The host lattice influence on the Jahn-Teller effect of the $Cu(H_2O)_6^{2+}$ complex studied by EPR in $K_2Zn(SO_4)_2.6H_2O$ and $(NH_4)_2Zn(SO_4)_2.6H_2O$ Tutton salt crystals

1999 J. Phys.: Condens. Matter 11 4391

(http://iopscience.iop.org/0953-8984/11/22/310)

J. Phys.: Condens. Matter **11** (1999) 4391–4400. Printed in the UK PII: S0953-8984(99)01602-1

The host lattice influence on the Jahn–Teller effect of the $Cu(H_2O)_6^{2+}$ complex studied by EPR in $K_2Zn(SO_4)_2 \cdot 6H_2O$ and $(NH_4)_2Zn(SO_4)_2 \cdot 6H_2O$ Tutton salt crystals

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Received 4 February 1999, in final form 8 April 1999

Abstract. The EPR investigations of Cu^{2+} doped $K_2Zn(SO_4)_2 \cdot 6(H_2O)$ and $(NH_4)_2Zn(SO_4)_2 \cdot 6(H_2O)$ Tutton salts in a temperature range of 4.2–300 K are reported. The analysis of the temperature dependences of the g-factors points to significant differences between Jahn–Teller $Cu(H_2O)_6^{2+}$ complexes in the ammonium and potassium compounds. In the ammonium salts the energy difference δ_{12}, between the ground and excited configurations, is found to be temperature dependent. This is explained by the lattice contribution to the adiabatic potential. Various mechanisms of such an influence are proposed. For the discussed case it is suggested that thermal librations of the ammonium groups will change the strength of the hydrogen bonds between the sulphate groups and water octahedra and in this way influence the Jahn–Teller complex.

1. Introduction

Paramagnetic ions doped into diamagnetic host crystals are commonly used as probes, which allow us to investigate various properties of the studied material assuming that the host lattice disturbance is negligible. Some of these probes can have, however, their own dynamics due to the Jahn–Teller effect. In such cases it is also commonly assumed that the vibronic complex does not disturb the lattice but the internal host lattice strains influence the geometry and dynamics of the doped complex. Moreover, the lattice strains are regarded as being not dependent on the temperature. This is the case of the Tutton salts, of general formula $A_2Me(XO_4)_2 \cdot 6(H_2O)$ (where A is K, Rb, Cs, NH_4; Me is divalent metal cation and X is S, Se), which are the subject of intensive EPR and structural studies. Their structure consists of $Me(H_2O)_6$ octahedra, bonded by the hydrogen bonds to the XO_4 groups. The octahedra are slightly compressed for the non-Jahn–Teller metal ions with shortest bond marked usually as the Me–O(9) bond. Distances Me–O(7) and Me–O(8) are nearly equal, with a slightly longer bond to O(7), in the zinc Tutton salts. In copper Tutton salts crystals the octahedra are strongly elongated, in either the Me–O(7) direction in the ammonium salt or Me–O(8) in all the others, due to the Jahn–Teller effect.

A fruitful approach to the description of the Jahn–Teller effect in the $K_2Zn(SO_4)_2 \cdot 6(H_2O)$ Tutton salt was suggested by Silver and Getz [1]. They interpreted the EPR data assuming

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0953-8984/99/224391+10$19.50

that the three Jahn–Teller configurations of rhombically distorted octahedra have different energies and are characterized by the same set of magnetic parameters. The transitions take place between these configurations over the whole temperature range and the observed EPR g-values are Boltzmann weighed averages over these configurations. The validity of this model was confirmed experimentally in other structures [2–5] as well as in the other Tutton [6–8] and Tutton-type salts [9, 10]. A theoretical description of the Jahn–Teller effect in tetragonally deformed octahedra was given by Bir [11] and Friebel *et al* [12], whereas, the case of an orthorhombic distortion was discussed by Yablokov *et al* [13].

