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Cite as: AIP Conference Proceedings **2313**, 030071 (2020); https://doi.org/10.1063/5.0032430

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Adiabatic Potential Energy Surface of the Jahn-Teller Complexes in SrF_2:Cr^{2+} Crystal

M. N. Sarychev[1], W. A. L. Hosseny[1, 2], A. S. Bondarevskaya[1],
G. S. Shakurov[3], V. A. Ulanov[4], V. T. Surikov[5], I. V. Zhevstovskikh[1, 6],
N. S. Averkiev[7] and V. V. Gudkov[1, a)]

[1]*Institute of Physics and Technology, Ural Federal University, Ekaterinburg, Russia*
[2]*Department of Physics, Faculty of Science, Benha University, Benha, Egypt*
[3]*Kazan E.K. Zavoisky Physical-Technical Institute of the Russian Academy of Sciences, Kazan, Russia*
[4]*Kazan State Power Engineering University, Kazan, Russia*
[5]*Institute of Solid State Chemistry, Ural Branch of Russian Academy of Sciences, Ekaterinburg, Russia*
[6]*M.N. Miheev Institute of Metal Physics, Ural Branch of the Russian Academy of Sciences, Ekaterinburg, Russia*
[7]*A.F. Ioffe Physical Technical Institute of the Russian Academy of Sciences, St. Petersburg, Russia*

a)Corresponding author: v.v.gudkov@urfu.ru

Abstract. Temperature dependence of attenuation of ultrasonic transverse normal modes, polarized propagating along the [110] crystallographic axis in SrF_2 crystal doped with Cr^{2+} ions was measured at the frequency of 52–162 MHz in the temperature range of 4–180 K. The results indicated the $T_{2g} \otimes \left(e_g + t_{2g}\right)$ Jahn-Teller effect problem with important impact of quadratic term in the vibronic Hamiltonian. The value of activation energy was derived from the temperature dependence of relaxation time of the sub-system of the Jahn-Teller complexes simulated with account of three mechanisms of relaxation: thermal activation, tunnelling through the potential energy barrier, and two-phonons mechanism similar to Raman scattering. The extrema points of adiabatic potential energy surface: six orthorhombic global minima, three tetragonal and four trigonal saddle points were calculated in 5-dimensional space of symmetrized coordinates.

INTRODUCTION

Significant properties of the Jahn-Teller effect (JTE) (see, e.g., [1]) was obtained by means of ultrasonic techniques recently in doped crystals. Important specificity of the JTE manifestation in such experiments is relaxation origin of the anomalies in dispersion and energy dissipation of ultrasonic waves caused by the JT subsystem [2]. Ultrasonic investigations make it possible to determine symmetry properties of the extrema points of the adiabatic potential energy surface (APES), their position in the space of symmetrized coordinates, and the magnitudes of the parameters entering the vibronic Hamiltonian such as linear and quadratic vibronic coupling constants.

In the fluorite type crystals doped with 3*d* ions, the APES was studied by the ultrasonic technique in SrF_2:Cr^{2+} [3, 4]. However, in [3], incorrect expressions were used for calculating the isothermal moduli those resulted in erroneous values of the vibronic coupling constants and the APES parameters, whereas in [4], the incorrect interpretation of the mechanisms of relaxation resulted in erroneous magnitudes of activation energy and, as well, of the APES parameters.

The VII International Young Researchers' Conference – Physics, Technology, Innovations (PTI-2020)
AIP Conf. Proc. 2313, 030071-1–030071-7; https://doi.org/10.1063/5.0032430
Published by AIP Publishing. 978-0-7354-4053-1/$30.00

In the present paper, we introduce the procedure of determination of the activation energy based on simulation of the temperature dependence of the relaxation time with account of three mechanisms. This procedure makes it possible to calculate the parameters of the APES more accurately.

