

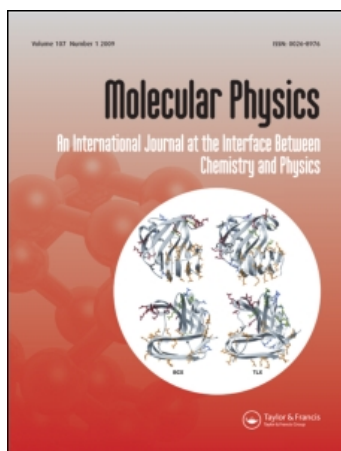
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Electron paramagnetic resonance evidence for Jahn-Teller glasses

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Single crystal E.P.R. studies of copper as a dopant in lithium potassium sulphate, lithium ammonium sulphate and lithium sodium sulphate have been carried out from room temperature down to 77 K. The three Jahn-Teller (JT) systems behave very similarly to one another. The room temperature dynamic JT spectra with $g_{\text{iso}} = 2.19 \pm 0.01$ and $A_{\text{iso}} = \pm(33 \pm 4) \times 10^{-4} \text{ cm}^{-1}$ transform around 247 K to spectra characterized by randomly frozen-in axial strains with $g_{\parallel} = 2.4307 \pm 0.0005$, $g_{\perp} = 2.083 \pm 0.001$, $A_{\parallel} = \pm(116 \pm 2) \times 10^{-4} \text{ cm}^{-1}$ and $A_{\perp} = \mp(14 \pm 4) \times 10^{-4} \text{ cm}^{-1}$. We proposed that the low temperature phase (below 247 K) of each of these systems provides an example of a Jahn-Teller glass.

1. Introduction

The electron paramagnetic resonance (E.P.R.) spectra of Jahn-Teller (JT) ions in crystals have attracted considerable attention in the past [1]. Apart from the spectra expected for normal dynamic and static JT effects [1], anomalous lineshapes were quite often observed [2]. Ham [3] and Chase [4-6] developed the model for strain-dependent behaviour of orbital doublet levels subject to the JT effect and showed that the nature of the low temperature E.P.R. spectra is determined by the relative strengths of the JT coupling and random strain (i.e. $\delta/3\Gamma$ for the particular case of the 2E vibronic ground state where 3Γ is the tunnelling splitting between the ground doublet and the nearest A_1 or A_2 excited singlet and δ is the average strain splitting of the ground state). Using Ham's effective hamiltonian formalism Boatner *et al.* [7] categorized the various JT effects into four types, ranging from static through quasi-static, quasi-dynamic to dynamic JT effect, as the above ratio decreases from a value above 5 to less than 0.1.

NH_3^+ as a paramagnetic dopant in LiKSO_4 (LKS) has served as a very faithful probe in a study of the low temperature phase transitions: PI (room temperature-(RT)); PII (below 204 K); PIII (below 190 K); PIV (below 138 K) [8-10]. When Cu^{2+} was tried as a paramagnetic probe the results were surprisingly different though persistently reproducible. There was a single transition at ~ 247 K. None of the phase transitions seen by NH_3^+ in LKS were indicated by Cu^{2+} as dopant. The spectra above the transition temperature of 247 K were typical of a dynamic Jahn-Teller (JT) effect. This by itself was not so surprising since Cu^{2+} is well known as a JT ion. Below the above mentioned transition the single crystal spectra were completely independent of magnetic field orientation and resembled powder spectra

with axially symmetric g and A tensors. We then studied the E.P.R. spectra of single crystals of LiNH_4SO_4 (LAS) and LiNaSO_4 (LSS) lightly doped with Cu^{2+} , and found similar results. The powder-like spectra of the low temperature phase seem to indicate the formation of a JT glass of the type proposed by Mehran and Stevens [21] for dilute JT systems with randomly frozen-in strain fields. A preliminary report on this work has been published [11].