A more general approach to the problem of the Jahn–Teller effect in Tutton salts has been proposed by Riley *et al* [14], who developed a model of the energy states and vibronic wavefunctions of a six-coordinate complex under the influence of both Jahn–Teller effect and lattice strain interactions. In this model the observed temperature dependence of g_y and g_z is ascribed to the rapid, on the EPR time scale, relaxation between thermally populated vibronic levels, characterized by different g-factors. This model was applied to interpretation of the EPR data of various Tutton salts [15]. For the $K_2Zn(SO_4)2 \cdot 6(H_2O)$ salt it confirms the main ideas of the Silver–Getz model.

Both models give a reasonably good description of experiments, allowing analysis of energetic and dynamic characteristics of Jahn–Teller centres. However, for Tutton salts other than $K_2Zn(SO_4)_2 \cdot 6(H_2O)$ some difficulties have been found in a theoretical description of the temperature dependences of the principal g-values [15]. They are explained either by thermal expansion of the lattice [6, 16], by the possible cooperative interaction [15, 17–20] or by the strong localization of the complex in the deepest potential well [21].

The other problem is the elongation direction of the $Cu(H_2O)_6^{2+}$ complexes doped into the diamagnetic host lattice. The configurational energy of the doped complex, resulting from three possible elongation directions, and, therefore, the depth of the potential wells are decided by the internal host lattice strains [13, 15]. It is generally accepted that these strains can be estimated from the deformation of the host complex. According to this, the $Cu(H_2O)_6^{2+}$ complex doped into $K_2Zn(SO_4)_2 \cdot 6(H_2O)$ should be elongated along the Zn–O(7) direction [22]. But the EPR data show that the copper complex exhibits elongation along the Zn–O(8) direction [1]. Such a comparison of the EPR and structural data shows the need to consider the mutual influence of the matrix and doped Jahn–Teller complexes.

In this paper we compare the temperature dependences of the principal values of g-factor, measured for Cu^{2+} doped $K_2Zn(SO_4)_2 \cdot 6(H_2O)$ and $(NH_4)_2Zn(SO_4)_2 \cdot 6(H_2O)$ Tutton salts. The results, together with the above mentioned question of the elongation direction, raise a problem of the host lattice influence on the $Cu(H_2O)_6^{2+}$ complex. We postulate that properties of the Jahn–Teller complex are determined also by the further surroundings, and this may result in a temperature modification of the adiabatic potential surface. We discuss possible reasons for this modification and propose an improvement of the Silver–Getz model allowing reproduction of the experimental g_y and g_z temperature dependences.

2. Experimental section

Crystals of $K_2Zn(SO_4)_2 \cdot 6(H_2O)$ and $(NH_4)_2Zn(SO_4)_2 \cdot 6(H_2O)$ were grown from water solutions containing 0.1% of the appropriate copper Tutton salt. However, obtained crystals contain 0.2% and 1.9% of Cu^{2+} ions, respectively.

Single crystals and powder EPR spectra were recorded with a RADIOPAN SE/X-2547 spectrometer with 100 kHz magnetic modulation, in the temperature range of 4.2–340 K using an Oxford ESR 900 flowing helium cryostat.

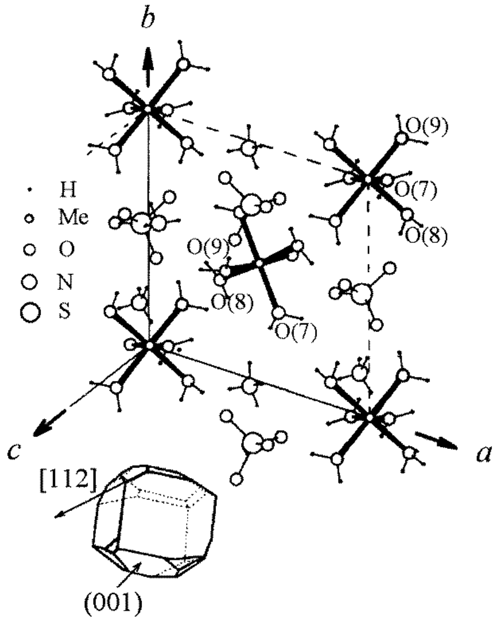

Figure 1. A partial projection of the ammonium Tutton salt structure along the [112] direction. The edge parallel to this direction is indicated in the drawing of the crystal habit. The Me–O(7) coordination bond lies almost exactly in the projected plane, whereas Me–O(8) and Me–O(9) of the other complex are only slightly inclined to this plane.

