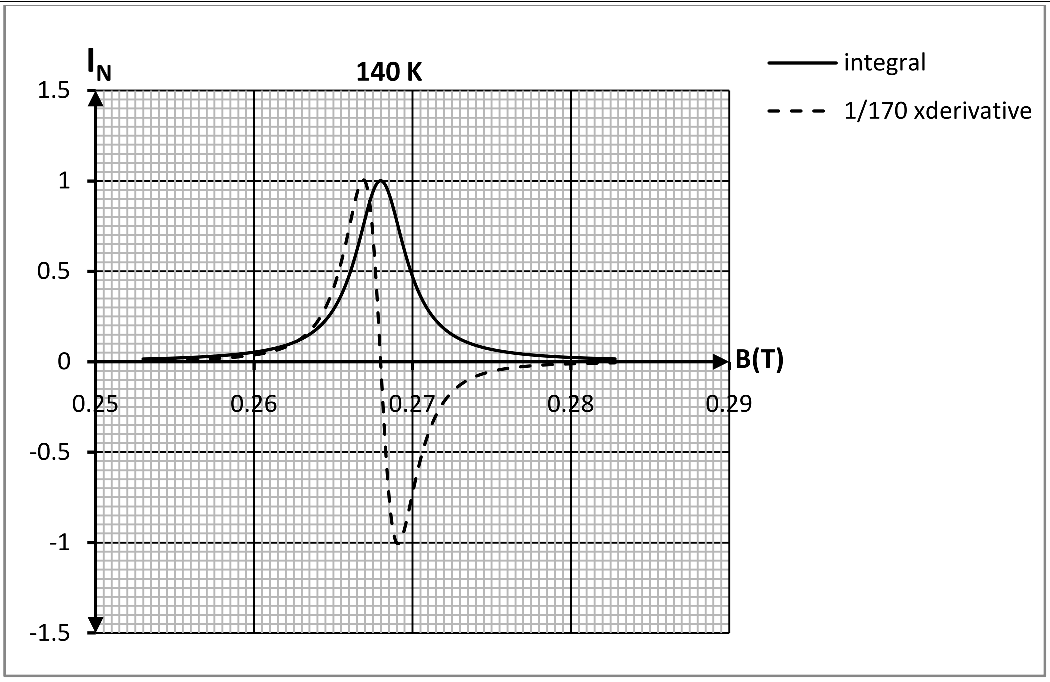
-1
-1.5
0.25
0.26
0.27
0.28
0.29
B(T)
integral
1/140 xderivative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140 K
integral
1/170 xderivative
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1
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0
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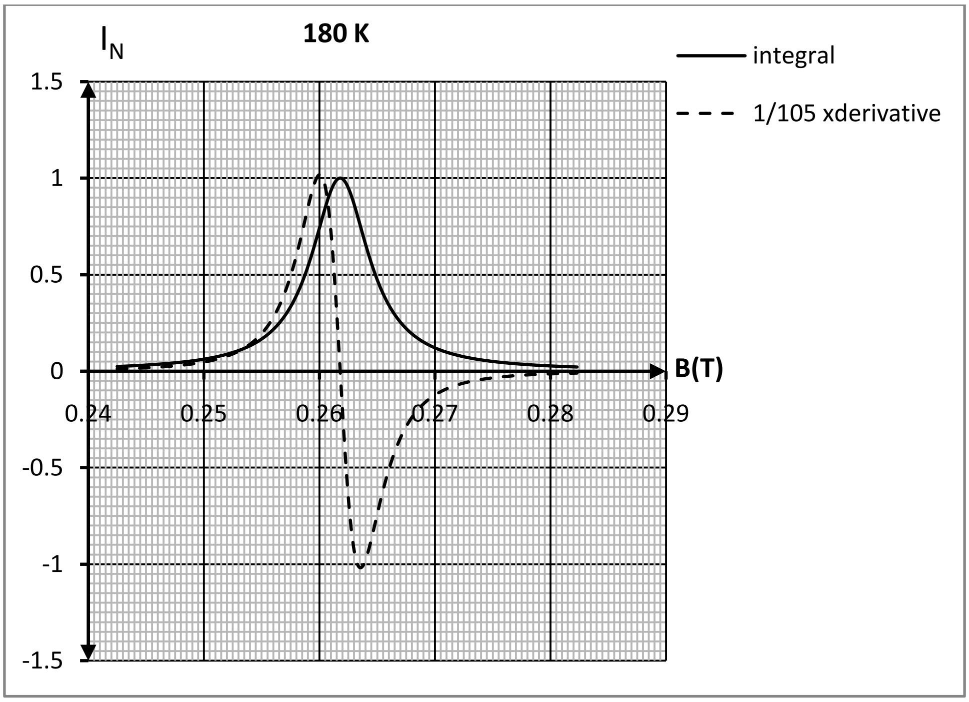
-1
-1.5
0.25
0.26
0.27
0.28
0.29
B(T)


