T. 85, № 1

V. 85, N 1

JANUARY—FEBRUARY 2018

## EVALUATION OF SPIN HAMILTONIAN PARAMETERS AND LOCAL STRUCTURE OF Cu<sup>2+</sup> DOPED ION IN $xK_2SO_4$ -(50 – x)Na<sub>2</sub>SO<sub>4</sub>-50ZnSO<sub>4</sub> GLASSES WITH VARIOUS K<sub>2</sub>SO<sub>4</sub> CONCENTRATIONS \*\*

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The spin Hamiltonian parameters (SHPs), i.e., g factors and hyperfine structure constants, and local structures are theoretically studied by analyzing tetragonally elongated  $3d^9$  clusters for  $Cu^{2+}$  in  $xK_2SO_4$ - $(50 - x)Na_2SO_4$ - $50ZnSO_4$  glasses with various  $K_2SO_4$  concentrations x. The concentration dependences of the SHPs are attributed to the parabolic decreases of the cubic field parameter Dq, orbital reduction factor k, relative tetragonal elongation ratio  $\tau$ , and core polarization constant  $\kappa$  with x. The  $[CuO_6]^{10-}$  clusters are found to undergo significant elongations of about 17% due to the Jahn-Teller effect. The calculated cubic field splittings and the SHPs at various concentrations agree well with the experimental data. **Keywords:** electron paramagnetic resonance, defect structures,  $Cu^{2+}$ ,  $K_2SO_4 \cdot Na_2SO_4 \cdot ZnSO_4$  glasses.

## ОЦЕНКА ПАРАМЕТРОВ СПИН-ГАМИЛЬТОНИАНА И ЛОКАЛЬНАЯ СТРУКТУРА ИОНОВ Cu<sup>2+</sup>, ДОПИРОВАННЫХ В СТЕКЛА *x*K<sub>2</sub>SO<sub>4</sub>-(50 – *x*)Na<sub>2</sub>SO<sub>4</sub>-50ZnSO<sub>4</sub> С РАЗЛИЧНЫМИ КОНЦЕНТРАЦИЯМИ K<sub>2</sub>SO<sub>4</sub>

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УДК 543.429.22

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(Поступила 19 мая 2016)

Теоретически изучены параметры спин-гамильтониана и локальные структуры удлиненных  $3d^9$  кластеров ионов  $Cu^{2+}$  в стеклах  $xK_2SO_4$ - $(50 - x)Na_2SO_4$ - $50ZnSO_4$  с различными концентрациями  $K_2SO_4$ . Концентрационные зависимости параметров спин-гамильтониана обусловлены уменьшением по параболическому закону кубического полевого параметра Dq, фактора редукции орбитального момента k, относительного тетрагонального растяжения  $\tau$  и поляризационной константы k с ростом x. Найдено, что группы  $[CuO_6]^{10-}$  подвергаются значительным удлинениям (на ~17 %) из-за эффекта Яна–Теллера. Рассчитанные кубические полевые расщепления и параметры спин-гамильтониана при различных концентрациях хорошо согласуются с экспериментальными данными.

**Ключевые слова:** электронный парамагнитный резонанс, дефект структуры,  $Cu^{2+}$ , стекла  $K_2SO_4 \cdot Na_2SO_4$  ZnSO<sub>4</sub>.

**Introduction.** Sulfate glasses, e.g.,  $K_2SO_4$ -Na<sub>2</sub>SO<sub>4</sub>-ZnSO<sub>4</sub> (KNZ) glasses, are an important subject in the investigations of physical and magnetic resonance properties when they are doped with transition-metal ions [1–3]. These ions significantly modify the optical properties and stipulate the exhibition of electron paramagnetic resonance (EPR) arising from the unfilled 3*d* energy levels [4–8]. Among the many 3*d* transition-metal ions, divalent copper is one of the most efficient dopants due to EPR signals recordable at room temperature. For example, the optical absorption and EPR experiments were employed for 1 mol.% Cu<sup>2+</sup>

<sup>&</sup>lt;sup>\*\*</sup> Full text is published in JAS V. 85, No. 1 (http://springer.com/10812) and in electronic version of ZhPS V. 85, No. 1 (http://www.elibrary.ru/title\_about.asp?id=7318; sales@elibrary.ru).

