# Nonlinear effect of uniaxial pressure in the EPR spectrum of a $Cr^0$ Jahn-Teller center in Si

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The uniaxial pressure effect in the EPR spectrum of a Cr impurity in Si is investigated at 1.2–2 K with an aim at determining the vibronic-state model and assessing the possible manifestation of the Jahn-Teller (JT) character of the center in this effect. An appreciable nonlinearity of the pressure effect is observed for a deep JT center in silicon. This nonlinearity is described in the spin-lattice Hamiltonian by terms that are quadratic in pressure. The linear spin-phonon constants and combinations of certain quadratic-in-pressure spin-phonon constants are determined. A connection is obtained between the spin-phonon constants that are quadratic in the pressure and the JT-interaction and anharmonicity constants. It is shown that the JT-Hamiltonian parameters corresponding to a strong JT effect can explain the observed quadratic-in-pressure effect in the EPR spectrum. As a result, the contributions of the quadratic JT interaction and of the anharmonicity to the adiabatic potential become substantial, in agreement with the model in which JT minima of different symmetry coexist for $Cr^0$ in Si.

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## INTRODUCTION

The investigation of the effect of pressure on the EPR spectrum is one of the most accurate methods of determining the characteristics of the spin-phonon interaction of a paramagnetic center. In the case of a degenerate triplet electronic state, the pressure effect in EPR can determine directly the constants of the orbit-lattice interaction of the center. This is particularly important in connection with the possible onset of the Jahn-Teller (JT) effect. Indeed, for electronic triplets, the spin-orbit interaction forms states that are shifted with respect to the spin and orbital degrees of freedom, and described by a total angular momentum $J$, and manifest themselves in the EPR. Therefore the coupling of such states with the lattice is determined, with good approximation, by the orbit-lattice interaction. Information on the orbit-lattice interaction permits ont only a description of the spin-lattice relaxation (SLR) but also a determination of the model of the vibronic states in the JT effect.

Interstitial $Cr^0$ in Si exhibits a dynamic JT effect. We have previously investigated[1,2] the spin-lattice relaxation of this center, which revealed anomalous properties that could be explained in a model wherein JT minima of different symmetry coexist. In the present paper we study in detail the effect of axial pressure on the EPR spectrum of $Cr^0$ in Si, for the purpose of determining the model of the vibronic states and interpreting the SLR data.

We describe the observation, for the first time ever, of an essentially nonlinear effect of uniaxial pressure in the EPR spectrum of a JT center in silicon. By investigating this effect and by obtaining the connection between the orbit-lattice interaction constants and the JT-Hamiltonian parameters, with account taken of the quadratic vibronic interaction and of the anharmonicity, we were able to determine the characteristics of the vibronic interaction and confirm the previously employed[2] model of a multiwell potential, and by the same token the model of the SLR of this JT center. The strong JT interaction explains the observed nonlinear pressure effect in the EPR spectrum.

## EXPERIMENT

The influence of uniaxial pressure on the EPR spectrum of interstitial $Cr^0$ in silicon was investigated at 9 GHZ and at temperatures 1.2–2 K. In the absence of pressure, at these temperatures and at a magnetic-field orientation $\mathbf{H} \parallel [100]$, the EPR spectrum of this center consists of two lines separated by 24.5 G.[1] At other directions of the magnetic field, the EPR lines become much broader and become more difficult to observe because of the low paramagnetic-center concentrations. In the apparatus constructed by us to produce axial pressure in a cylindrical EPR resonator operating in the $H_{100}$ mode[1] at 1.2–78 K, a pressure up to 1 10 kgF/cm was reached for samples measuring $3\times 3\times 10$ mm with inhomogeneity not exceeding 5%. The pressure was perpendicular to the direction of the magnetic field, at two sample orientations, $\mathbf{P} \parallel [100]$ and $\mathbf{P} \parallel [110]$. At the two pressure directions and at $\mathbf{H} \parallel [001]$, the EPR lines shift in opposite directions in the magnetic-field, and at pressures 15–20 kg they merge into a single broad line, while an intense narrow EPR line due to the two-photon transition is observed with increasing power. With further increase of pressure, the narrower EPR line shifts towards a stronger resonant magnetic field, while the strong field line shifts towards the weaker field. The arithmetic mean of the resonant magnetic fields of the two lines ($H_{12}$) shifts towards the weaker magnetic field (Fig. 1).

