Low-energy resonances in Jahn-Teller impurity centers

Yu. B. Rozenfel'd and A.V. Vaĭsleĭb

Center for Automation of Scientific Research and of Metrology, Academy of Sciences of the Moldavian SSR
(Submitted 11 July 1983)

A theoretical study is made of a Jahn-Teller impurity center whose electrons interact with the phonon continuum. Analysis of the renormalized Born approximation for the scattering of phonons by the impurity center yields criteria for the occurrence of low-frequency resonances and establishes the symmetry of these resonances. The dispersion relations for an impurity center found in an orbital doublet state and interacting with phonons of tetragonal symmetry are solved analytically for arbitrary values of the vibronic coupling. A study is made of the change in the single-particle vibronic spectrum as the coupling force increases. The position and broadening of the low-frequency rotational resonances are determined.

1. INTRODUCTION

The theory of the dynamic Jahn-Teller effect has been worked out rather thoroughly for molecular or cluster problems (see Refs. 1–4 for review). Interest has recently arisen in impure crystals, which exhibit acoustic and magnetic anomalies that find explanation in the Jahn-Teller effect (or pseudo-Jahn-Teller effect).[5] For the case in which the electrons of the impurity center interact with the phonon continuum, such a theory has been developed for the case of weak electron-phonon coupling.[6–9] Several problems have also been examined in the strong-coupling limit.[10–12] It was shown in Refs. 6–9 that the dynamic Jahn-Teller effect can lead to the appearance of local and resonant electron-phonon states, but the criteria for the appearance of these states require a rather strong electron-phonon interaction, particularly for the occurrence of low-frequency resonances. On the other hand, the applicability criteria for perturbation theory require a rather weak coupling, and so there are no grounds for hoping that reliable results can be obtained for the low-frequency resonances in the weak-coupling theory.

In the present paper we attempt to describe the lowest excited states of Jahn-Teller impurity centers for arbitrary values of the electron-phonon coupling.

2. CRITERIA FOR THE OCCURRENCE OF LOW-FREQUENCY RESONANCES

Let us consider a small-radius impurity center in a degenerate isolated electronic ground state whose wave functions transform according to row p of an irreducible representation P. The Hamiltonian of the impurity-phonon system is of the form

$$H = H_0 + V = \sum \int d\omega \{ b_{Ll}^+(\omega) b_{Ll}(\omega) + \alpha_L(\omega)$$

$$\times [b_{Ll}^+(\omega) + b_{Ll}(\omega)] v_{Ll} \}, \quad (1)$$

$$\alpha_L(\omega) = \alpha_L \hbar \Omega_L (2^{-1} \omega^{-1} \Omega_L \rho_L(\omega))^{1/2}.$$

Here the first term is the free-phonon Hamiltonian, the second term is the vibronic interaction, $b_{Ll}^+(\omega)$ and $b_{Ll}(\omega)$ are phonon creation and annihilation operators, transforming according to row l of irreducible representation L (i.e., having fixed values of the quasi-angular momentum L and its projection l), ω is the phonon frequency, α_L is the dimen-

sionless vibronic-coupling constant, $\rho_L(\omega)$ is the projected frequency density of effective symmetrized phonons.

$$\Omega_L^{-2} = \int_0^\infty d\omega \, \omega^{-1} \rho_L(\omega),$$

and the v_{Ll} are the electron operators in the basis of the electronic functions $|Pp\rangle$ of the term under consideration.[7]

With the aid of the equations of motion for the phonon operators, one can establish a relationship between the T matrix for elastic phonon scattering and the Fourier transform of the electron Green-function matrix G at a temperature of absolute zero:

$$T_{p'L'l', \, pLl}(\omega) = \hbar^{-1} \alpha_L(\omega) \alpha_{L'}(\omega) G_{p'L'l', \, pLl}(\omega), \quad (2)$$

$$G_{p'L'l', \, pLl}(t) = -i\theta(t)\hbar^{-1}\langle Pp'| [v_{L'l'}(t), v_{Ll}] |Pp\rangle. \quad (3)$$

