relation function yields a frequency spectrum $f(\omega)$ which in the case of the harmonic solid is the frequency spectrum of the normal modes. The frequency spectrum for the silver subsystem is, by definition,

$$f(\omega) = (2/\pi)\int_0^\infty \Psi_{\mathrm{Ag}^+}(t')\cos\omega t'\,dt', \tag{11}$$

where $f(\omega)$ is normalized to unity. $f(\omega)$ is where in Fig. 2(b). In principle, $f(\omega)$ can be measured by inelastic neutron scattering experiments.[17] A rough estimation of the position of the main peak of $\sigma(\omega)$ from $\varphi_{\mathrm{AgI}}(t)$ leads to 81 cm^{-1}. The experimentally observed value[18] is 90 cm^{-1}.

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Jahn-Teller Effect in an Orbital Triplet Coupled to Both E_g and T_{2g} Modes of Vibration: Experimental Evidence for the Coexistence of Tetragonal and Trigonal Minima

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We have observed magnetic resonance in the ${}^3T_{1u}$ excited levels of Ga^+ in KBr using an optical detection technique. The A_T and A_X emissions take place from excited states which display tetragonal and trigonal symmetries respectively. A model assuming nearly equal linear coupling to E_g and T_{2g} modes and an additional bilinear coupling to totally symmetric modes, A_{1g}, accounts for the available data: magnetic resonance spectra, and temperature and pressure dependence of the optical spectra.

Characteristic phenomena caused by the Jahn-Teller effect have been observed in (KI:Tl^+)-type phosphors.[1] The luminescent center is of O_h symmetry in its ground state (s^2) and has simple unrelaxed excited states (sp): ${}^3T_{1u}$ and ${}^1T_{1u}$. Öpik and Pryce[2] studied the linear Jahn-Teller effect in ${}^3T_{1u}$ and ${}^1T_{1u}$ states and concluded that either of the tetragonal or trigonal distortion, but not both, will occur. Actually, however, excitation of ${}^3T_{1u}$ through the A absorption band generally

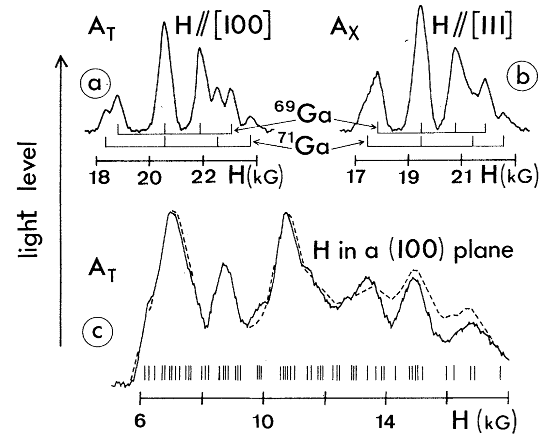

FIG. 1. Light intensity vs magnetic field $\vec{H}$ at $T=1.6$ K. Optical detection is along $\vec{H}$. (a) A_T with $\vec{H} \parallel [100]$ and $\nu = 34.6$ GHz; (b) A_X with $\vec{H} \parallel [111]$ and $\nu = 3.46$ GHz; (c) A_T with $\vec{H}$ in a (100) plane at an angle of 30° from [001] and $\nu = 70.2$ GHz. Dashed line in (c) represents the calculated spectrum using the parameters in Table I. Small vertical ines in (a), (b), and (c) indicate the computed transitions between the two lowest electonic spin levels for the two isotopes of Ga.

produces two emission bands designated as A_T and A_X in order of decreasing energy. Many investigations made so far clearly indicate that the relaxed excited states (RES) responsible for A_T is distorted tetragonally. Recently, Dang *et al.*[3] and Fukuda[4] showed experimentally that the A_X RES are quite similar to the A_T RES; due to the spin degeneracy ($S=1$) they consist of a doubly degenerate level with a nondegenerate trap level below. They further pointed out that the A_X RES may probably be distorted trigonally. In this Letter we report results of electron paramagnetic resonance (EPR) which show for the first time without ambiguity that the A_X RES in KBr:Ga$^+$ is indeed trigonally distorted. To explain most of the characteristic features of A_T and A_X emissions, a model is also proposed based on the bilinear Jahn-Teller coupling which allows for the coexistence of the tetragonal and trigonal distortions.[4,5]

At 1.6 K, optical pumping in the A band at 37 000 cm^{-1} yields a strong emission band A_T at 22 200 cm^{-1} and a much weaker emission band A_X at 18 200 cm^{-1}. The technique for optical detection of magnetic resonance in excited levels has been described elsewhere.[6] Because of the large zero-field splittings expected,[3] EPR was carried out at 70 and 35 GHz in a split-coil superconducting magnet.