2. Experimental work

Single crystals of Cu^{2+} doped LiKSO_4 (LKS) were grown by taking $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and K_2SO_4 in the molar ratio 3.5 : 1 along with at least 5 mole per cent of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in aqueous solution, and slowly evaporating at room temperature (RT). LiNH_4SO_4 (LAS) crystals doped with Cu^{2+} were grown from an aqueous solution of equimolar amounts of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{SO}_4$ and 0.5 mole per cent of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. LiNaSO_4 (LSS) crystals doped with Cu^{2+} were crystallized at 343 K from a solution containing $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and Na_2SO_4 in stoichiometric amounts, and 0.5 mole per cent of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. The crystals of LKS were hexagonal, of LAS pseudo-hexagonal and LSS trigonal in habit. They were as expected [12–14]. These three types of crystals were characterized by their X-ray powder patterns. It seemed very difficult however to obtain solution grown crystals of either LKS, LAS and LSS with reproducibly varying concentrations of Cu^{2+} in them.

Since it was difficult to introduce varying concentrations of Cu^{2+} into solution grown host crystals, this was tried in melt grown LKS crystals. Accordingly analar grade $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and K_2SO_4 were taken in stoichiometric amounts and heated to around 900°C to prepare pure LiKSO_4 (LKS). The LKS was mixed with the required amount of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in platinum crucibles, and heated in a furnace to $\sim 775^\circ\text{C}$ at which it was soaked for 4 hours. Care was taken not to exceed this temperature since Cu^{2+} tends to be reduced to Cu^+ at higher temperatures. The temperature was then slowly decreased at the rate of 15°C per hour over a period of 48 hours. The crystals so obtained were checked under the polarizing microscope and confirmed to be single crystals. Some crystals were powdered and the X-ray diffraction pattern was taken. The powder pattern confirmed that the crystals were of LKS.

The E.P.R. spectra of the Cu^{2+} doped LKS, LAS, and LSS crystals were recorded on a Varian E-109 spectrometer operating at X-band and employing a 100 kHz magnetic field modulation. The spectra were recorded in three orthogonal planes from RT (300 K) to 77 K.

3. Results

3.1. Solution grown crystals

Figures 1, 2 and 3 show the E.P.R. spectra of Cu^{2+} in solution grown LKS, LAS and LSS single crystals respectively. These spectra were found to have the following features in common. At RT (300 K) partially resolved hyperfine lines due to Cu^{2+} were seen. The widths of these hyperfine lines decreased towards the high field side and the amplitudes correspondingly increased. The line positions were independent of magnetic field orientation. For all these three systems (LKS, LAS and LSS doped

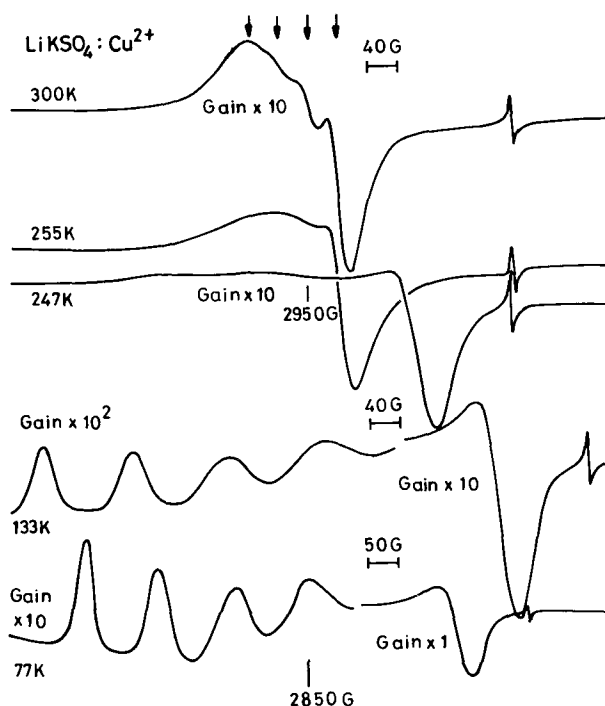


Figure 1. The E.P.R. spectra of Cu^{2+} doped in LKS single crystals (grown from solution) have been recorded at various temperatures. At around 247 K there is a JT transition. The spectra are independent of magnetic field orientation both above and below the JT transition.