(in the form of CuSO<sub>4</sub> · 5H<sub>2</sub>O) doped  $xK_2SO_4$ -(50 – x)Na<sub>2</sub>SO<sub>4</sub>-50ZnSO<sub>4</sub> (KNZ) glasses [9]. The *d*-*d* transition bands and the spin Hamiltonian parameters (SHPs) were measured for various K<sub>2</sub>SO<sub>4</sub> concentrations: x = 10, 25, 30, and 40 mol.% (corresponding to the samples  $R_1, R_2, R_3$ , and  $R_4$ , respectively) [9]. In detail, both the *d*-*d* optical transitions and the parallel component of the hyperfine structure constants  $A_{\parallel}$  exhibit approximately parabolic decreases with x, while the decreases of the parallel ( $g_{\parallel}$ ) and perpendicular ( $g_{\perp}$ ) g factors are insignificant [0]. These EPP signals were tontatively assigned to the tatragonally elongated  $Cu^{2^+}$ 

factors are insignificant [9]. These EPR signals were tentatively assigned to the tetragonally elongated  $Cu^{2+}$  centers of KNZ glasses, with various molecular orbital coefficients (i.e., adjustable  $\beta_1^2$  as well as fixed  $\alpha^2 \approx 0.77$  and  $\beta^2 \approx 1$ ) obtained by fitting the two measured g factors based on the simple g formulas [9]. Later on, the theoretical analysis was performed on the SHPs and the local structure for  $Cu^{2+}$  in KNZ glasses [10]. However, the above treatments dealt with the averages of the SHPs for different concentrations, while the concentration dependences of the SHPs and local structure were not quantitatively examined.

As compared with conventional borate and silicate glasses, sulfate glasses have only been scarcely studied. Thus, the investigation of the optical and EPR properties as well as their concentration dependences for KNZ glasses with Cu<sup>2+</sup> dopants would reveal important impurity behaviors in these systems. Moreover, the information on the local structures for Cu<sup>2+</sup> impurity can be helpful to understand the properties of these and any other relevant glasses containing copper. So, the SHPs and the local structure for Cu<sup>2+</sup> in KNZ glasses at various K<sub>2</sub>SO<sub>4</sub> concentrations x are worth further study. In this article, the EPR spectra and the local structure as well as their concentration dependences for Cu<sup>2+</sup> doped KNZ glasses are theoretically investigated from the high order perturbation calculations of the SHPs for a tetragonally elongated octahedral 3d<sup>9</sup> cluster. In particular, the parabolic relationships with concentration x are proposed for the relevant quantities (i.e., cubic field parameter Dq, orbital reduction factor k, relative tetragonal elongation ratio  $\tau$ , and core polarization constant  $\kappa$ ) so as to illustrate the variations of the measured d-d optical transitions and the SHPs. The properties of the SHPs and the local structure as well as the microscopic mechanisms of the parabolic relationships between the relevant quantities and concentration x are discussed.

**Calculations.** The Cu<sup>2+</sup> impurity (in the form of CuSO<sub>4</sub> · 5H<sub>2</sub>O) in KNZ glasses is located at appropriate oxygen octahedral sites of the three-dimensional network [9]. As regards a Cu<sup>2+</sup> (3d<sup>9</sup>) ion in an octahedron, the two-fold orbital degenerated  ${}^{2}E_{g}$  level is the ground state [11, 12], and thus the [CuO<sub>6</sub>]<sup>10-</sup> cluster can undergo the Jahn–Teller effect via the vibrational interactions [13, 14]. For example, the two Cu<sup>2+</sup>–O<sup>2-</sup> bonds can exhibit the relative elongation along the  $C_{4}$  axis and lead to a local tetragonal ( $D_{4h}$ ) point symmetry, yielding a tetragonally elongated octahedron. For convenience, the local structure of Cu<sup>2+</sup> in KNZ glasses can be described as the relative tetragonal elongation ratio  $\tau$ . Consequently, the original two-fold orbital degeneracy of the cubic ground state  ${}^{2}E_{g}$  is cancelled and brings forward two orbital singlets  ${}^{2}A_{1g}(\theta)$  and  ${}^{2}B_{1g}(\varepsilon)$ , with the latter lying lowest. On the other hand, the original excited orbital triplet  ${}^{2}T_{2g}$  may split into an orbital singlet  ${}^{2}B_{2g}(\zeta)$  and an orbital doublet  ${}^{2}E_{g}(\xi, \eta)$  [11, 12]. The perturbation formulas of the SHPs for a tetragonally elongated octahedral  $3d^{9}$  cluster can be written as [15, 16]