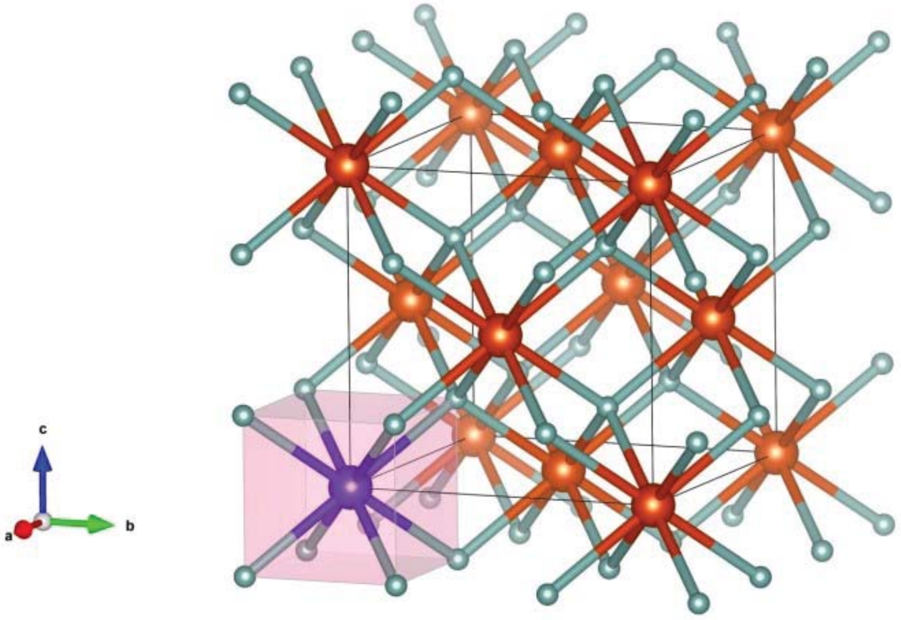

FIGURE 1. The SrF_2 crystal with fluorite structure. The Cr^{+2} ion (violet color) substitutes strontium (orange) ions in the lattice site. It is surrounded by eight fluorine (green) ions in the corners of the cube. The CrF_8 JT complex is outlined by pink

EXPERMENTAL METHOD AND RESULTS

The single crystals of SrF_2:Cr^{2+} were grown in Kazan E.K. Zavoisky Physical-Technical Institute of the RAS by Czochralski method in a helium atmosphere. Concentration of the impurities $n_{Cr} = 1.6 \cdot 10^{19}$ cm^{-3} was determined in the Institute of Solid State Chemistry, Ural Branch of the RAS.

Ultrasonic experiments were done at the Ural Federal University. Ultrasonic waves were generated and detected by $LiNbO_3$ piezoelectric transducers at the frequency of 52–162 MHz. Ultrasonic waves propagated along the [110] crystallographic axis. The transverse normal modes associated with this direction were investigated: polarized along the [001] axis (trigonal modulus $c_T = c_{44}$) and polarized along the [1,-1,0] axis (tetragonal modulus $c_E = \left(c_{11} - c_2\right)/2$). The setup functioned as a frequency variable bridge. The temperature variation of attenuation $\Delta\alpha = \alpha\left(T\right) - \alpha\left(T_0\right)$ was measured (T_0 is the reference temperature). Description of the setup can be found in [4].

Chromium ions substitute strontium ions surrounded by eight fluorine ions (see Fig. 1) in the lattice site of the O_h-symmetry. The ground state of Cr^{2+} ion in this case is orbitally threefold degenerate $^5T_{2g}$ subject to the $T_{2g} \otimes \left(e_g + t_{2g}\right)$ JT problem with the APES defined in the five-dimensional space of symmetrized coordinates [1].

Total attenuation of the wave α_β (the subscript indicates the type of normal mode according to corresponding modulus: $\beta = E, T$) can be introduced as the sum of the contribution of JT subsystem α_{JT} and the background attenuation α_b coursed by other subsystems of the crystal. Contribution of the JT subsystem to attenuation is given by [2]

$$\left(\alpha_\beta\right)_{JT} = -\frac{1}{2} k_{\beta 0} \frac{\left(c_\beta^T\right)_{JT}}{c_{\beta 0}} \frac{\omega\tau}{1 + \left(\omega\tau\right)^2} \ , \tag{1}$$

where $c_{\beta 0} = c_{\beta}\left(T_o\right)$ is the reference magnitude of the dynamic (i.e., frequency dependent) modulus c_{β}, (note, $c_{\beta 0}$ represents the total modulus, i.e., defined with account of all the subsystems of the crystal), $\left(c_{\beta}^{T}\right)_{JT}$ is the isothermal contribution of the JT subsystem to the elastic modulus, $k_{\beta 0} = k_{\beta}\left(T_0\right)$ is the reference magnitude of the wave number, ω is the cyclic frequency of the wave, and τ is the relaxation time .