I_N
180 K
integral
1/105 xderivative
1.5
1
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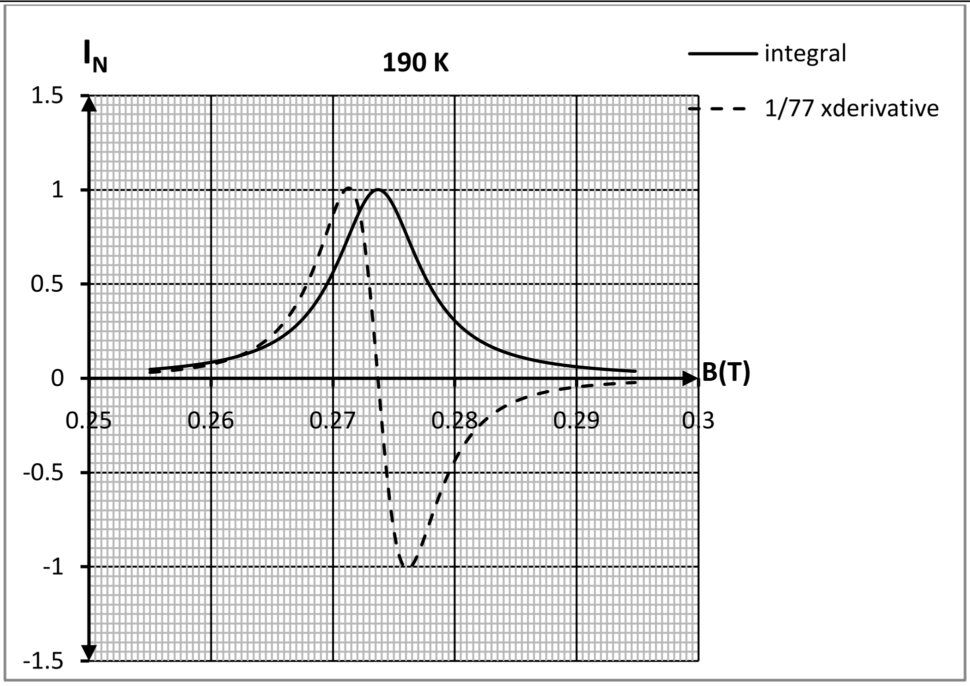
0.24
0.25
0.26
0.27
0.28
0.29
B(T)


I_N
190 K
integral
1/77 xderivative
1.5
1
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0
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-1
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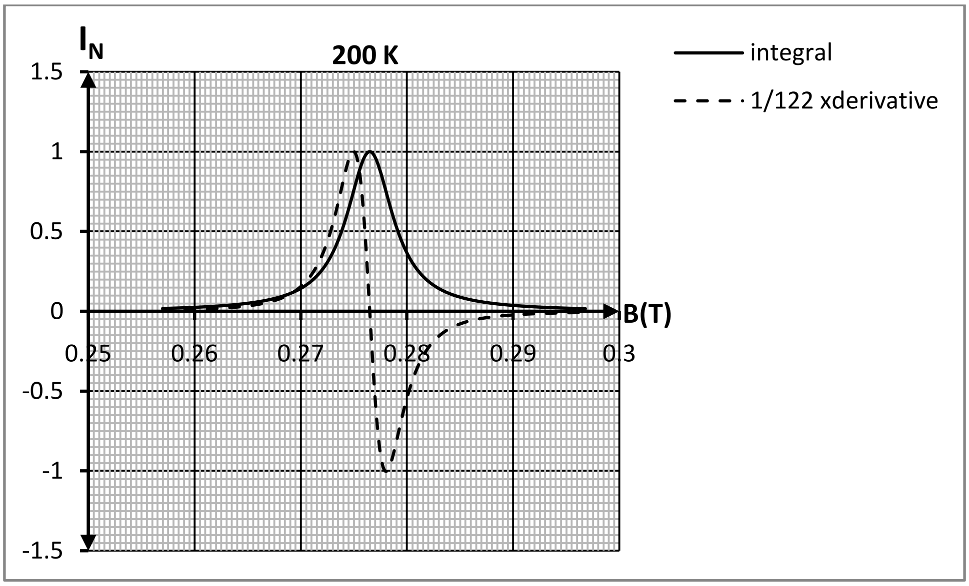
0.25
0.26
0.27
0.28
0.29
0.3
B(T)