with Cu^{2+}) $g_{\text{iso}} = 2.19 \pm 0.01$ and $A_{\text{iso}} = \pm(33 \pm 4) \times 10^{-4} \text{ cm}^{-1}$. These spectra resemble the E.P.R. spectra of Cu^{2+} in MgO, recorded at temperatures above 4 K [2]. On cooling from RT, the resolution of the hyperfine lines decreased as can be seen from the spectrum at 255 K for LKS, 253 K for LAS and 251 K for LSS (figures 1, 2 and 3). At around 247 K and for all these crystals, there occurred a transition. This transition temperature was dependent on the thermal history of the samples, and was in the range 247 ± 5 K. Below the transition the spectrum consisted of a strong line at $g_{\perp} = 2.083$. Further cooling led to the gradual development of four additional weak and broad hyperfine lines on the low field side. This is recorded at 133 K for LKS, LAS and LSS in Figures 1, 2 and 3. These low temperature spectra given by solution grown crystals were also independent of magnetic field orientation and in fact resembled power-like E.P.R. spectra with axially symmetric tensors. Accordingly, we have determined

$$g_{\parallel} = 2.4307 \pm 0.0005, \quad g_{\perp} = 2.083 \pm 0.001,$$

$$A_{\parallel} = \pm(116 \pm 2) \times 10^{-4} \text{ cm}^{-1}, \quad A_{\perp} = \mp(14 \pm 4) \times 10^{-4} \text{ cm}^{-1}.$$

Any further cooling only led to an increase in the intensity of the individual components, as can be seen from Figure 1 for the E.P.R. spectrum of LKS at 77 K. Unlike the high temperature spectra (above the transition temperature ~ 247 K) the spectra of solution grown crystals below the transition temperature had the four

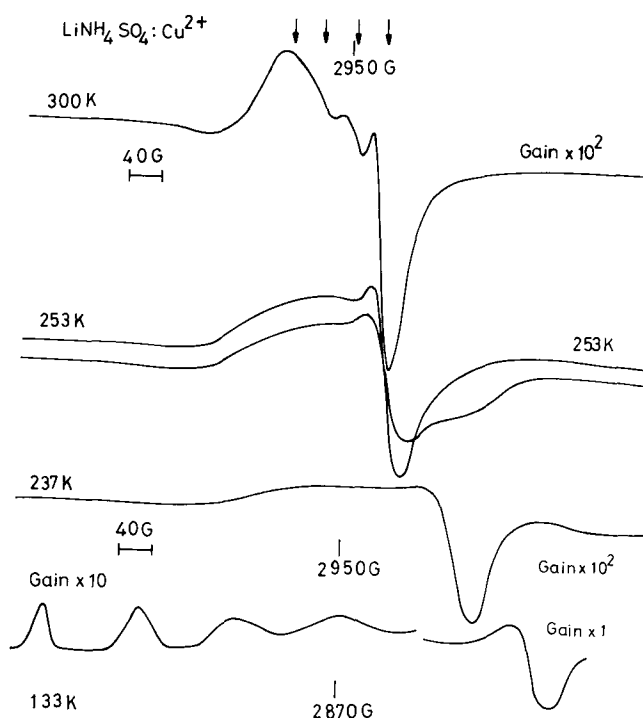


Figure 2. The E.P.R. spectra of Cu^{2+} doped in LAS single crystals (grown from solution) have been recorded at various temperatures. Around 247 K there is a JT transition. The spectra are independent of magnetic field orientation both above and below the JT transition.

parallel hyperfine lines increasing in linewidth, and decreasing in intensity as the magnetic field increased. The spectra of LSS however contained some weak additional lines (as shown in figure 3) due to a trace of some chance impurity in the chemicals used. This impurity spectrum however was dependent on the orientation of the magnetic field; and as we show later actually helped in the interpretation of our results. It must be mentioned here that in some crystals of LKS, LAS and LSS (but not all) there was an additional signal due to Cu^{2+} with $g \sim 2.10$, as shown in figure 4 for LKS. The signal was independent of magnetic field orientation and also did not show any temperature variation in the range 300 K–77 K studied by us (not shown here).