The temperature dependences of the principal g-values were measured along the three directions in the crystal plane perpendicular to the [112] direction. The normal to this plane is nearly perpendicular to the Me–O(7) bond of the one of two complexes in the unit cell. The Me–O(8) and Me–O(9) bonds of the second complex are slightly inclined (about 15°) to the plane (figure 1). The g-values measured in these directions are very close to the principal values obtained from the g-tensor diagonalization, and allow a very precise measurement of the g-factor temperature dependences. Moreover, by an angular variation of EPR spectra in this crystal plane we may easily distinguish between the two possible directions of the $Cu(H_2O)_6^{2+}$ elongation.

3. Results

The temperature dependences of the principal g-tensor values, measured for single crystals of $K_2Zn(SO_4)_2 \cdot 6(H_2O)$:0.2% Cu^{2+} and $(NH_4)_2Zn(SO_4)_2 \cdot 6(H_2O)$:1.9% Cu^{2+}, are presented in figures 2(a) and 3(a). A comparison shows that the difference between the low temperature values of g_x and g_y is larger in the potassium salt than in the ammonium one. This means that the rhombicity of the g-tensor in the first case is higher. In the ammonium salt, the low temperature g-factors are practically the same as for the copper analogue [6, 23]. But for the potassium compound the significant differences of g-factors are observed for the concentrated and diluted compounds [6, 23]. There are also significant differences between the temperature dependences of the principal g-factor in both salts. In the potassium crystal, the g-factor averaging starts at low temperatures and the dependences are somewhat concave. For the ammonium crystal, averaging of g-factors is observed above 100 K and the temperature dependences are rather convex.

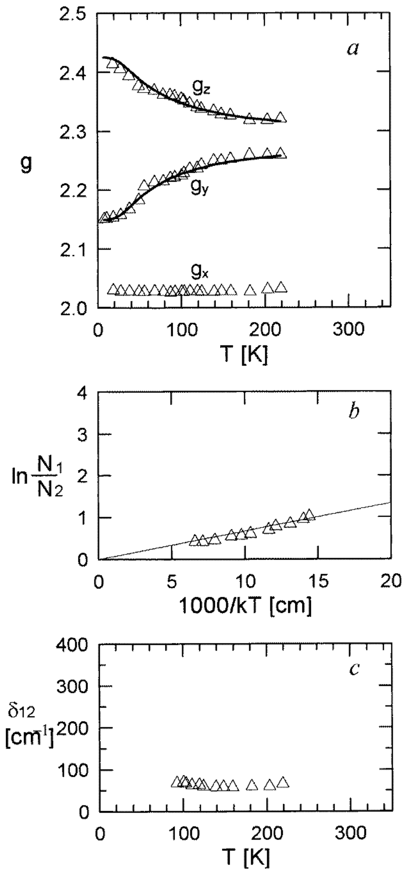

Figure 2. (a) The temperature dependences of the principal values of g-factor, (b) $\ln(N_1/N_2)$ versus $1000/kT$ and (c) $\delta_{12}(T)$ for $K_2Zn(SO_4)_2 \cdot 6(H_2O)$:$Cu^{2+}$. Symbols represent the experimental data, and the solid lines represent g_y- and g_z-fits obtained for $\delta_{12} = 68$ cm^{-1}.