Simultaneously diagonalizing the T and G matrices, we introduce the partial Green functions $G_{L'L}^\Gamma$ (the representation Γ is contained in the direct product $P \times L$);[7] this is equivalent to isolating the partial contributions to the scattering amplitude. Using the analytical properties of the G matrix, in particular, the Goldberger crossing symmetry,[13]

$$G_{p'L'l', \, pLl}(z) = G_{p'Ll, \, pL'l'}(-z), \quad (4)$$

we obtain a system of dispersion relations for the partial Green functions:

$$G_{L'L}^\Gamma(z) = \frac{1}{\hbar z} R_{L'L}^\Gamma + \frac{1}{\pi} \int_0^\infty k\omega \left\{ \frac{1}{\omega - z} \, \mathrm{Im}\, G_{L'L}^\Gamma(\omega) \right.$$

$$\left. - \frac{1}{\omega + z} \sum_{\bar\Gamma} [\bar\Gamma] \begin{bmatrix} L' & P & \Gamma \\ L & P & \bar\Gamma \end{bmatrix} \mathrm{Im}\, G_{LL'}^{\bar\Gamma}(\omega) \right\}, \quad (5)$$

$$R_{L'L}^\Gamma = i^{L+L'} \left\{ (-1)^{L'} \delta_{Pr} \delta(LPP) \delta(L'PP) [P]^{-1} \right.$$

$$\left. - (-1)^L \begin{bmatrix} L' & P & \Gamma \\ L & P & P \end{bmatrix} \right\} K_P(L) K_P(L'). \quad (6)$$

Here $[P]$ is the dimensionality of representation P, $[:::]$ is the 6Γ symbol, and the $K_P(L)$ are vibronic reduction factors.[3] This system of equations is analogous to the familiar Low equations for the static model of the pion-nucleon interaction. The techniques of obtaining equations of this type can be found in Ref. 14. The first term in expression (5) describes the contribution of the Born approximation with a renormalized coupling constant (the coupling constant is multi-

plied by the vibronic reduction factor, which here has the meaning of a renormalization parameter). The corresponding term in the **T** matrix is

$$F_{L'L}^{\Gamma}/\hbar z = \alpha_{L'}(z)\alpha_L(z)R_{L'L}^{\Gamma}/\hbar z. \tag{7}$$

The negative sign of the eigenvalues of matrix **F** corresponds to attraction of the phonon to the impurity center, the positive sign to repulsion from it, and the absolute values of the eigenvalues characterize the strength of the attraction or repulsion of the phonon. Therefore, low-frequency resonances should be expected to occur in states with the largest (in absolute value) negative eigenvalues of the matrix $\mathbf{F}^{\Gamma}$.

Let us examine the typical Jahn-Teller problems.

1) The $E \times e$ problem is the case in which the electrons of the impurity center in the degenerate orbital doublet E state interact with the e phonons of tetragonal symmetry. In this case $L' = L = P = E$. Substituting the values of the 6Γ symbols[15] into Eq. (6), we obtain $R^{A_1} = R^{A_2} = -R^E = -1/2$. Thus the low-frequency resonance should be expected to occur in states A_1 and A_2. The fact that the effective coupling constant is the same in these states is due to axial symmetry that obtains when the vibronic interaction includes only terms linear in the coordinates of the nuclei.[7] These states are described by an angular-momentum projection $J = \pm 3/2$. As we shall show, this resonance, which occurs at a rather strong coupling, describes a "rotational" polaron.

2) The $E \times (b_1 + b_2)$ problem. The impurity-center electrons are in the orbital doublet E state of the tetragonal group and interact with b_1 and b_2 phonons. For this problem $P = E$; $L', L = b_1, b_2$; $\Gamma = E$. Diagonalizing the matrix $\mathbf{F}^E$, we obtain for the negative eigenvalue

$$F^E = -\alpha_{b_1}(z)\alpha_{b_2}(z)K_E(b_1)K_E(b_2). \tag{8}$$

If $\alpha_{b_1}(z) = \alpha_{b_2}(z)$, the $E \times (b_1 + b_2)$ problem formally coincides with the $E \times e$ problem examined above. At large, unequal (but comparable in order of magnitude) values of the coupling constant there will be, in addition to the low-frequency rotational resonance, a high-frequency resonance state corresponding to perturbed rotations (in the adiabatic approximation this motion appears when the groove on the lower sheet of the adiabatic potential gives way to two shallow minima and two saddle points). If, on the other hand, one of the coupling constants is much larger than the other, then $|F^E|$ becomes small as a result of the sharp decrease in the reduction factor for vibrations with which the interaction is weaker. This conclusion agrees with the results of direct calculations in the framework of the static Jahn-Teller effect; no low-frequency resonances occur in this case.