The isothermal contribution of the JT subsystem to the elastic moduli of different symmetry in the fluorite type crystal is given in [4]. All these non-vanishing moduli are proportional to $1/T$. Therefore, eq. (2) can be written as

$$\left(\alpha_{\beta}\right)_{JT} = 2\frac{\left[\alpha_{\beta}\left(T_1\right)\right]_{JT} T_1}{T}\frac{\omega\tau}{1+\left(\omega\tau\right)^2} , \tag{2}$$

where T_1 is the temperature which corresponds to the condition $\omega\tau\left(T_1\right)=1$. Solutions of eq. (2) give the expression for the temperature dependence of relaxation time on the basis of data on ultrasonic attenuation:

$$\tau\left(T\right) = \frac{1}{\omega}\left\{\frac{\left[\alpha_{\beta}\left(T_1\right)\right]_{JT} T_1}{\left[\alpha_{\beta}\left(T\right)\right]_{JT} T} \pm \sqrt{\left[\frac{\left[\alpha_{\beta}\left(T_1\right)\right]_{JT} T_1}{\left[\alpha_{\beta}\left(T\right)\right]_{JT} T}\right]^2 - 1}\right\} , \tag{3}$$

Positive sign is taken for $T \le T_1$ and negative sign is used for $T > T_1$.

The temperature dependences of attenuation related to the trigonal c_T and tetragonal c_E modes are given in Fig. 2. One can see a big anomaly in the case of c_T mode and a small anomaly in the case of c_E mode. Contribution of the JT subsystem $\left(\alpha_{\beta}\right)_{JT}$ is defined as subtraction of the background attenuation $\alpha_b\left(T\right)$ from the measured one $\alpha\left(T\right)$. The background attenuation is simulated by a smooth function approaching to the measured one at low and high temperatures. Justification of such simulation originates from eq. (2) which indicates vanishing $\left(\alpha_{\beta}\right)_{JT}$ at both $\omega\tau \gg 1$ (low temperatures) and $\omega\tau \ll 1$ (high temperatures). In the case of the c_T mode, we simulated the background attenuation by $\Delta\alpha_b / k_0 = 2.07\cdot 10^{-8} T^{-2}$ (Fig. 2a, curve 2).

Anomalies in both c_T and c_E modes, according to [4], indicate the $T_{2g} \otimes \left(e_g + t_{2g}\right)$ JTE problem. The isothermal contribution of the JT subsystem to the elastic moduli entering eq. (3) are given as follows [4]

$$\left(c_E^T\right)_{JT} = -\frac{1}{72}\frac{n_{Cr} a_0^2 F_E^2}{k_B T}, \qquad \left(c_T^T\right)_{JT} = -\frac{4}{9}\frac{n_{Cr} a_0^2 F_T^2}{k_B T}. \tag{4}$$

Here F_E and F_T are tetragonal and trigonal linear vibronic coupling constants, respectively, a_0 is the distance between chromium and fluorine ions in the JT complex, and k_B is the Boltzmann constant. The linear vibronic coupling constants can be calculated with the use of the expressions derived from eq. (1), (2) and (4):

$$F_E^2 = 18\frac{c_{E0} k_B T_1}{n_{Cr} a_0^2}\frac{\left[\alpha_E\left(T_1\right)\right]_{JT}}{k_{E0}}, \qquad F_T^2 = \frac{27}{4}\frac{c_{T0} k_B T_1}{n_{Cr} a_0^2}\frac{\left[\alpha_T\left(T_1\right)\right]_{JT}}{k_{T0}}. \tag{5}$$