3.2. Melt grown crystals

The spectra of Cu^{2+} in melt grown LKS crystals which were the only ones tried are given in figure 5 for 0.5 mole per cent Cu^{2+} . The spectra for 0.05 mole per cent, 0.1 mole per cent and 1 mole per cent Cu^{2+} were similar and are not shown separately. The spectra have been recorded from 473 K to 77 K and found to be virtually independent of temperature. There was therefore no transition at ~ 247 K (or any other temperature) as in the case of solution grown crystals. The spectra were also independent of magnetic field orientation (not shown in the figure). A single broad line indicated a tetragonal distortion with $g_{\perp} \sim 2.10$. The parallel

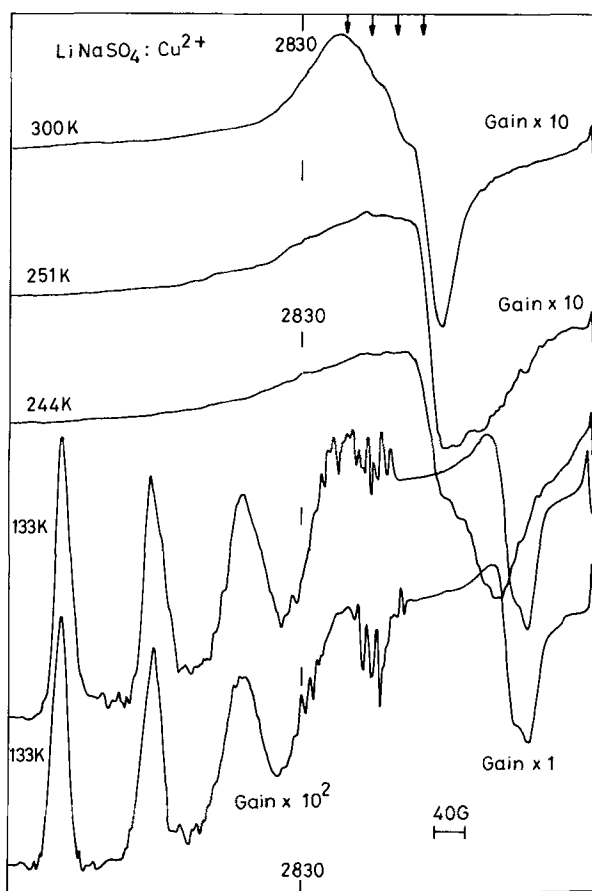


Figure 3. The E.P.R. spectra of Cu^{2+} doped in LSS single crystals (grown from solution) have been recorded at various temperatures; and at 133 K for two different orientations. (Note the impurity spectrum is dependent on the orientation of the magnetic field).

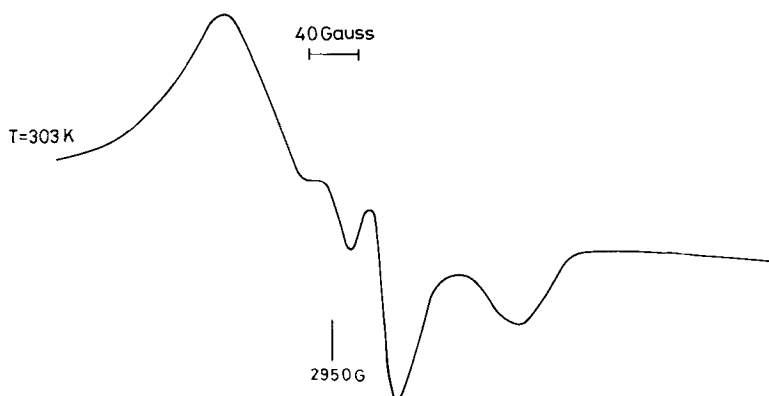


Figure 4. LKS single crystals doped with Cu^{2+} grown from solution. At 303 K, in this crystal, there are spectra due to Cu^{2+} in two different sites. One of the sites shows the usual dynamic JT spectrum with $g_{\text{iso}} = 2.19$, $A_{\text{iso}} = (33 \pm 4) \times 10^{-4} \text{ cm}^{-1}$; the second site is characterized by a $g \sim 2.10$.