3) The $T \times t$ problem. The electrons of an impurity center in the orbital triplet T_2 state interact with trigonal t_2 phonons. In this case $L' = L = P = T_2$; $R^{A_1} = -1/3$, $R^{T_1} = -1/6$, $R^E = R^{T_2} = 1/6$. Here if the vibronic coupling is strong enough one should expect a low-frequency resonance to arise in the A_1 state, since the effective attraction in this state is twice as large as in the T_1 state. This resonance corresponds to a tunneling state.

4) The $T \times (e + t_2)$ problem. The electrons of an impurity center found in the orbital triplet T_2 state interact with

tetragonal e phonons and trigonal t_2 phonons. Then $P = T_2$; $L', L = E, T_2$; $\Gamma = A_1, E, T_1, T_2$. In the states A_1 and E we have

$$F^{A_1} = -\tfrac{1}{3}\alpha_{T_2}^2(z)K_{T_2}^2(T_2), \quad F^E = \tfrac{1}{6}\alpha_{T_2}^2(z)K_{T_2}^2(T_2). \tag{9}$$

We diagonalize the matrices $\mathbf{F}^{T_1}$ and $\mathbf{F}^{T_2}$ and write out only the negative eigenvalues:

$$F^{T_1} = -\frac{1}{12}\alpha_{T_2}^2(z)K_{T_2}^2(T_2)\left\{1+\left[1+12\frac{K_{T_2}^2(E)\alpha_E^2(z)}{K_{T_2}^2(T_2)\alpha_{T_2}^2(z)}\right]^{1/2}\right\}, \tag{10}$$

$$F^{T_2} = -\frac{1}{12}\alpha_{T_2}^2(z)K_{T_2}^2(T_2)\left\{1+\left[1+36\frac{K_{T_2}^2(E)\alpha_E^2(z)}{K_{T_2}^2(T_2)\alpha_{T_2}^2(z)}\right]^{1/2}\right\}. \tag{11}$$

Recognizing that in the long-wavelength region the projected densities of states of the trigonal and tetragonal phonons coincide, we obtain

$$|F^{T_2}| > |F^{T_1}| > |F^{A_1}| \tag{12}$$

for

$$K_{T_2}^2(E)\alpha_E^2 > \tfrac{2}{3}K_{T_2}^2(T_2)\alpha_{T_2}^2 ; \tag{13}$$

in the opposite case the inequalities in (12) are reversed. Knowing the behavior of the vibronic reduction factors $K_{T_2}(E)$ and $K_{T_2}(T_2)$ as functions of the vibronic coupling constant,[16] we can reach the following conclusions:

a) If the interactions with the tetragonal e phonons is predominant over the interaction with the trigonal t_2 phonons, the low-frequency resonances will not occur, because the absolute values of F^{Γ} in the case of strong coupling with the tetragonal vibrations turn out to be extremely small since $K_{T_2}(T_2)\ll 1$ in this case (the interaction with the trigonal vibrations is suppressed). For the case of a weak interaction with the trigonal vibrations this conclusion agrees with the familiar assertion that tunneling states do not occur in the case of a strong tetragonal Jahn-Teller effect for molecular problems.[2]

b) If the coupling with the trigonal vibrations is the stronger [i.e., if the inequality opposite in sense to (13) holds], then there is every reason to expect a completely symmetric low-frequency resonance, since the effective attraction in the A_1 state grows stronger with the coupling constant α_{T_2} while $K_{T_2}(T_2)\to 2/3, K_{T2}(E)\to 0$.

c) If, on the other hand,

$$\alpha_E^2 = \tfrac{2}{3}\alpha_{T_2}^2, \tag{14}$$

then in this case, as we know,[17] the symmetry of the point center increases to spherical and formally describes the interaction of an $S = 1$ electronic "pseudospin" with five-dimensional d phonons (their angular momentum is equal to 2). Here the vibronic reduction factors $K_{T_2}(E) = K_{T_2}(T_2)$ go to 2/5 at large values of the vibronic coupling constant.[1] In this situation one expects that a low-frequency resonance will appear in a state with an angular momentum of 3 (the states A_1, T_1, and T_2 coalesce). This resonance corresponds to a low-lying metastable rotational state. At small deviations from exact equality in (14) and for a strong coupling, one expects that there will be three low-frequency resonances, deriving from a split rotational F state and describing distorted rotations. The lowest will be the T_2 state if inequality (13) holds, or state A_1 in the opposite case.