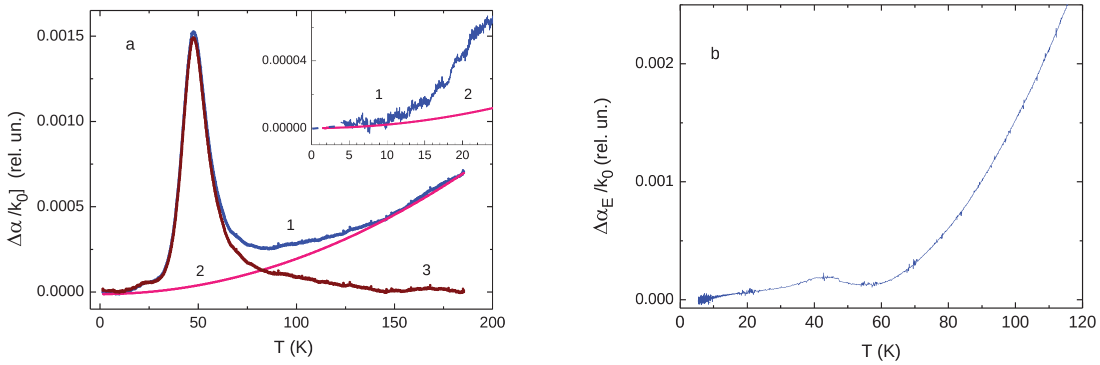

FIGURE 2. Temperature dependence of ultrasound attenuation in the SrF2:Cr^{2+} crystal: (a) the c_T mode at $\omega / 2\pi = 105$ MHz and (b) the c_E mode at $\omega / 2\pi = 56$ MHz. $\Delta\alpha_T / k_0 = \left[\alpha_T(T) - \alpha_T(T \to 0)\right] / k_0$ (curve 1), the background attenuation $\Delta\alpha_b / k_0 = 2.07 \cdot 10^{-8} T^{-2}$ (curve 2), and contribution of the JT subsystem $\left(\alpha_T\right)_{JT} / k_0$ (curve 3)

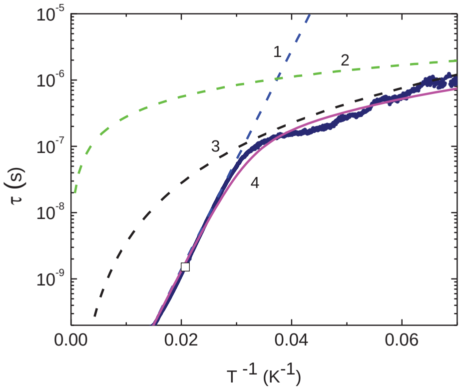

FIGURE 3. Temperature dependence of relaxation time in SrF2:Cr^{2+} crystal determined with the use of the data given in Fig. 1a (curve 2). Dark solid line is experimental data, curve 1 is activation relaxation time $\tau_a = 7 \cdot 10^{-13} \exp\left(380 / T\right)$, curve 2 is tunneling relaxation time $\tau_t = 2.8 \cdot 10^{-5} T^{-1}$, curve 3 is relaxation time due to two-phonon mechanism $\tau_R = 3.5 \cdot 10^{-3} T^{-3}$, curve 4 is total relaxation time $\tau = \left(\tau_a^{-1} + \tau_t^{-1} + \tau_R^{-1}\right)^{-1}$. The square symbol corresponds to $\omega\tau\left(T\right) = 1$

Discussing possible mechanisms of relaxation Sturge [2] took into consideration thermal activation over the potential barrier, tunneling through the barrier, and two-phonons process analogous to Raman scattering. Relaxation rates related to these mechanisms are the following: $\tau_a^{-1} = \nu_0 \exp\left(-V_0 / T\right)$, $\tau_t^{-1} = BT$, and $\tau_R^{-1} = \left(B / \theta^2\right) T^3$. Temperature dependence of relaxation time calculated with the use of eq. (3) is given in Fig. 3 by the curve 1. Account of different mechanisms of relaxation makes it possible to determine the value of activation energy V_0 .