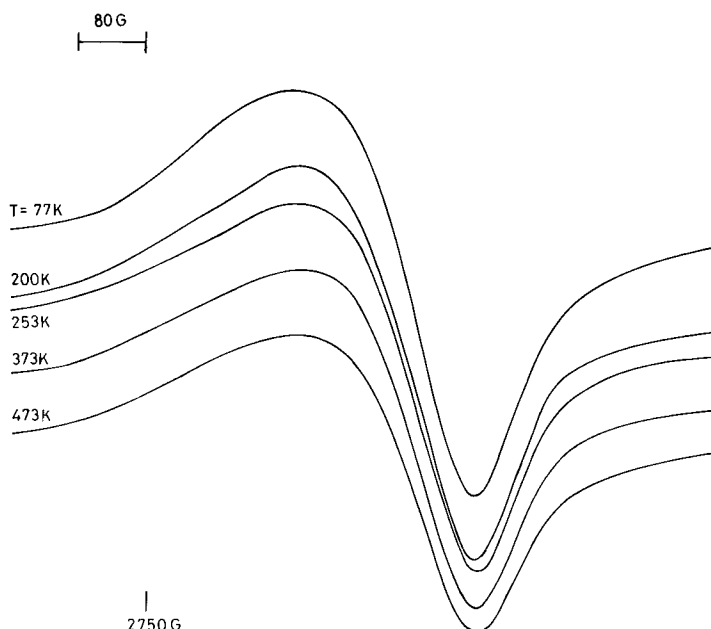


Figure 5. Single crystal E.P.R. spectra of LKS doped with Cu^{2+} (grown from melt) are shown from 77 K to 473 K. The spectra do not show any temperature dependence as indicated.

components could not be seen with the highest possible sensitivity of the spectrometer. In fact even the g_{\perp} component was weak. The above observations pertain to all the concentrations of Cu^{2+} (0.05, 0.1 and 1 mole per cent) studied.

4. Discussion

4.1. Spectra of solution grown crystals

As mentioned in the §3.1 RT E.P.R. spectra (figures 1, 2 and 3 of Cu^{2+} in LKS, LAS and LSS single crystals (solution grown) resemble the high temperature spectrum of Cu^{2+} in MgO which exemplifies the dynamic JT effect [2]. In addition, we note that the spin-hamiltonian parameters satisfy

$$g_{\text{iso}} = (2.19) = (1/3)(2 \times 2.083 + 2.4307) = (1/3)(2g_{\perp} + g_{\parallel})$$

as expected for a dynamic to static JT transition [1] for an orbital doublet E crystal-field ground state of Cu^{2+} . These spin-hamiltonian parameters indicate that Cu^{2+} has an octahedral/near octahedral environment undergoing a tetragonal distortion. It is also significant that the E.P.R. spectrum of Cu^{2+} is the same in all the solution grown host crystals LKS, LAS and LSS whose crystal structures are different from one another as shown in the table. Also, NH_3^+ introduced together with Cu^{2+} in these crystals shows the expected dependence on magnetic field orientation. Even the chance impurity in LSS shows the expected anisotropy of the spectra as shown in figure 3. The observed isotropy of the E.P.R. spectrum of Cu^{2+} in all these crystals (with respect to the magnetic field orientation) is therefore unique for Cu^{2+}

The room temperature crystal structure, number of molecules per unit cell and the site symmetry around the cations in LKS, LAS and LSS.