The energetic levels of the $Cu(H_2O)_6^{2+}$ Jahn–Teller complex can be found from the vibrational Hamiltonian:

$$H_{vib} = H_0 + H_{JT} + H_{ST} \tag{1}$$

where H_0 is a pure vibrational Hamiltonian of undistorted geometry and determines the potential energy surface when no vibronic coupling operates and H_{JT} is a Jahn–Teller Hamiltonian. These two terms give rise to the well known ‘Mexican hat’ shape of the adiabatic potential surface, which warped form results from the nonlinear, second order Jahn–Teller coupling and anharmonic terms of the pure vibrational Hamiltonian. H_{ST} describes the influence of the host lattice strains, resulting in non-equivalence of the three potential wells.

The schematic drawing of an adiabatic potential surface, shown in figure 4, is characterized by the Jahn–Teller radius ρ_0, the stabilization energy E_{JT}, the barrier height 2β between the potential wells and the energy difference δ_{ij} between the lowest states in ith and jth wells. It is generally assumed that for the local Jahn–Teller effect the potential energy surface is temperature independent.

The experimental EPR data may be analysed in terms of the fluxional Silver–Getz [1] model. As the experimental g_x-values are practically not temperature dependent we conclude

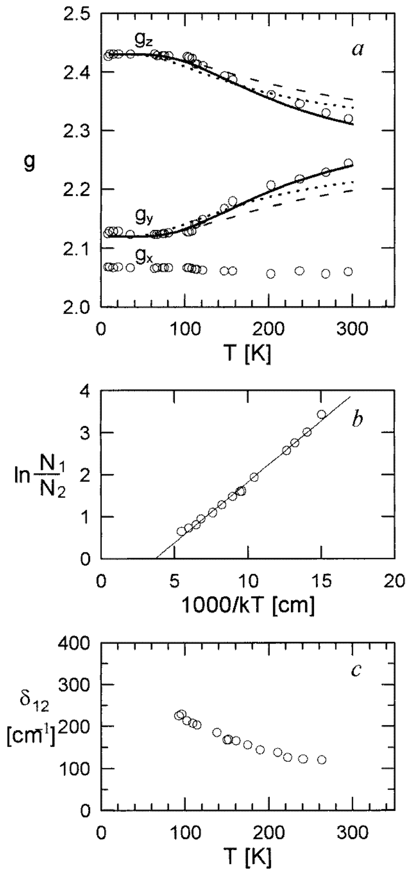

Figure 3. (a) The temperature dependences of the principal values of g-factor, (b) $\ln(N_1/N_2)$ versus $1000/kT$ and (c) $\delta_{12}(T)$ for $(NH_4)_2Zn(SO_4)_2 \cdot 6(H_2O)$:Cu^{2+}. Symbols represent the experimental data, and the solid lines represent g_y- and g_z-fits obtained for the temperature dependent $\delta_{12} = \Delta E^0_{12} - Ak(T - T_B)$, for $\Delta E^0_{12} = 220$ cm^{-1}, $A_1 = 0.98$, $T_B = 100$ K. The dashed lines represents theoretical plots for $\delta_{12} = 230$ cm^{-1} as determined by Petrashen *et al* [6], and the dotted line for $\delta_{12} = 181$ cm^{-1} as was estimated by Riley *et al* [15].

that only the two lowest wells are effectively populated. The observed g_y- and g_z-values may be described by the formula proposed by Silver and Getz [1].

$$g_z(T) = \frac{N_1(T)}{N} g^{(1)}_{max} + \frac{N_2(T)}{N} g^{(2)}_{med}$$

$$g_y(T) = \frac{N_1(T)}{N} g^{(1)}_{med} + \frac{N_2(T)}{N} g^{(2)}_{max} \qquad (2)$$

where $N_1(T)$ and $N_2(T)$ are temperature dependent populations of the first and second well, and $g^{(i)}_{max}$ and $g^{(i)}_{med}$ are the maximum and medium principal g-value the in the ith well. In calculations it is assumed that $g^{(1)}_{med} = g^{(2)}_{med} = g^{(1)}_y$ and $g^{(1)}_{max} = g^{(12)}_{max} = g^{(1)}_z$.