At the orientation $\mathbf{H} \perp \mathbf{P} \parallel [110]$, a linear splitting (within the limits of experimental error) of the EPR line is observed, as well as a shift of $H_{12}$, which can be described by using the Hamiltonian $\hat{\mathcal{H}}_e^{(1)}$. This Hamiltonian is obtained from $\hat{\mathcal{H}}_e$, defined in Refs. 3 and 4, to which one adds terms that are quadratic in spin and

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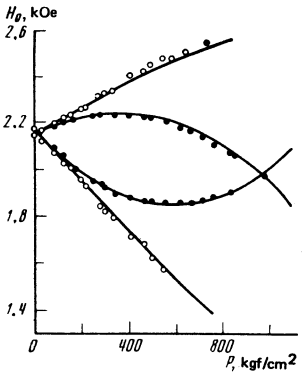


FIG. 1. Resonant magnetic fields of two EPR lines of $Cr^0$ in Si vs pressure at H ∥ [001]: ● – P ∥ [100], ○ – P ∥ [110].

are obtained from $\hat{\mathcal{H}}_e$ by making the substitutions $H_k \to \hat{J}_k$ and $\beta g_{ij} \to G_{ij}$, and also by adding a term quadratic in the magnetic field, which described the splitting of the EPR line of $Cr^0$ in Si at zero pressure.[5]

In this orientation, we succeeded in observing the angular dependence of the pressure effect on the magnetic-field direction (Fig. 2). The angular dependence of the splitting $\Delta H$ between the lines and of the shift of $H_{12}$ ($\delta H$) is described by the expressions

$$\Delta H = \frac{P}{2g\beta}\left[(G_{11}-G_{12})(S_{12}-S_{11})(3\cos^2\varphi-1) - \frac{3}{2}G_{44}S_{44}\sin^2\varphi\right], \quad (1)$$

$$\delta H = -\frac{PH}{2g}\left\{\left[g_{11}(S_{11}+S_{12}) + g_{12}(S_{11}+3S_{12}) - \frac{1}{2}g_{44}S_{44}\right]\sin^2\varphi + 2\left[g_{11}S_{12}+g_{12}(S_{11}+S_{12})\right]\cos^2\varphi\right\}. \quad (2)$$

The quantity $\delta H$ is assumed to be positive if $H_{12}$ increases.

On the basis of the obtained angular dependence of the pressure effect, Eqs. (1) and (3) were used to determine the linear-in-pressure spin-phonon constants for $Cr^0$ in Si:

$$G_{11}-G_{12} = -230\pm30\ \text{cm}^{-1}, \quad G_{44} = -85\pm10\ \text{cm}^{-1};$$
$$g_{11} = -800\pm100, \quad g_{12} = 400\pm50, \quad g_{44} = -300\pm80. \quad (3)$$

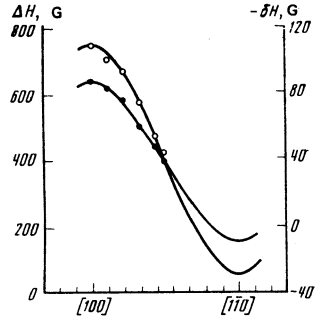


FIG. 2. Angular dependence of the splitting of two EPR lines (●) and shift of arithmetic mean of the resonant magnetic fields of these lines $H_{12}$ (○) of $Cr^0$ in Si at P = 400 kgf/cm, H ⊥ P ∥ [110]. The solid lines correspond to the theoretical expressions (1) and (2).

It is assumed here, in analogy with the preceding paper,[3] that $g_{11} + 2g_{12} = 0$, corresponding to the absence of influence of the fully symmetrical deformation.

At orientations H ⊥ P ∥ [100] one observes an effect that is essentially nonlinear in pressure, namely the splitting of the EPR lines and a shift of $H_{12}$, corresponding within the limits of experimental error to a dependence on the direction of the magnetic field. To describe this experiment at P ∥ [100] and H ∥ [001] we used the quadratic-in-pressure spin-phonon Hamiltonian from the paper of Koloskova,[6] in the form

$$\hat{\mathcal{H}}_e^{(2)} = {}^3/_2\beta P^2 J_x H\left[{}^1/_2 g_{111}(S_{12}^2 - S_{11}^2) + 2g_{112}S_{12}^2\right] + {}^3/_2 P^2 J_z^2\left[\frac{1}{2}G_{111}(S_{12}^2 - S_{11}^2) + 2G_{112}S_{12}^2\right]. \quad (4)$$

For the orientations P ∥ [110] and H ∥ [001] the quadratic-in-pressure Hamiltonian is of the form

$$\hat{\mathcal{H}}_e^{(2)} = {}^3/_2\beta P^2 J_x H\{g_{111}[S_{12}^2 - {}^1/_4(S_{11}+S_{12})^2] + {}^1/_2 g_{112}(S_{12}^2 - S_{11}^2) - 2g_{166}S_{44}^2\} + {}^3/_2 P^2 J_z^2\{G_{111}[S_{12}^2 - {}^1/_4(S_{11}+S_{12})^2] + {}^1/_2 G_{112}(S_{12}^2 - S_{11}^2) - 2G_{166}S_{44}^2\}. \quad (5)$$

We have discarded in (4) and (5) the terms with off-diagonal matrix elements.