DISCUSSION

Depth of the saddle points are determined from the value of tetragonal (E_E) and trigonal (E_T) JT stabilization energy (see, e.g., [1]): $E_E = F_E^2 / 2K_E$, $E_T = 2F_T^2 / 3K_T$, where, K_E and K_T are tetragonal and trigonal primary force constants. The JT stabilization energy for orthorhombic minima (i.e., the depth of the global minima of the APES) is $E_{OR} = E_T + V_0 + \left(1/2\right)\hbar$, where ω_R is the radial vibronic frequency. It can be accepted as equal to local trigonal-type vibrational frequency ω_τ. The energy of the vibrations for SrF$_2$ $\hbar$ cm^{-1} was reported in [5]. In our calculation, we used $\omega_R = 100\ \text{cm}^{-1}$. The force constant K_T is defined by the product of ω_R^2 and the reduced mass of the CrF$_8$ complex M =6.43·10^{-23} g. The relation between primary force constants should match the relation between corresponding symmetry elastic moduli. In our crystal, $K_E / K_T = 0.815$. As a result, $K_T = 1.85 \cdot 10^4$ dyn/cm and $K_E = 2.29 \cdot 10^4$ dyn/cm. Positions of orthorhombic global minima can be calculated introducing the dimensionless parameters $A = W_{ET} / \sqrt{K_E K_T}$ and $B = W_{ET} F_E / K_E F_T$ [6], where W_{ET} is the quadratic vibronic coupling constant. The values of A are defined by the quadratic equation

$$E_{OR} / E_E = \left[\left(A/B \right)^2 - \left(A/B \right) A + 1/4 \right] \left(1 - A^2 \right)^{-1}. \tag{7}$$

while $B = AF_E / \sqrt{K_E K_T}$. Position of the first orthorhombic minimum is defined as follows $Q_1^{OR} = \left(-\left[F_E \left(B - 2A^2 \right) \right] \cdot \left[2K_E B \left(1 - A^2 \right) \right]^{-1}, 0, 0, 0, -\left[F_T \left(2 - B \right) \right] \cdot \left[2K_T \left(1 - A^2 \right) \right]^{-1} \right)$. The other five minima can be obtained according to the Table 1. Coordinates of the saddle points are given in Tables 2 and 3. Numerical data which characterize the JTE and the APES in SrF$_2$:Cr^{2+} obtained in our study are given in Tables 4 and 5.

TABLE 1. Positions of six orthorhombic minima in coordinates $\left(Q_\vartheta, Q_\varepsilon, Q_\xi, Q_\eta, Q_\zeta \right)$.

	Q_ϑ	Q_ε	Q_ξ	Q_η	Q_ζ
Q_1^{OR}	$Q_{0\vartheta}^{OR}$	0	0 0	0	$Q_{0\zeta}^{OR}$
Q_2^{OR}	$Q_{0\vartheta}^{OR}$	0	0	0	$-Q_{0\zeta}^{OR}$
Q_3^{OR}	$-\frac{1}{2} Q_{0\vartheta}^{OR}$	$\frac{\sqrt{3}}{2} Q_{0\vartheta}^{OR}$	0	$Q_{0\zeta}^{OR}$	0
Q_4^{OR}	$-\frac{1}{2} Q_{0\vartheta}^{OR}$	$\frac{\sqrt{3}}{2} Q_{0\vartheta}^{OR}$	0	$-Q_{0\zeta}^{OR}$	0
Q_5^{OR}	$-\frac{1}{2} Q_{0\vartheta}^{OR}$	$-\frac{\sqrt{3}}{2} Q_{0\vartheta}^{OR}$	$Q_{0\zeta}^{OR}$	0	0
Q_6^{OR}	$-\frac{1}{2} Q_{0\vartheta}^{OR}$	$-\frac{\sqrt{3}}{2} Q_{0\vartheta}^{OR}$	$-Q_{0\zeta}^{OR}$	0	0

TABLE 2. Positions of three tetragonal saddle points in coordinates $\left(Q_\vartheta, Q_\varepsilon, Q_\xi, Q_\eta, Q_\zeta\right)$. $Q_0^E = F_E / K_E$.