$$g_{\parallel} = g_{s} + 8k\zeta/E_{1} + k\zeta^{2}/E_{2}^{2} + 4k\zeta^{2}/E_{1}E_{2} - g_{s}\zeta^{2}[1/E_{1}^{2} - 1/(2E_{2}^{2})] + k\zeta^{3}(4/E_{1} - 1/E_{2})/E_{2}^{2} - - 2k\zeta^{3}(2/E_{1}E_{2} - 1/E_{2}^{2})/E_{1} + g_{s}\zeta^{3}[1/(E_{1}E_{2}^{2}) - 1/(2E_{2}^{3})],$$

$$g_{\perp} = g_{s} + 2k\zeta/E_{2} - 4k\zeta^{2}/(E_{1}E_{2}) + k\zeta^{2}[2/(E_{1}E_{2}) - 1/E_{2}^{2}] + 2g_{s}\zeta^{2}/E_{1}^{2} + k\zeta^{3}(2/E_{1} - 1/E_{2}) \times \times (1/E_{2} + 2/E_{1})/2E_{2} - k\zeta^{3}(1/E_{1}^{2} - 1/E_{1}E_{2} + 1/E_{2}^{2})/2E_{2},$$

$$A_{\parallel} = P [-\kappa - 4k/7 + (g_{\parallel} - g_{s}) + 3(g_{\perp} - g_{s})/7] ,$$

$$A_{\perp} = P[-\kappa + 2k/7 + 11(g_{\perp} - g_{s})/14].$$
(1)

Here  $g_s \approx 2.0023$  is the pure spin g value. Equivalent to covalency factor N, k is the orbital reduction factor that characterizes the covalency of the systems,  $\zeta$  and P are the spin-orbit coupling coefficient and the dipolar hyperfine structure parameter of the 3d<sup>9</sup> ion in the glasses, respectively,  $\kappa$  is the core polarization constant, which is the characteristic of the isotropic Fermi contact interactions arising from the central ion 3d-3s (4s) orbital admixtures, and  $E_1$  and  $E_2$  are the energy separations between the excited  ${}^2B_{2g}$  and  ${}^2E_g$  and the ground  ${}^2B_{1g}$  states in tetragonal crystal-fields, respectively. They can be expressed from the energy matrices for a tetragonal  $3d^9$  cluster with the cubic field parameter Dq and the tetragonal field parameters Dsand Dt [15, 16]:

$$E_1 \approx 10Dq,$$
  

$$E_2 \approx 10Dq - 3Ds + 5Dt.$$
 (2)

As for the  $[CuO_6]^{10-}$  clusters, due to the Jahn–Teller elongation distortions the impurity-ligand distances parallel and perpendicular to the C<sub>4</sub> axis are expressed as  $R_{\parallel} \approx R(1 + 2\tau)$  and  $R_{\perp} \approx R(1 - \tau)$ , where *R* is the reference impurity-ligand distance. Based on the superposition model [17–19] and the local geometry, the tetragonal field parameters are determined as follows:

$$Ds \approx (4/7) \,\overline{A}_2(R) \,[(1-\tau)^{-t_2} - (1+2\tau)^{-t_2}],$$
  
$$Dt \approx (16/21) \,\overline{A}_4(R) \,[(1-\tau)^{-t_4} - (1+2\tau)^{-t_4}].$$
(3)

Here  $\overline{A}_2(R)$  and  $\overline{A}_4(R)$  are the intrinsic parameters, and  $t_2 \approx 3$  and  $t_4 \approx 5$  [17] are the power-law exponents. For the octahedral 3d<sup>n</sup> clusters, the relationships  $\overline{A}_4(R) \approx (3/4)Dq$  and  $\overline{A}_2(R) \approx 12 \overline{A}_4(R)$  [20–22] have proved reliable in many systems and are suitably adopted here. Thus, the local structure of the impurity Cu<sup>2+</sup> can be quantitatively related to the tetragonal field parameters and hence to the SHPs of the systems, especially anisotropy  $\Delta g = g_{\parallel} - g_{\perp}$ .