To take into account the nonlinearity that can appear in the quadratic in the magnetic field in the case of a spin-phonon Hamiltonian that is linear in pressure, the problem was solved numerically with a computer. The solid lines in Fig. 1 show the computer-calculated resonant magnetic fields of two EPR lines as function of pressure, using the Hamiltonin $\hat{\mathcal{H}}_e^{(1)} + \hat{\mathcal{H}}_e^{(2)}$, for two orientations of the pressure, P ∥ [100] and P ∥ [110] and at a magnetic field direction H[001]. The spin-phonon constants (3) were used in this case. The calculated resonant magnetic fields agreed with the experimental ones at the following values of the combinations of the spin-phonon constants:

$$g_{112} - 2.92g_{111} = -(25\pm5)\cdot10^5,$$
$$g_{111} + 9.1g_{112} + 106g_{166} = (2\pm1)\cdot10^5,$$
$$G_{112} - 2.92G_{111} = (90\pm10)\cdot10^4\ \text{cm}^{-1},$$
$$G_{111} + 9.1G_{112} + 106G_{166} = -(3\pm2)\cdot10^4\ \text{cm}^{-1}. \quad (6)$$

The calculations have shown that at the considered splittings of the EPR lines under pressure the contribution of the off-diagonal matri elements from $\hat{\mathcal{H}}_e^{(1)}$ and of the term quadratic in the magnetic field, which we have assumed to be independent of pressure, leads to a negligible nonlinearity up to 900 kgf/cm (Fig. 1, P ∥ [110]). However, the contribution of the off-diagonal linear-in-pressure terms $G_{ij}$ and the shift $H_{12}$ turn out to be comparable with the contribution of the diagonal quadratic-in-pressure terms $g_{ijk}$. If we neglect this circumstance, then the sign of the linear combination $g_{ijk}$ (6) is reversed.

## ORBIT–LATTICE INTERACTION OF JT IMPURITIES

The observed considerable quadratic effect of the pressures in the EPR spectrum of $Cr^0$ in Si is evidence of a large quadratic orbit-lattice interaction with the long-wave deformations. On the other hand, the given center exhibits a strong JT effect, so that it can be assumed that the appreciable quadratic interaction of the center with the long-wave deformation is common in

character with the vibronic interaction. To clarify this question, we analyze the connection between the orbit-lattice constants and the parameters of the JT Hamiltonian.

The initial electronic state of the considered KT paramagnetic center is the triplet $T_2$. When account is taken of the linear and quadratic JT interactions as well as of the anharmonicity, this leads to the following JT Hamiltonian in the quasimolecular approximation:

$$\begin{aligned}\hat{\mathcal{H}}_{JT}=&-2\cdot3^{-1/4}[bQ_2+b_{\varepsilon\varepsilon}Q_2Q_3+{}^1/_2b_{\tau\tau}(Q_4^2-Q_5^2)]\hat{\varepsilon}_\varepsilon\\&-3^{-1/2}[2bQ_3+b_{\varepsilon\varepsilon}(Q_2^2-Q_3^2)+3^{-1/2}b_{\tau\tau}(2Q_6^2-Q_4^2-Q_5^2)]\hat{\varepsilon}_\theta\\&-(cQ_4+c_{\tau\tau}Q_5Q_6)\hat{T}_4-(cQ_5+c_{\tau\tau}Q_4Q_6)\hat{T}_5\\&-(cQ_6+c_{\tau\tau}Q_4Q_5)\hat{T}_6+{}^1/_2[K_\varepsilon(Q_2^2+Q_3^2)+K_\tau(Q_4^2+Q_5^2+Q_6^2)\\&+K_AQ_4^2]J-{}^1/_6K_\varepsilon'(3Q_2^2Q_3-Q_3^3)J-{}^1/_6K_\tau'Q_4Q_5Q_6J\\&+{}^1/_2w[Q_4(3^{1/2}Q_2-Q_3)\hat{T}_4-Q_5(3^{1/2}Q_2+Q_3)\hat{T}_5+2Q_3Q_6\hat{T}_6]\\&-2\cdot3^{-1/2}b'(Q_2Q_1\hat{\varepsilon}_\varepsilon+Q_3Q_1\hat{\varepsilon}_\theta)-c'(Q_4Q_1\hat{T}_4+Q_5Q_1\hat{T}_5+Q_6Q_1\hat{T}_6).\end{aligned}\tag{7}$$