3. DYNAMIC JAHN-TELLER EFFECT IN AN ORBITAL DOUBLET FOR AN ARBITRARY VIBRONIC COUPLING

For the $E \times e$ problem the exact dispersion equations (5) amit an analytical solution in the low-frequency approximation for a vibronic coupling of arbitrary strength. In this case these equations are of the form

$$G^{1/2(3/2)}(z) = \pm \frac{K_E^2(E)}{2\hbar z}$$
$$+ \frac{1}{\pi} \int_0^\infty d\omega \left\{ \frac{\operatorname{Im} G^{1/2(3/2)}(\omega)}{\omega - z} - \frac{\operatorname{Im} G^{3/2(1/2)}(\omega)}{\omega + z} \right\},$$

(15)

where $G^{A_1} = G^{A_2} = G^{3/2}$ and $G^e = G^{1/2}$ by virtue of the presence of a conserved angular-momentum projection

$$J_z = -i \int d\omega [b_u^+(\omega) b_v(\omega) - b_v^+(\omega) b_u(\omega)] - {}^1/_2 \sigma_v. \quad (16)$$

The lower sign on the right-hand side of (15) pertains to the angular-momentum values given in parentheses in the superscripts to G. Let us solve dispersion equations (15) by Dyson's method.[14] To do this, we write the approximate unitarity condition implied by the relationship between the T matrix for the phonon scattering and the electron Green function, where only the contribution of the exact no-phonon and one-phonon states is taken into account:

$$\operatorname{Im} G^J(z) = -\pi\hbar^{-1} C\alpha_E^2(z) |G^J(z)|^2. \quad (17)$$

The coefficient C will then be found from the condition $J = 1/2$ in the ground state. With allowance for (17) the solution of the dispersion equations is of the form

$$G^{1/2(3/2)}(z) = \pm \frac{1}{2\hbar z} K_E^2(E)$$
$$\times \left\{ 1 \pm \frac{1}{2} C\alpha_E^2 K_E^2(E) \Omega_E^3 z \int_0^\infty \frac{d\omega \rho_E(\omega)}{\omega^2 (\omega^2 - z^2)} \right\}^{-1}.$$

(18)

The approximation under study is equivalent to the summation of the ladder diagrams and a subsequent renormalization. Converting expression (16) to a matrix of the exact eigenfunctions $|+1/2\rangle$ with the use of the equations of motion for the phonon operators, we obtain the relation

$$\frac{1}{2} [1 - K_E(A_2)] = \iint d\omega \, d\omega' [\operatorname{Im} G^{1/2}(\omega) - \operatorname{Im} G^{1/2}(\omega)]$$
$$\times \frac{\alpha_E^2(\omega')}{\pi\hbar(\omega + \omega')^2}, \quad (19)$$

which, together with (18), makes it possible to determine the coefficient C. Analysis of expression (19) in the limit of weak and strong coupling yields the approximate formula for C:

$$C = K_E^{-1}(E). \quad (20)$$

The final expression for the electron Green functions is

$$G^{1/2(3/2)}(z) = \pm \frac{1}{2\hbar z} K_E^2(E)$$
$$\times \left\{ 1 \pm \frac{1}{2} \alpha_E^2 K_E(E) \Omega_E^3 z \int_0^\infty \frac{d\omega \rho_E(\omega)}{\omega^2 (\omega^2 - z^2)} \right\}^{-1}. \quad (21)$$