The well populations N_1 and N_2 can be calculated from equation (2), and the δ_{12} may be obtained assuming the Boltzmann distribution:

$$\frac{N_1}{N_2} = \exp \frac{\delta_{12}}{kT}. \qquad (3)$$

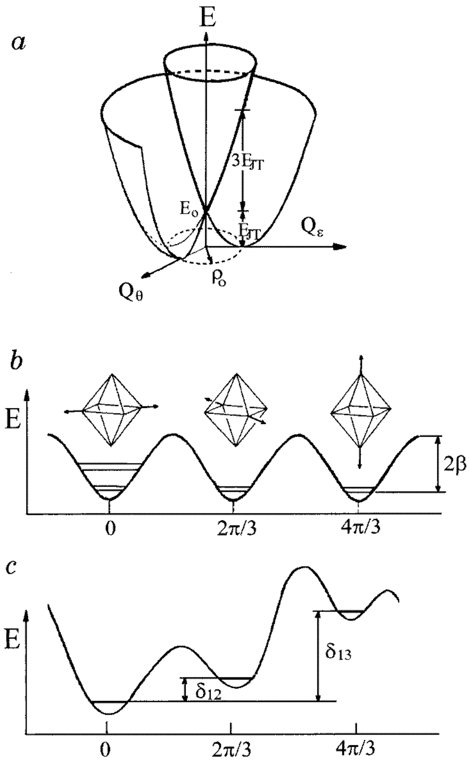

Figure 4. The shape of the adiabatic potential: (a) a Mexican hat, (b) intersection of the surface 'warped' due to the anharmonic and second order terms of vibronic and Jahn–Teller Hamiltonians, (c) the case of an orthorhombic distortion with non-equivalent wells.

For $K_2Zn(SO_4)_2 \cdot 6(H_2O)$ we found $\delta_{12} = 68$ cm^{-1}. This value is closed to the value obtained by Silver and Getz [1]. The theoretical temperature dependence of g_z and g_y with this value of δ_{12} is shown by a solid line in figure 2(a).

Application of the Silver–Getz model to the EPR results obtained for $(NH_4)_2Zn(SO_4)_2 \cdot 6(H_2O)$ leads to surprising results. Theoretical plots of g_y and g_z temperature dependences obtained using $\delta_{12} = 230$ cm^{-1} estimated by Petrashen *et al* [6] (dashed line in figure 3(a)) as well as those obtained for values estimated by Riley *et al* [15] i.e. $\delta_{12} = 181$ cm^{-1} and $g^{(1)}_{max} = 2.427$, $g^{(2)}_{max} = 2.422$, $g^{(1)}_{med} = 2.117$ and $g^{(2)}_{med} = 2.143$, (dotted line in figure 3(a)), do not reproduce details of the experimental dependences. According to equation (3) the plot of $\ln(N_1/N_2)$ should be linearly dependent on $1/kT$ (figure 3(b)), and pass through the origin of the coordinate system, just as it does in the case of potassium compounds (figure 2(b)). However, for the ammonium salt $\ln(N_1/N_2) = \delta_{12}/kT - A$. This means that $N_1 = N_2$ at finite temperature. These results may be also presented in the form of the temperature dependence of δ_{12} shown in figures 2(c) and 3(c). One may notice that for the potassium compounds δ_{12} is practically not dependent on the temperature, whereas a temperature dependence of δ_{12} is found for the ammonium crystals.

4. Discussion

In the existing models of vibronic g-factor averaging in the Jahn–Teller complexes [1, 15], it is assumed that the vibronic complex is not influenced by the crystal lattice. The effect of the lattice is limited to the shape of the adiabatic potential only, which is assumed to be not dependent on temperature. It is commonly accepted in Tutton salts that a doped complex adopts the position of the host complex. The deviation of the host ion octahedron from cubic symmetry is treated as an initial deformation which is enhanced by the Jahn–Teller effect of the doped $Cu(H_2O)_6^{2+}$ complex.