Here $Q_1$, $Q_2$, $Q_3$ and $Q_4$, $Q_5$, $Q_6$ are the normal vibrations of the cluster and transform in accord with the irreducible representations of the cubic symmetry-group representations $A_1$, $E$, and $T$, respectively. The electron operators $\hat{\varepsilon}_\varepsilon$, $\hat{\varepsilon}_\theta$, $\hat{T}_4$, $\hat{T}_5$, $\hat{T}_6$ on the basis of the electronic state of the triplet $T_2$ were determined in the book of Abragam and Bleaney.[12] The constants $b$ and $c$ correspond to linear JT interaction with trigonal deformations of the cluster. The constants $w$, $b_{\varepsilon\varepsilon}$, $b_{\tau\tau}$, $c_{\tau\tau}$ are connected with the quadratic JT interaction for the $T$ term,[7-9] and $K_\varepsilon'$ and $K_\tau'$ are the cubic-anharmonicity constants.[10] In (7) we took into account also the new terms in the quadratic $JT$ interaction of the term $T$, which intertwine the tetragonal and trigonal deformations with the fully symmetric one. This interaction is described by the constants $b'$ and $c'$.

In the adiabatic approximation we write down the shift of the atoms of the cluster $Q_i$ in the form of a sum of a shift $Q_i'$ that varies rapidly with frequency $\omega_c$ and a shift $Q_i''$ that varies with the frequency of the long-wave acoustic oscillations, and expand $Q_i''$ in terms of the components of the strain tensor. Substituting $Q_i=Q_i'+Q_i''$ in the JT Hamiltonian and calculating its matrix elements on the vibronic wave functions, we obtain the effective Hamiltonian of the orbit-lattice interaction. Thus, for tetragonal JT minima and for an octahedral cluster, the effective Hamiltonians $\mathcal{H}_{OL}^{(1)}$ and $\mathcal{H}_{OL}^{(2)}$ for the linear and quadratic orbit-lattice interactions, respectively, are given by

$$\mathcal{H}_{OL}=\mathcal{H}_{OL}^{(1)}+\mathcal{H}_{OL}^{(2)},\tag{8}$$

$$\mathcal{H}_{OL}^{(1)}=-(4\cdot3^{-1/2}bR+2K_\varepsilon Q_0R)(e_\varepsilon\hat{\varepsilon}_\varepsilon+e_\theta\hat{\varepsilon}_\theta),\tag{9}$$

$$\begin{aligned}\mathcal{H}_{OL}^{(2)}=&-\{8\cdot3^{-1/2}R^2[b_{\varepsilon\varepsilon}e_\theta e_\varepsilon+{}^1/_2b_{\tau\tau}(e_{yz}^2-e_{xz}^2)]+2^{1/2}R^2K_\varepsilon'Q_0e_\theta e_\varepsilon\}\hat{\varepsilon}_\varepsilon\\&-2R^2\{2\cdot3^{-1/2}[b_{\varepsilon\varepsilon}(e_\varepsilon^2-e_\theta^2)+b_{\tau\tau}3^{-1/2}(2e_{xy}^2-e_{xz}^2-e_{yz}^2)]\\&+K_\varepsilon'Q_0(e_\theta^2-e_\varepsilon^2)\}\hat{\varepsilon}_\theta-8\cdot3^{-1/2}R^2b'e[e_\varepsilon\hat{\varepsilon}_\varepsilon+e_\theta\hat{\varepsilon}_\theta],\end{aligned}\tag{10}$$

$e_{ij}$ are the components of the strain tensor, $e_\theta=(2e_{zz}-e_{xx}-e_{yy})$, $e_\varepsilon=3^{1/2}(e_{xx}-e_{yy})$, $e=e_{xx}+e_{yy}+e_{zz}$, $Q_0$ is the equilibrium deformation of the cluster at one of the minima of the adiabatic potential, and $R$ is the distance between the impurity and the ligand of the cluster.