Systems	RT crystal structure			Site symmetry around		
	Space group	Z	Li ⁺	K ⁺	NH ₄ ⁺	Na ⁺
LKS	<i>P6₃</i>	2	Tetrahedral	Trigonal		
LAS	<i>P2₁cn</i>	4	Tetrahedral		No symmetry greater than 2 fold	
LSS	<i>P31c</i>	6	Irregular arrangements of 4 oxygens around it			Irregular arrangements of 8 oxygens around it

which incidentally is well known as a JT ion. In fact Tl^{2+} in LKS [15] gives E.P.R. spectra varying with magnetic field orientation and also reflecting the known phase transitions of LKS. We have also recorded in figure 6 the E.P.R. spectrum of Fe^{3+} in LKS at 300 K and at two different orientations of the magnetic field (i and ii). The spectra (i) and (ii) clearly show their dependence on the direction of the magnetic field. It is therefore highly improbable that the isotropic nature of Cu^{2+} E.P.R. spectra in LKS etc. with respect to magnetic field orientation could be due to randomly distributed crystal-fields caused by charge compensating vacancies. The spectra also remained unchanged even after annealing the crystals at 475 K to eliminate any possible inclusions of mother liquor in them. The conclusion that the high temperature spectra (above 247 K) of Cu^{2+} in LKS, LAS and LSS are of the dynamic JT type seems therefore ineluctable.

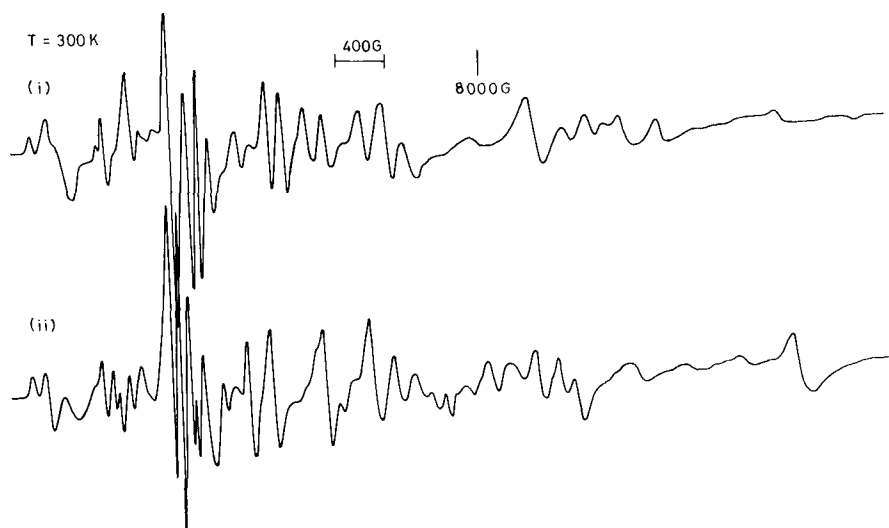


Figure 6. E.P.R. spectra of LKS single crystals (grown from solution) doped with Fe^{3+} ; (i) and (ii) represent spectra recorded in two different orientations at 300 K. These spectra clearly indicate the anisotropy of the Fe^{3+} centre in LKS with respect to the magnetic field H.

As mentioned in the last paragraph, the g -value of Cu^{2+} in LKS, LAS and LSS indicates a near octahedral surrounding. The cations in LSS (table) have much lower site symmetries [14]; Li^+ in LAS has a tetrahedral environment [13] and if Cu^{2+} were to substitute it the ground state would be an orbital triplet and the observed g -values would be different [16]. LKS has of course K^+ in a trigonal environment; but we have to take account of the fact that all these three host crystals give the same E.P.R. spectra for Cu^{2+} in them. It is therefore likely that Cu^{2+} is not in a substitutional but in an interstitial site in all these crystals. This is not surprising in view of the fact that the optical absorption spectra of Mn^{2+} and Co^{2+} in LAS [17, 18] indicate interstitial site occupation.

Coming now to the spectra below the transition at ~ 247 K (indicated by the solution grown crystals) the g -values indicate (as mentioned earlier) a tetragonal environment around Cu^{2+} . That means to say there is a JT distortion of the complex. This low temperature spectrum as also the transition temperature ~ 247 K is the same for Cu^{2+} in all the three solution grown host crystals. NH_3^+ as a dopant side by side with Cu^{2+} in some crystals (figures 7 and 8) does not indicate any phase transition at ~ 247 K while Cu^{2+} does not indicate any of the well known low temperature phase transitions of LKS indicated by NH_3^+ (figure 9). It follows from all these experimental facts that the transition at ~ 247 K is unique for Cu^{2+} as dopant and is virtually independent of the host crystal (LKS, LAS and LSS). The spectrum is also independent of magnetic field orientation while the g and A tensors indicate axial symmetry. This is therefore a powder-like spectrum given by a single crystal. This type of spectrum does not correspond to any of the known type of spectra [7].