These electron Green functions describe the vibronic spectrum for arbitrary strength of the electron-phonon coupling in the low-frequency approximation. For weak coupling expression (21) agrees with the results of Refs. 6 and 7 up to terms of second order in the coupling constant. For extremely strong coupling a low-freqency resonance is observed in the state with $J = 3/2$ at a frequency

$$z_r = 4(\alpha_E^2 \Omega_E^3 \overline{\omega^{-4}})^{-1}, \quad (22)$$

corresponding to a transition to the rotational level with $J = 3/2$, in agreement with the result of Ref. 10. Here $\overline{\omega^{-4}}$ is the inverse fourth moment of the projected phonon density. The broadening of this level due to direct single-phonon decay processes,

$$\gamma = {}^1/_8 \pi \alpha_E^2 \rho_E(z_r) \Omega_E^3 z_r^{-1}, \quad (23)$$

was not obtained in Ref. 10. The multimode $E \times e$ problem for a weak vibronic coupling was first considered by Slonczewski.[12] In studying the lower sheet of the adiabatic potential, Slonczeweski noticed that when the rotational energy was included in the case of a continuous phonon continuum, one does not obtain finite quantities for the equilibrium values of the vibrational coordinates. Accordingly, one does not obtain a finite value for the ground-state energy. The result presented above implies that the "resonance" of the rotational state and the vibrational states discussed by Slonczewski is actually a metastable rotational state. At a sufficiently strong coupling, the broadening of the rotational level is small by virtue of the small phonon density near z_r. As the coupling increases, so does the moment of inertia of the "rotational" polaron which is formed, and this leads to a decrease in the energy of the rotational metastable state with $J = 3/2$, which decays with the emission of phonons having angular-momentum projection ± 1, undergoing a transition to the ground state with $J = 1/2$. Unlike the case of an ordinary polaron, the cloud of virtual phonons leads to a renormalization not of the effective mass, but of the moment of inertia.

The poles of the electron Green function, owing to its relationship to the T matrix, also describe changes in the phonon spectrum. The positions of the local and pseudolocal vibronic states are determined in the general case from the equation

$$1 \pm \frac{1}{2} \alpha_E^2 K_E(E) \Omega_E^3 z \cdot$$
$$\times \int_0^\infty \frac{d\omega \rho_E(\omega)}{\omega^2 (\omega^2 - z^2)} = 0. \quad (24)$$

The states which arise in the case of a weak coupling are discussed in Refs. 6 and 7. The spectrum of the system in a superposition of almost purely phononic partial spectra characterized by the angular-momentum values $J = 1/2$ and $3/2$. Such a superposition of phonon spectra in problems with phonon dispersion is analogous to the Moffitt-Thorson splitting of the single-quantum electronic-vibrational states in the molecular problem.[18] For the case of strong coupling, in addition to the rotational polaron described above there arises a renormalized part of the phonon spectrum, whose singularities are determined by the equation

$$\int_0^\infty \frac{d\omega\rho_E(\omega)}{\omega^2(\omega^2-z^2)} = 0. \tag{25}$$

This result was obtained in Ref. 10. We note that Eq. (25) is identical to the equation for the change which occurs in the phonon spectrum upon the formation of the extreme low-frequency pseudolocal vibration when the elastic coupling corresponding to the e mode is broken off completely.

The phonon Green functions are expressed exactly in terms of the electron Green functions.[7] Analysis of the phonon Green functions reveals the existence of an unrenormalized phonon spectrum as well, with an intensity proportional to $1-K_E(E)$, i.e., changing from zero for weak coupling to 1/2 for strong coupling.

Passing in Eq. (24) to the case of no dispersion, $\rho_E(\omega) = \delta(\omega - \omega_0)$, we can obtain, for arbitrary values of the vibronic coupling, an analytical expression for the gap between the ground state and first excited state:

$$z_r/\omega_0 = (1+\beta^2)^{1/2}-\beta, \quad \beta = {}^1/_4\alpha_E{}^2 K_E(E). \tag{26}$$

Comparison of the results of a calculation by formula (26) (curve 1 in Fig. 1) with the calculated results of Muramatsu[19] (curve 2) shows that the results are in satisfactory agreement over the entire range of coupling constants. In the molecular limit one can also obtain an expression for the ground-state energy,
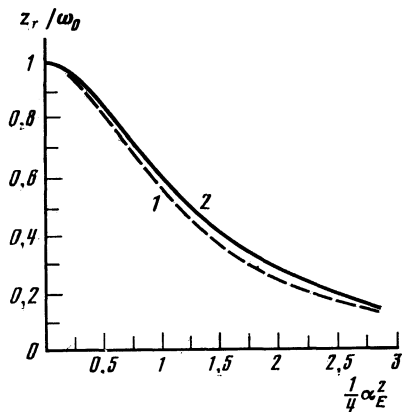

FIG. 1. Curve 1 is our theoretical result [Formula (26) in main text] and curve 2 shows the result of numerical calculations.[19]

$$\Delta\varepsilon/\hbar\omega_0 = -K_E(E)\{1+\beta+(\beta^2-1)(1+\beta^2)^{-1/2}\}, \tag{27}$$

also in good agreement with numerical calculations.[19,20]

Since expression (24) is valid for any phonon dispersion law, it can be used to find the energy of the lowest excited states of the multimode molecular problem. The symmetry of these states is described by angular momenta 1/2 and 3/2.