The first hint that these assumptions may not be correct results from the earlier mentioned elongation direction of the $Cu(H_2O)_6^{2+}$ complex doped into the potassium zinc Tutton salt. This direction is different from the longest bond direction of the host $Zn(H_2O)_6^{2+}$ complexes. It is possible that the direction of the largest deformation of metal complexes, both Jahn–Teller and non-Jahn–Teller, is determined by the same forces. We assume that the main role is played by the packing effects of all constituents of the crystal structure, together with the requirement of the minimum energy of the hydrogen bond system between water and sulphate oxygens. The crystal structure of the zinc Tutton salts is built from nearly regular $Zn(H_2O)_6^{2+}$ octahedra, which are slightly deformed due to the interactions with the other constituents of the structure. In the copper compound, the $Cu(H_2O)_6^{2+}$ octahedra are strongly elongated. The Zn–O(7) bond is longest in the zinc lattice whereas the Cu–O(8) is longest in the copper compound. The EPR data show that for $Cu(H_2O)_6^{2+}$ doped into the zinc potassium compound the largest g-factor value is observed along the Cu–O(8) direction indicating that this is the longest bond. This means that doping of the Cu^{2+} ion changes the conditions of the minimum energy in the surrounding structural fragment. The depth of the adiabatic potential wells is determined by the structural internal strains which, in Tutton salts, result from non-equivalent hydrogen bonds between the complex and SO_4 groups. Therefore, we suppose that the modified structural fragment consists of the Jahn–Teller complex and surrounding sulphate groups. The fact that in the ammonium compounds the Me–O(7) direction is preserved as the longest both in the zinc and copper salts draws our attention to a role of the hydrogen bonds between NH_4 and SO_4 groups. There are no direct connections between ammonium groups and metal complex, but the comparison of the ammonium crystal structures with those of the potassium salts shows that in the ammonium compounds the O–H $\cdots$ O hydrogen bonds between the complex and the sulphate groups are modified due to interactions between ammonium and sulphate groups.

All these facts lead to the conclusion that the behaviour of the Jahn–Teller complex in the Tutton salts is determined by both the Jahn–Teller effect of the $Cu(H_2O)_6^{2+}$ unit and its interaction with the surrounding SO_4 groups and monovalent cations. It should be also noticed that such an approach may explain the difference in the δ_{12}-values in these compounds. The δ_{12} is small for the copper complex built into the potassium lattice and elongated in the opposite way than the lattice requires, and quite large in the ammonium compounds, where the lattice requirements are satisfied. Also the rhombicity of the g-tensor of the $Cu(H_2O)_6^{2+}$ complex in the zinc–potassium compound may be a result of the interactions between the guest and host complexes.

Results presented in this paper show that both the Silver–Getz model and a model introduced by Riley *et al* [14] cannot reproduce the temperature dependences of the g-factor in some cases. This is illustrated in figure 3(a), where dashed and dotted lines represent theoretical plots of $g_y(T)$ and $g_z(T)$, obtained from equations (2), for the various values of δ_{12}. Also the plots obtained for the g-factor temperature dependency in the ammonium zinc Tutton salt and presented in the paper of Riley *et al* [15] are the poorest in the series. However, the great number of data confirm the basic assumptions of both these models, thus we suppose that after some modifications the models should describe g-factor averaging effect in all Tutton salts.

There are two potential sources of inaccuracy. The first is an assumption that all the possible configurations and potential wells corresponding to them are characterized by the same set of g-factors. Indeed, the experimental $g(T)$ may be reproduced on the assumption that g-values in the first and second well are not the same. The plot most similar to the experimental dependency was obtained for $\delta_{12} = 230$ cm^{-1} and g-values in the first well $g_{max}^{(1)} = 2.433$, $g_{med}^{(1)} = 2.120$ and in the second well $g_{max}^{(2)} = 2.611$ and $g_{med}^{(2)} = 1.990$. These values in the second well seem to be completely unreasonable. The second source of the error may be an assumption that the form of the adiabatic potential is temperature independent. In our opinion it may be modified by the temperature and, therefore, equation (3) should be written as $N_1/N_2 = \exp(\delta_{12}(T)/kT)$.