In view of the unexpected nature of the above results the experiments were carefully repeated several times to check their reproducibility. The crystals were also annealed at ~ 475 K overnight in order to eliminate any possible inclusions of mother liquor in the crystals. The crystals were also checked under the polarizing

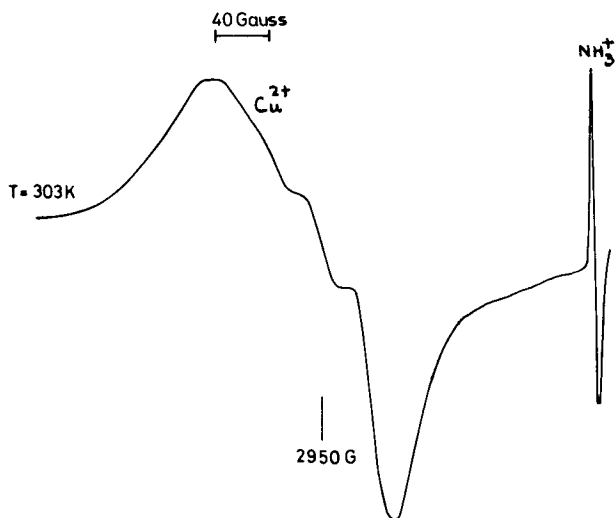


Figure 7. LKS single crystals doped with Cu^{2+} and NH_3^+ grown from solution. The dynamic JT spectrum of Cu^{2+} in LKS is shown along with the first line (lowest field) of the twelve line NH_3^+ E.P.R. spectrum; both are recorded at 303 K.

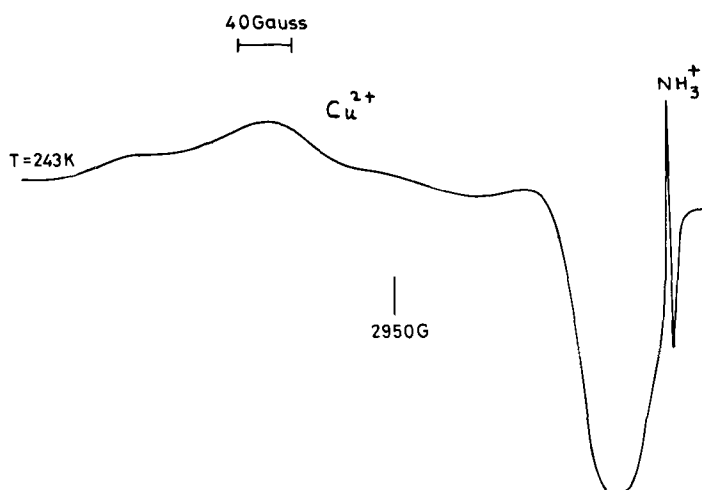


Figure 8. LKS single crystals doped with Cu^{2+} and NH_3^+ grown from solution. The NH_3^+ E.P.R. spectrum in LKS however, remains unchanged at this temperature (243 K). The dynamic JT spectrum of Cu^{2+} in LKS is shown.

microscope and confirmed to be single crystals (as mentioned earlier the chance impurity in LSS shows a spectrum dependent on magnetic field orientation and further substantiates the fact that LSS is still a single crystal below the transition temperature). The only possible explanation of this powder-like behaviour under E.P.R. of the above dilute JT systems in their low temperature phases, seems to be that they are probably JT glasses and the transition at ~ 247 K is a JT glass transition.