According to the measured d-d optical transitions for  $Cu^{2+}$  in KNZ glasses [9], the cubic field splitting  $E_1$  or the cubic field parameter Dq shows the approximately parabolic decrease with increasing the K<sub>2</sub>SO<sub>4</sub> concentration x. This can be suitably described as the modifications of the structures and properties of the glasses by means of the mixed alkali effect [23]. This may modify the coordination number of B<sup>3+</sup> in the B<sub>2</sub>O<sub>3</sub> networks, the local crystal-field strength arising from the nearest neighbor oxygen ligands and the electronic cloud distributions around Cu<sup>2+</sup>, and hence the Cu<sup>2+</sup>–O<sup>2-</sup> electron cloud admixtures and copper 3d-3s (4s) orbital admixtures. Considering the decrease of the denominator  $E_1$  in Eq. (1), the slightly decreasing g factors [9] with x may require the decreases of both the orbital reduction factor k and the spin-orbit coupling coefficient  $\zeta$  in the numerators. This can be illustrated by the decreasing averages  $\approx 0.85$ , 0.84, 0.84, and 0.83 of the adjusted molecular orbital coefficient  $\beta_1^2$  and fixed  $\alpha^2 \approx 0.77$  by fitting the experimental SHPs [9]. So, the concentration dependences of the spectral parameters Dq and k are suitably expressed as parabolic functions of x:

$$Dq \approx Dq_0(1 + a_1 x^2), k \approx N_0(1 + a_1 x^2).$$
(4)

Here the adjustable proportionality coefficient  $a_1$  is usually determined by fitting the concentration dependences of the experimental d-d optical spectra and SHPs. In view of the slightly decreasing  $E_1$  and g factors [9],  $a_1$  is expected to be negative. The reference values  $Dq_0 \approx 1191 \text{ cm}^{-1}$  and  $k_0 \approx 0.846$  are obtained from the optical spectral measurements for Cu<sup>2+</sup> in the oxides [11, 24].

The spin-orbit coupling coefficient  $\zeta$  is calculated from the free-ion value  $\zeta_0 \approx 829 \text{ cm}^{-1}$  [25] and the corresponding k at various x. Since the variation of the K<sub>2</sub>SO<sub>4</sub> concentration can influence the Cu<sup>2+</sup>–O<sup>2-</sup> bonding characterized by the parabolic-type modifications of Dq and k, the degree of the Jahn–Teller distortion and hence the relative tetragonal elongation ratio can be similarly modified. Therefore, the concentration dependence of the relative elongation ratio can be determined with the reference (initial) value  $\tau_0$ :

$$\mathbf{t} \approx \mathbf{\tau}_0 (1 + a_1 x^2). \tag{5}$$

Inputting the relevant values into Eq. (1) and fitting the theoretical g factors to the experimental data for various concentrations, one can obtain the optimal reference elongation ratio and proportionality coefficient:  $\tau_0 \approx 17.4\%$ ,  $a_1 \approx -0.075$ . The corresponding *d*-*d* optical transitions  $E_1$ , orbital reduction factors *k*, and relative elongation ratios  $\tau$  for various concentrations x = 10, 25, 30, and 40 mol.% are shown in Table 1, and the concentration dependences of the *g* factors are compared with the experimental data in Table 2.

TABLE 1. The Cubic Field Splittings  $E_1$  (cm<sup>-1</sup>), Orbital Reduction Factors k, Relative Tetragonal Elongation ratios  $\tau$  and Core Polarization Constants  $\kappa$  for Cu<sup>2+</sup> in KNZ Glasses with Various K<sub>2</sub>SO<sub>4</sub> Concentrations x (10  $\leq x \leq 40$  mol.%)

<i>x</i> , mol.%	$E_1^{\text{ calc}}$	$E_1^{\exp[9]}$	k	τ, %	к
10	11901	11902	0.845	17.4	0.210
25	11854	11845	0.842	17.4	0.200
30	11830	11817	0.840	17.3	0.194
40	11767	11775	0.836	17.2	0.181

For the hyperfine structure constants, the dipolar hyperfine structure parameter *P* is obtained from the free-ion value  $P_0 \approx 402 \times 10^{-4}$  cm<sup>-1</sup> for Cu<sup>2+</sup> [26] by multiplying *k*. The variation of *x* would modify the distribution of the electronic cloud around the impurity Cu<sup>2+</sup>, and thus the isotropic Cu<sup>2+</sup> 3*d*–3*s* (4*s*) orbital admixtures and the core polarization constant  $\kappa$  can be modulated. As the approximately parabolic decrease of  $A_{\parallel}$  can indicate the similarly parabolic decrease of  $\kappa$  with *x*, the core polarization constant is expressed as a parabolic-type decreasing function of *x* with another coefficient *a*<sub>2</sub>:

$$\kappa \approx \kappa_0 (1 + a_2 x^2). \tag{6}$$

Here the reference value  $\kappa_0$  can be approximately obtained from the empirical relationship  $\kappa_0 \approx -2\chi/(3\langle r^{-3}\rangle)$ , where  $\chi$  is characteristic of the density of unpaired spins at the nucleus of the central ion, and  $\langle r^{-3}\rangle$  is the expectation value of the inverse cube of the impurity 3d radial wave function [26]. Using the values  $\langle r^{-3}\rangle \approx 8.252$  a.u. [11] and  $\chi \approx 2.62$  a.u. [26] for Cu<sup>2+</sup> in some oxides, one can obtain  $\kappa_0 \approx 0.212$ , which is close to that ( $\approx 0.26-0.30$  [27]) for divalent copper in Tutton's salt and can be considered as suitable. Inserting these values into the formulas of the hyperfine structure constants and matching the calculated concentration dependence of  $A_{\parallel}$  to the observed result [9], we have  $a_2 \approx -0.9$ . The corresponding hyperfine structure constants are given in Table 2.

TABLE 2. The Concentration Dependences of g Factors and Hyperfine Structure Constants  $(10^{-4} \text{ cm}^{-1})$  for Cu<sup>2+</sup> in KNZ Glasses

<i>x</i> , mol.%	$g_{\parallel}^{ m \ calc}$	$g_{\parallel}^{\exp[9]}$	$g_{\perp}^{\mathrm{cal}}$	$g_{\perp}^{\exp[9]}$	$A_{\parallel}^{\ \  ext{cal b}}$	$A_{\parallel}^{\exp[9]}$	$A_{\perp}^{\rm \ cal \ b}$	$A_{\perp}^{\exp[9]}$
10	2.399	2.40(2)	2.054	2.06(2)	-91.81	-91.35(100)	24.22	-
25	2.398	2.39(2)	2.054	2.05(2)	-88.61	-88.74(100)	27.49	-
30	2.397	2.39(2)	2.054	2.05(2)	-86.94	-85.62(100)	29.20	-
40	2.395	2.39(2)	2.054	2.04(2)	-82.72	-83.46(100)	33.49	-

**Discussion.** Table 2 reveals that the theoretical d-d optical transitions  $E_1$  and SHPs as well as their concentration dependences based on the represented calculations are in good agreement with the experimental data. So, the measured optical and EPR spectra are reasonably explained for KNZ:Cu<sup>2+</sup> glasses. Information on the local structures in the vicinity of copper dopants is obtained for various K<sub>2</sub>SO<sub>4</sub> concentrations in this paper. There are several points that can be discussed here.

As for the properties of the SHPs for  $Cu^{2^+}$  in KNZ glasses, the low  $g_{\perp}$  is ascribed to the large tetragonal elongation ratios  $\tau \approx 17\%$ , which induce large negative *Ds* and hence a large denominator  $E_2$  in the  $g_{\perp}$  formula. Interestingly, the large tetragonal elongation distortions of the studied systems can account for the large ratios  $g_{\parallel}/A_{\parallel} \approx 274 \ 1/cm^{-1}$  [9], which suitably reflect significant tetragonal distortions for  $3d^9$  ions in the octahedra [28]. Similar large tetragonal elongation ratios ( $\approx 19\%$  [29] or 18% [30] and 12% [31]) were also reported for  $Cu^{2^+}$  in alkali lead tetraborate and KRbB<sub>4</sub>O<sub>7</sub> glasses, corresponding to analogous low  $g_{\perp}$  ( $\approx 2.032-2.041$  [32] and 2.059 [33]), respectively. Unlikely,  $Cu^{2^+}$  in  $xMgO \cdot (30 - x) \cdot Na_2O \cdot 69B_2O_3$  ( $5 \le x \le 17 \text{ mol.}\%$ ) glasses exhibits higher  $g_{\perp}$  ( $\approx 2.09$  [34]) and much smaller relative elongation ratios ( $\approx 0.4\%$  [35]), despite similar parabolic relationships of Dq and the SHPs with concentration x [34]. The anisotropy of the EPR spectra for KNZ: $Cu^{2^+}$  glasses can be described as the positive anisotropies  $\Delta g = g_{\parallel} - g_{\perp}$  of the lowest  ${}^2B_{1g}$  state for a tetragonally elongated octahedral  $3d^9$  cluster owing to the Jahn–Teller effect. On the other hand, the signs of hyperfine structure constants and the magnitudes of  $A_{\perp}$  were not determined experimentally in [9]. Based on the present calculations and the relevant measured results [26] for  $Cu^{2^+}$  in tetragonally elongated octahedra, one can find that  $A_{\parallel} < 0$  and  $A_{\perp} > 0$  for  $Cu^{2^+}$  in KNZ glasses here. Of course, the theoretical values of  $A_{\perp}$  in this paper need verification with further experimental measurements, even though the positive anisotropy  $\Delta A = |A_{\parallel}| - |A_{\perp}| > 0$  for the calculated hyperfine structure constants in Table 2 exhibits the same sign as  $\Delta g$  and can be regarded as suitable.