I_N
200 K
integral
1/122 xderivative
1.5
1
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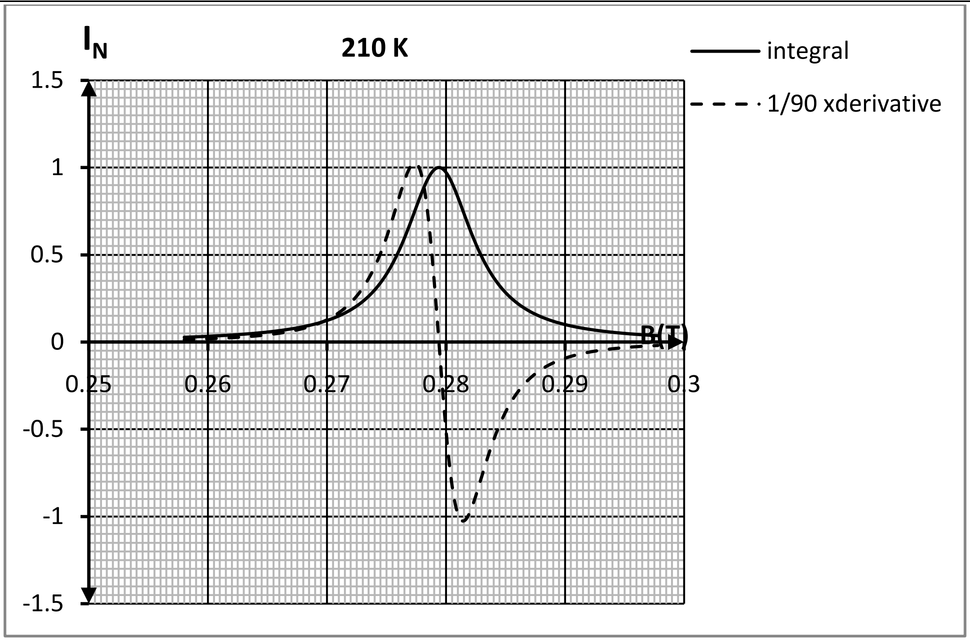
0
-0.5
-1
-1.5
0.25
0.26
0.27
0.28
0.29
0.3
B(T)



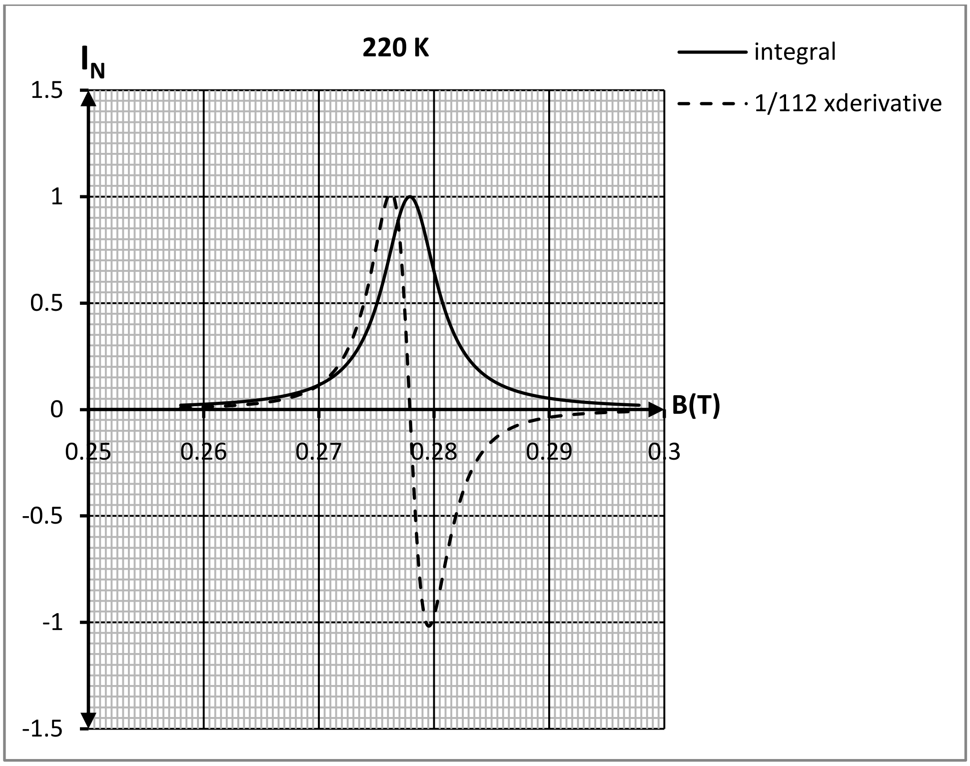


Fig. 3 Temperature dependence of the normalized intensity and lowmagnetic field in the M=-3/2 or x-direction

Conclusion

In this paper, we have carried out computer simulation of the Cu^{2+}:CAS spectra in the low magnetic field in the x-direction for M=-3/2 at different temperatures. The normalized intensity obtained from the simulated spectra decreases with temperature showing a phase transition temperature of about 195 K. The calculated activation energy varies with temperature in the same way as the normalized intensity. In another vein, we observed that the peak to peak linewidth and resonance field vary in the form of polynomials as opposed to exponential behaviour in our earlier studies of the linewidth and intensity of this system in all directions.

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