Q_1^E	Q_2^E	Q_2^E
$Q_0^E\left(1,0,0,0,0\right)$	$Q_0^E\left(-\frac{1}{2},\frac{\sqrt{3}}{2},0,0,0\right)$	$Q_0^E\left(-\frac{1}{2},-\frac{\sqrt{3}}{2},0,0,0\right)$

TABLE 3. Positions of four trigonal saddle points in coordinates $\left(Q_\vartheta, Q_\varepsilon, Q_\xi, Q_\eta, Q_\zeta\right)$. $Q_0^T = 2F_T / \left(3K_T\right)$.

Q_1^T	Q_2^T	Q_3^T	Q_4^T
$Q_0^T\left(0,0,1,1,1\right)$	$Q_0^T\left(0,0,-1,1,-1\right)$	$Q_0^T\left(0,0,1,-1,-1\right)$	$Q_0^T\left(0,0,-1,-1,1\right)$

TABLE 4. Stabilization energies for tetragonal trigonal and orthorhombic energies.

E_E, cm^{-1}	E_T, cm^{-1}	E_{OR}, cm^{-1}
225	440	754

TABLE 5. Vibronic coupling constants and parameters entering Tables 1–3 (for positive F_T).

F_E, dyn	F_T, dyn	W_{ET}, dyn/cm	Q_0^E, Å	Q_0^T, Å	$Q_{0\vartheta}^{OR}$, Å	$Q_{0\zeta}^{OR}$, Å
$5.3\cdot10^{-5}$	$5.5\cdot10^{-5}$	$-1.3\cdot10^{4}$	0.19	0.16	0.17	-0.41
		$2.3\cdot10^{4}$			-1.0	0.83
$-5.3\cdot10^{-5}$	$5.5\cdot10^{-5}$	$-2.3\cdot10^{4}$	-0.19	0.16	1.0	-0.83
		$1.3\cdot10^{4}$			-0.17	-0.41

CONCLUSIONS

The anomaly which was observed in the temperature dependence of attenuation in SrF_2:Cr^{2+} single crystal was interpreted as due to relaxation in the subsystem of the JT complexes $Cr^{2+}F_8^-$. The temperature dependence of relaxation time was obtained and interpreted with account of three mechanisms. The magnitudes of the JT stabilization energies, the vibronic coupling constants, positions of the extrema points were calculated.

ACKNOWLEDGMENTS

In Ural Federal University this work was supported by the RFBR (grant 18-02-00332_a), UrFU Center of Excellence “Radiation and Nuclear Technologies” (Competitiveness Enhancement Program), the Ministry of Education and Science of the Russian Federation (Program 5-100). In M.N. Miheev Institute of Metal Physics, this work was carried out within the state assignment of the Ministry of Education and Science of the Russian Federation (theme “Electron” No. AAAA-A18-118020190098-5).

REFERENCES

1. I. B. Bersuker, *The Jahn-Teller effect*. (Cambridge University Press, Cambridge, 2006), pp. 45–106.
2. M. D. Sturge, Solid State Physics **20,** 92 (1967).

3. I.V. Zhevstovskikh, I.B. Bersuker, V.V. Gudkov, N.S. Averkiev, M.N. Sarychev, S. Zherlitsyn, S. Yasin, G.S. Shakurov, V.A. Ulanov, V.T. Surikov, J. Appl. Phys. **119**, 225108 (2016).
4. N.S. Averkiev, I.B. Bersuker, V.V. Gudkov, I.V. Zhevstovskikh, M.N. Sarychev, S. Zherlitsyn, Sh. Yasin, G.S. Shakurov, V. A. Ulanov, V.T. Surikov, "Manifestation of the Jahn-Teller effect in elastic moduli of cubic crystals. Application to strontium fluorite doped with chromium ions," in *Fluorite. Structure, Chemistry and Applications, edited by* Moritz van Asten (Nova Science Publishers, New York, 2019), pp. 111–159.
5. W. Kaiser, W.G. Spitzer, R. H. Kaiser, L.E. Howarth, Phys. Rev. **127**, 1950 (1962).
6. I.B. Bersuker and V.Z. Polinger, Zh. Eksp. Teor. Fiz. **66**, 2078 (1974) [Sov. Phys. JETP **39**, 1023 (1974)].