The calculated d-d optical transitions  $E_1$  and the SHPs for various concentrations x based on the SHPs formulas in Eq. (1) and the parabolic relationships of the relevant quantities in Eqs. (4), (5), and (7) (with only two adjustable coefficients  $a_1$  and  $a_2$ ) show good agreement with the measured values. So, the represented calculations for the concentration dependences of  $E_1$  and the SHPs seem superior to the previous treatments of the g factors based on the simple g formulas with the adjustable molecular orbital coefficients  $\beta_1^2$  as well

as the fixed  $\alpha^2 \approx 0.77$  and  $\beta^2 \approx 1$  [9]. Numerically, the above parabolic relationships of the relevant quantities can be illustrated by Eq. (1). The influence of the parabolic decrease of Dq (in the denominator  $E_1$  of  $g_{\parallel}$  formula) would be largely offset by the parabolic decrease of k (in both the numerators k and  $\zeta$ ) and bring forward nearly unchanging but slightly declining  $g_{\parallel}$  in view of large experimental uncertainties. As regards  $g_{\perp}$ , the influences of the decreases in the numerators k and  $\zeta$  can be nearly canceled by the decrease in the denominator  $E_2$  due to the decrease of Dq (and also Ds) and thus lead to an almost constant but slightly decreasing  $g_{\perp}$  with x. With decrease in P due to decreasing k, the parabolic decrease of  $\kappa$  (relevant to the dominant isotropic parts of hyperfine structure constants) also accounts for the decreasing magnitude of  $A_{\parallel}$ .

The concentration dependences of the *d*-*d* transition optical and EPR spectra as well as the relevant quantities are ascribed to the mixed alkali effect [23]. The variations of the K<sub>2</sub>SO<sub>4</sub> concentration can modify the boron-oxygen network by converting some BO<sub>3</sub> units into BO<sub>4</sub> ones [9] and the local environments (e.g., the crystal-field strength arising from the nearest oxygen ligands,  $Cu^{2+}-O^{2-}$  orbital admixtures and copper 3d-3s (4s) orbital admixtures). Firstly, the increase in x can induce decreases in the crystal-field strength and the orbital reduction factor, as illustrated by the parabolic relationships of Dq and k in Eq. (4). Secondly, the decrease in the crystal-field strength is associated with the decrease of the vibration interactions of  $Cu^{2+}-O^{2-}$  bonds and hence the parabolic decreasing  $\tau$  in Eq. (5). Finally, the increase in x can lead to decrease in the isotropic  $Cu^{2+} 3d-3s$  (4s) orbital admixtures and hence the parabolic admixtures and hence the parabolically decreasing core polarization constant  $\kappa$  in Eq. (7). Thus, the concentration dependences of the above spectral and local structural properties can be explained as being due to the impurity  $Cu^{2+}$  in KNZ glasses.

**Conclusion.** The SHPs and the local structure are theoretically investigated for  $Cu^{2+}$  in KNZ glasses with various  $K_2SO_4$  concentrations. The concentration dependences of the SHPs are attributed to the parabolic decreases of the cubic field parameter Dq, orbital reduction factor k, relative tetragonal elongation ratio  $\tau$ , and core polarization constant  $\kappa$  with x. The  $[CuO_6]^{10-}$  clusters are subject to the significant elongations of about 17% owing to the Jahn–Teller effect. The microscopic mechanisms of the above concentration dependences for the relevant quantities are illustrated by the modifications of the local crystal fields and the electron cloud distribution around the impurity  $Cu^{2+}$  due to the mixed alkali effect.

Acknowledgment. This work was financially supported by the Sichuan Province Academic and Technical Leaders Support Fund [Y02028023601032] and the Fundamental Research Funds for the Central Universities [ZYGX2014J136].

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