[1] We note that if the electron operators were defined in terms of the matrix of Clebsch-Gordan coefficients rather than in terms of the 3Γ symbol, the case under discussion would correspond to equality of the coupling constant, i.e., to identical interactions with the tetragonal and trigonal vibrations.

[1] Yu. E. Perlin and B. S. Tsukerblat, Effekty Elektronno-Kolebatel'nogo Vzaimodeĭstviya v Opticheskikh Spektrakh Primesnykh Paramagnitnykh Ionov [Effects of the Electronic-Vibrational Interaction in the Optical Spectra of Paramagnetic Impurity Ions], Shtiintsa, Kishinev (1974).

[2] I. B. Bersuker, Elektronnoe Stroenie i Svoistva Koordinatsionnykh Soedinenii [Electronic Structure and the Properties of Coordination Compounds], Khmimiya, Leningrad (1976).

[3] F. S. Ham, in: Electron Paramagnetic Resonance, Plenum Press, New York (1972), pp. 1–119.

[4] R. Englman, The Jahn-Teller Effect in Molecules and Crystals, Wiley-Interscience, New York (1972).

[5] S. V. Maleev, Zh. Eksp. Teor. Fiz. 79, 1995 (1980); 84, 260 (1983) [Sov. Phys. JETP 52, 1008 (1980); 57, 149 (1983)].

[6] Yu. B. Rozenfel'd and V.Z. Polinger, Zh. Eksp. Teor. Fiz. 70, 597 (1976) [Sov. Phys. JETP 43, 310 (1976)].

[7] A. V. Vaĭsleĭb, V. P. Oleĭnikov, and Yu. B. Rozenfel'd, Fiz. Tverd. Tela (Leningrad) 24, 1074 (1982) [Sov. Phys. Solid State 24, 609 (1982)].

[8] A. V. Vaisleib, V. P. Olejnikov, and Yu.B.Rozenfeld, Phys. Lett. A 89, 41 (1982)

[9] A. V. Vaisleib, Yu. B. Rozenfeld, and V. P. Olejnikov, Phys. Status Solidi B 109, K35 (1982).

[10] V. Z. Polinger and G. I. Bersuker, Phys. Status Solidi B 95, 403 (1979); 96, 153 (1979).

[11] V. Z. Polinger, Zh. Eksp. Teor. Fiz. 77, 1503 (1979) [Sov. Phys. JETP 50, 754 (1979)].

[12] J. C. Slonczewski, Phys. Rev. 131, 1596 (1963).

[13] M. Gell-Mann and M. L. Goldberger, Phys. Rev. 96, 1433 (1954).

[14] E. Henley and W. Thirring, Elementary Quantum Field Theory, McGraw-Hill, New York (1962), Ch. 17,18.

[15] J. C. Griffith, The Irreducible Tensor Method for Molecular Symmetry Groups, Prentice-Hall, Englewood Cliffs, N.J. (1962).

[16] A. V. Vaĭsleĭb, Author's Abstract, Candidate's Dissertation [in Russian], Kazan (1982).

[17] M. C. M. O'Brien, J. Phys. C 4, 2524 (1971); Phys. Rev. 187, 407 (1969).

[18] M. Moffitt and W. Thorson, Phys. Rev. 108, 1251 (1957).

[19] S. Muramatsu and N. Sakamoto, J. Phys. Soc. Jpn. 44, 1640 (1978).

[20] H. C. Longuet-Higgins, U. Öpik, M. H. L. Pryce, and R. A. Sack, Proc. R. Soc. (London) Ser. A 244, 1 (1958), M. S. Child and R. C. Longuet-Higgens, Trans. R. Soc. A 254, 259 (1961).

Translated by Steve Torstveit

621   Sov. Phys. JETP 59 (3), March 1984

Yu. B. Rozenfel'd and A. V. Vaĭsleĭb   621