There are many factors which may influence the shape of the adiabatic potential of the Jahn–Teller complex making it temperature dependent. As for now, two mechanisms have been proposed to explain the experimentally observed temperature dependence of δ_{12}:

(i) The anisotropy of the thermal lattice expansion in non-cubic crystals [6, 16] modifying the local strains. This effect in some lattices the may be strong, but in others can be compensated by other factors.

(ii) The cooperative interactions between Jahn–Teller complexes [15, 17–20].

The cooperative interactions are expected for the concentrated crystals. In some cases they may be observed even in diluted compounds. There are results for $K_2Zn_{0.8}Cu_{0.2}F_4$ showing an influence of cooperative interactions on the EPR spectra [24]. Interactions between vibronic centres may be observed even in very diluted compounds. It was shown that the formation of the cooperative interaction in copper doped $ZnZrF_6 \cdot 6H_2O$, $ZnSiF_6 \cdot 6H_2O$ and K_2ZnF_4 starts from the pair formation of the neighbour [25] or distant [24] Jahn–Teller complexes and increases in the mixed crystals with the increase of copper concentration [9]. The character of correlations between nearest neighbours is managed by the competing vibronic contributions with different signs [26] and may result in ferrodistortive [24] or antiferrodistortive [27] ordering of coupled complexes. The energy of coupling is rather high. In $ZnSiF_6 \cdot 6H_2O$ it is destroyed by thermal motions above $T \approx 95$ K [27]. Thermal breakdown of such cooperative couplings should lead to changes in the adiabatic potential surface manifesting themselves in a change of the relative energy of the Jahn–Teller complex configurations. However, the number of pairs in diluted crystals is very low and we doubt whether vanishing of their coupling would influence the isolated complexes. It has already been shown [27] for $ZnZrF_6 \cdot 6H_2O$ and $ZnSiF_6 \cdot 6H_2O$ that the temperature dependences of the EPR spectra of both kinds of centre are different and independent one from the other.

Therefore we would like to propose two other possible mechanisms:

(iii) Temperature dependent changes in the elastic interactions between the Jahn–Teller complex and the crystal lattice resulting from the thermal librations of the complex. At low temperature the copper complex has an effectively elongated shape and this configuration corresponds to the minimum energy of the complex and its nearest surroundings but not necessary of the whole lattice. Tension exerted by the lattice on the guest complex may be treated as an internal strain and determines the energy of the adiabatic potential wells. At high temperatures the thermal motion of the complex averages its shape and changes the space occupied by the complex in the lattice. Consequently, the magnitude and the direction of internal strains may be distinct from those at low temperatures. As a result, the adiabatic potential surface may be modified. This mechanism has a universal character, but its magnitude will strongly depend on the crystal lattice properties. It should be more effective in rigid lattices.

(iv) The internal dynamics of the crystal lattice can lead to its instability. In this case the doped complex acts as a paramagnetic probe and its dynamics reflects the crystal lattice properties. We suppose that this phenomenon is observed in the zinc–ammonium Tutton salts. Unfortunately, the temperature dependent structural data set is available for