Mehran and Stevens (1983) have recently considered the possibility of JT glass formation. They make use of the displaced oscillator transformation [19] to decouple the spins and the interacting lattice oscillators; thus replacing the interaction by an Ising type exchange interaction among the pseudo-spins (representing the JT ions) themselves. They put forward a physical argument to demonstrate that in dilute JT systems, the effective Ising type exchange interaction among the pseudo-spins is oscillatory in sign as a function of distance; and such an interaction can, in a manner analogous to the RKKY interaction in the case of spin glasses, lead to random freezing of the JT strains. Mehran and Stevens have, in their model, JT

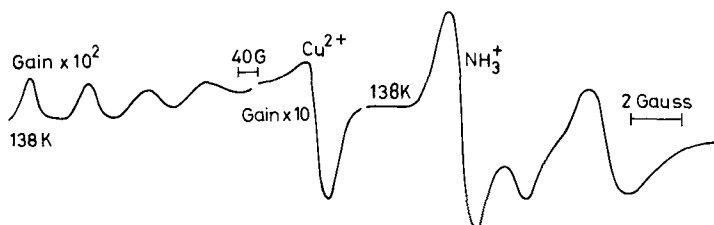


Figure 9. LKS single crystals doped with Cu^{2+} and NH_3^+ grown from solution. The E.P.R. spectrum of NH_3^+ in LiKSO_4 (LKS) at 138 K shows the PIII–PIV low temperature phase transition whereas Cu^{2+} does not reveal the phase transitions of LKS.

crystals diluted with non-JT ions in view; while the systems dealt with in this paper are non JT crystals doped lightly with JT ions. There is no essential difference between these two.

4.2. Spectra of melt grown crystals

The melt grown crystals of LKS with varying concentrations of Cu^{2+} were grown essentially because the solution grown crystals (in which it was difficult to introduce known different concentrations of Cu^{2+}) indicated a JT glass transition; and the temperature of such a transition is expected to be concentration dependent. The results on these crystals mentioned in §3.2 turned out to be rather unexpected since such melt grown crystals did not indicate the transition at $\sim 247\text{ K}$ or at any other temperature.

It was mentioned at the end of §3.1 (figure 4) that a small number of solution grown crystals have broad weak line with $g \sim 2.10$ in addition to the lines in figures 1, 2 and 3 which have been discussed in §4.1. This additional line appearing in some solution grown crystals but not all, resembles the spectrum (figure 5) of melt grown LKS doped with Cu^{2+} . This only means that the latter type of spectra are caused by Cu^{2+} occupying lattice sites different from those giving the spectra of figures 1, 2 and 3. In other words, Cu^{2+} is capable of occupying two different types of crystal sites in LKS for example. We will call them *A* and *B* for purposes of illustration. When crystals are grown from aqueous solution at RT the site preference of Cu^{2+} seems to be mostly for *A* and to a small extent for *B*. This site preference seems to change almost totally in favour of *B* when the crystals are grown at a high temperature from the melt. The reason seems to be that LKS undergoes several phase transitions above room temperature [20]. It is not surprising that the site-preference of a dopant such as Cu^{2+} depends on the crystal structure of the host crystal. Once a dopant enters a certain preferred site at a high temperature, the large potential barriers between different sites do not allow the dopant to change over easily to the thermodynamically preferred site at a lower temperature. Such changes of site occupancy in a crystal involve large energies of activation and are not easy.

5. Conclusion

The solution grown crystals were difficult to dope with different concentrations of Cu^{2+} as the crystals seemed to accept only constant amounts of Cu^{2+} ; and the melt grown crystals in which it was easy to introduce known different concentrations of Cu^{2+} gave different spectra. There seems to be no way of accounting for the unique transition in three separate host crystals (LKS, LAS and LSS) at $\sim 247\text{ K}$ nor the type of spectra below this temperature other than to assume a JT glass transition. The melt grown samples did not however, indicate any transition at $\sim 247\text{ K}$ (or any other temperature). So the expected concentration dependence of the transition temperature could not be shown. However, in view of the fact that the transition temperature of the same sample varies by as much as $\pm 5\text{ K}$, it is possible that the concentration dependence of the transition temperature is within this range.

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