The choice of an octahedral cluster for the JT interstitial impurity in silicon corresponds to the second coordination sphere; this is justified by the fact that the dominant role in the formation of the spectrum of the electronic state of an interstitial impurity in silicon is played apparently by the crystal field of the second octahedral sphere.[5]

It follows from (9) that the linear orbit-lattice interaction is determined not only by the constants of the linear vibronic interaction, as customarily assumed,[11] but also by the product of the harmonic elastic constant $K_\varepsilon$ by the JT shift, and both contributions are comparable in magnitude.

Within the framework of the expansion in powers of the displacements, we have disregarded in (9) the quadratic vibronic interaction and the anharmonicity. These interactions, however, as follows from (10), determine the quadratic orbit-lattice interaction, whose constants are proportional to the constants of the quadratic vibronic interaction and of the anharmonicity. The contribution of the anharmonicity in (10), just as the contribution of the harmonic oscillations in (9), is proportional to $Q_0$ and does not contain the vibronic reduction.

We assume for estimates $b_{\tau\tau}$, $b_{\varepsilon\varepsilon}$, $b'\sim10^4$ cm$^{-1}$/Å$^2$, $K_\varepsilon'\approx10^4$ cm$^{-1}$/Å$^3$, and $Q_0\sim1$ Å, reasonable values for a strong JT effect. For an octahedral cluster of the second coordination sphere, using (10), we then obtain the values of the orbit-lattice constants corresponding to the values of the experimentally determined linear combinations (6). Thus, the parameters of the JT Hamiltonian corresponding to the strong JT effect can explain the observed quadratic-in-pressure effect in the EPR spectrum of $Cr^0$ in Si.

The anomalously large quadratic-in-deformation orbit-lattice constants obtained in the present paper point to a considerable magnitude of the constants of the quadratic vibronic interaction and of the anharmonicity for $Cr^0$ in silicon. On the other hand, the quadratic vibronic interaction and the anharmonicity for the JT effect of the triplet states leads to the possible coexistence of JT minima of different symmetry.[9,10] This model was used by us earlier to explain the anomalous spin-lattice relaxation of this center. Thus, the appreciable contribution of the quadratic orbit-lattice interaction in the EPR spectrum, obtained in the present paper, agrees with our model of the vibronic states for $Cr^0$ in Si.[2]


[1] A. A. Bugaĭ, V. S. Vikhnin, V. E. Kustov, V. M. Maksimenko, and B. K. Krulikovskiĭ, Zh. Eksp. Teor. Fiz. 74, 2250 (1978) [Sov. Phys. JETP 47, 1170 (1978)].

[2] A. A. Bugaĭ and V. S. Vikhnin, Fiz. Tverd. Tela (Leningrad) 21, 3332 (1979) [Sov. Phys. Solid State 21, 1924 (1979)].

[3] A. A. Bugaĭ and V. S. Vikhnin, Fiz. Tverd. Tela (Leningrad) 21, 2022 (1979) [Sov. Phys. Solid State 21, 1159 (1979)].

[4] G. W. Ludwig and F. S. Ham, Paramagnetic Resonance (Proc. 1st Internat. Conf., Jerusalem, 1962), Academic, Vol. 2, 620 (1963).

[5] G. W. Ludwig and H. A. Woodbury, Russ. transl. in: Elec-

tronnyi spinovyi rezonans v poluprovodnikov (Electrons Spin Resonance in Semicondutors), Mir, 1964, Chap. 3 [Solid State Phys. 13, 223 (1964)].
[6]N. G. Kolskova, in: Paramagnitnyĭ rezonans (Paramagnetic Resonance), S. A. Al'tshuler, ed., Kazan' Univ. Press, 1964, p. 117.
[7]I. B. Bersuker, Élektronnoe stroenie is svoĭstva koordinatsionnykh soedineniĭ (Electronic Structure and Properties of Coordination Compounds), Khimiya, L., 1976.
[8]I. B. Bersuker and V. Z. Polinger, Zh. Eksp. Teor. Fiz. **66**, 2078 (1974) [Sov. Phys. JETP **39**, 1023 (1974)].
[9]M. Bacci, A. Ranfagni, M. P. Fontana, and G. Viliani, Phys. Rev. B **12**, 5907 (1975).
[10]M. Bacci, A. Ranfagni, M. Cetica, and G. Viliani, Phys. Rev. B **12**, 5907 (1975).
[11]F. S. Ham, Phys. Rev. **166**, 307 (1968).
[12]A. Abragam and B. Bleaney, Electron Paramagnetic Resonance of Transition Ions, Oxford, 1970, Vol. 2. [Russ. transl. Mir, 1973, p. 285].

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