$(ND_4)_2Cu(SO_4)_2 \cdot 6D_2O$ [18, 29–31] only, which has not been the subject of our EPR studies. This compound is supposed to be strongly influenced by the cooperative Jahn–Teller interactions between $Cu(D2O)_6^{2+}$ complexes [20]. In such an approach the crystal structure of the compound would be determined by the cooperative interactions. But temperature changes of the shape and dynamics of the ammonium groups, which are not bonded to the copper complexes, might be treated as independent. Moreover, despite the cooperative interactions the symmetry and the general structure of all the Tutton salts are the same as in the other Tutton salts. Therefore, the crystal data for the $(ND_4)_2Cu(SO_4)_2 \cdot 6D_2O$, especially those concerning the ammonium groups, provide information which may be valid for all ammonium Tutton salts. Neutron diffraction data show that before the Cu–O(7) and Cu–O(8) start to average, an increase of the longest Cu–O(8) distance is observed, and the shortest Cu–O(9) distance continuously decreases [18]. These effects cannot be explained by the thermal averaging resulting from the Jahn–Teller centre reorientations. As they are observed in a copper crystal there is a temptation to interpret them as a manifestation of the cooperative interaction. But they are accompanied by the changes in the strength of the $N \cdots O$ hydrogen bonds between ammonium and sulphate groups, which weaken considerably with increase of temperature [18]. Some oxygens from SO_4 groups are involved in the hydrogen bonds with both the $Cu(H_2O)_6^{2+}$ octahedra and ammonium groups, forming bifurcated bonds. Weakening of the $N–H \cdots O$ bonds (between ammonium and sulphate groups) results, therefore, in strengthening of the $O–H \cdots O$ bonds (between sulphate groups and complexes). As the weakening of $N–H \cdots O$ hydrogen bonds results from internal dynamics of ammonium groups it can be expected also in diamagnetic crystals. This concept of the ammonium group dynamics influence on the adiabatic potential should be verified by other methods, such as x-ray structural investigations, NMR and Raman spectroscopy of $(NH_4)_2Zn(SO_4)_2 \cdot 6H_2O$.

Factors pointed above are not independent one from the other but may manifest themselves with various magnitudes and can even compensate. The first three are general ones and may be expected in all compounds. The last reason may be expected for the lattices with the dynamics overruled by their definite parts, such as the ammonium groups, possessing their own internal dynamics.

All these factors can introduce some temperature dependent contributions to the adiabatic potential. Therefore, the temperature dependent $\delta_{12}(T)$ may be written in the form:

$$\delta_{12}(T) = \Delta E_{12} + \Delta(T) \qquad (4)$$

where ΔE_{12} represents the energy difference between two lowest wells of the invariant form of the adiabatic potential surface, and $\Delta(T)$ is the contribution from the various factors.

The character of the $\Delta(T)$-dependency cannot be determined on the basis of these results. With the same accuracy as the assumption that δ_{12} for the potassium compound is not dependent on temperature (figure 2(c)) we may assume that as presented in figure 3(c) $\delta_{12}(T)$ decreases linearly. Such an approach demands an additional parameter T_B—the starting temperature of this dependency. Thus, for $T > T_B$ the temperature dependent part of the separation energy may be written as: $\Delta(T) = Ak(T - T_B)$. The theoretical plots of g_y and g_z resulting from this assumption are represented by the solid lines in figure 3(a). It is visible that they reproduce better the experimental data than the other two theoretical plots. It is not perfect yet, but our approximation of $\Delta(T)$ does not pretend to be the best and the only possible one. We want only to show that even such a simplified approach can improve agreement between the experiment and the model. The temperature dependency of Δ would be described in a more complicated way, taking into account the changes of the hydrogen bond strength. We can only speculate that an analytic description of this dependency (if possible) will be represented by a function weakly dependent on temperature below T_B and linearly approximated above.

5. Conclusions

From the above discussion we may draw the following conclusions:

- The analysis of the vibronic effects in Tutton salts should concern not only the Jahn–Teller $Cu(H_2O)_6^{2+}$ complex but also the hydrogen bonded neighbouring SO_4 groups and in the case of ammonium salts also the NH_4 groups.
- The temperature dependency of the energy interval between the two lowest wells of the adiabatic potential surface should be taken into account when the Jahn–Teller complexes in slightly distorted positions are studied. The analysis of reasons for such dependency yields important information about interactions of the Jahn–Teller complexes with both the nearest crystal lattice constituents and the whole crystal lattice.

Acknowledgments

We wish to thank Professors S K Hoffmann and Yu V Yablokov for most valuable discussion. This work was supported by the Scientific Research Committee under grant KBN-2-PO3B-122-14 and the Russian Foundation for Basic Research (grant 98-02-16588).

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