For an arbitrary orientation of the magnetic field $\vec{H}$, the EPR spectra are very complex and are spread over nearly 30 kG. They become much simpler when $\vec{H}$ is along a [100] direction for A_T, or along a [111] direction for A_X (see Fig. 1). This strongly suggests that the corresponding EPR spectra have an axial symmetry along these directions. Detailed analysis of the data obtained with $\vec{H}$ along the main crystallographic directions [100], [111], and [110] allowed determination of the parameters (see Table I) of the usual spin Hamiltonian:

$$\mathcal{H}_S = \mu_B \vec{H}\cdot g\vec{S} + D(S_z^2 - \tfrac{2}{3}) + E(S_x^2 - S_y^2) + \vec{I}\cdot A\vec{S}, \qquad (1)$$

where $S=1$ and $I=\frac{3}{2}$ for both isotopes ^{69}Ga and ^{71}Ga, which are present in the natural abundances of 60.2% and 39.8%, respectively.

Although the parameter values of spin Hamiltonian (1) are about the same for A_T and A_X, it should be noted that A_X is of purely trigonal symmetry while A_T is actually of orthorhombic symmetry with its principal axes along [100], [010], and [001]. Because the symmetry of the spectra is lower than cubic and the g values are close to that of the free spin, we have strong evidence for a static Jahn-Teller effect in both A_T and A_X RES's. Actually axial symmetry is expected when an orbital triplet $^3T_{1u}$ is coupled primarily to E_g or T_{2g} modes.[7] In both cases, second-order effects of the spin-orbit interaction give rise to a zero-field splitting[6]:

$$D_{so} = \zeta^2/12E_{JT} - \zeta'^2/4\Delta, \qquad (2)$$

TABLE I. Spin Hamiltonian (1) parameter values for A_T and A_X.

	Direction of axis					D	E	$^{69}A_{x(y)}$	$^{69}A_z$
	x	y	z	$g_x\,(y)$	g_z	(GHz)	(GHz)	(GHz)	(GHz)
A_T	[100]	[010]	[001]	2.00^a	2.02^b	93.6^a	8.0^a	3.6^b	4.04^c
A_X			[111]	2.00^a	2.01^b	90.0^a	<0.2	3.4^c	3.80^c

[a] Ref. 5. [b] Ref. 1. [c] Ref. 2.

where ζ and ζ' are the p-electron spin-orbit matrix elements inside the ${}^3T_{1u}$ and between the ${}^3T_{1u}$ and ${}^1T_{1u}$ states, respectively. $3E_{JT}$ is the Jahn-Teller splitting, and Δ the energy splitting between, say, the relaxed ${}^3T_{1u,z}$ state and the ${}^1T_{1u,x}$ and ${}^1T_{1u,y}$ states.

Dipole-dipole interaction between the electrons of the unfilled shell also contributes to the fine structure.[6] The magnitude of this interaction cannot be evaluated since the wave functions are not known well enough. This contribution to D is negative so that by use of (2) one may deduce an upper limit for E_{JT}: With assumption of the same electron-lattice coupling for the singlet and triplet states, Δ is the sum of the exchange energy (approximately 7200 cm^{-1}) and $3E_{JT}$. Taking $\zeta \approx \zeta' \approx 1000\ \text{cm}^{-1}$, one gets $E_{JT} \lesssim 8000\ \text{cm}^{-1}$, a value which looks reasonable when compared to half the Stokes shift. The contribution of the dipolar interaction to D is expected to be the same for A_T and A_X, so that from the near equality of the D values (see Table I) one can conclude that E_{JT} for A_T and A_X RES's are about the same. The occurence of a nonzero E value for A_T is puzzling. It is true that the adiabatic potential-energy surfaces (APES) in case of coupling of a ${}^3T_{1u}$ to a E_g mode can have six orthorombic minima.[2] However there is no way to stabilize one of the corresponding distortions simultaneously for the three spin levels.

The near equality of the two E_{JT} should not be considered as mere coincidence. Moreover, we think it is connected with the strong temperature dependence of the ratio of the A_T and A_X emission intensities.[1] We shall develop a model for the vibronic coupling which accounts for (i) the activation energy $B = 540\ \text{cm}^{-1}$ which characterizes this temperature dependence.[3] (ii) the values of the A_T and A_X Stokes shifts, (iii) the near equality of the two E_{JT} and their common upper limit, and (iv) the fact that, even at high temperatures, the A_T RES is not thermally populated which is equivalent to saying that the energy difference ΔE between A_T and A_X RES's is larger than 1000 cm^{-1}. We shall follow the usual adiabatic calculations of the electron-lattice interaction by introducing six "interaction-mode" coordinates spanning A_{1g} (Q_1), E_g (Q_2, Q_3), and T_{2g} (Q_4, Q_5, Q_6).[1]

Öpik and Pryce[2] have already investigated the shape of the APES inside the five-dimensional space $(Q_2, \ldots, Q_6)$ and showed that there are two kinds of stationary points of interest. One kind consists of three purely tetragonal distortions corresponding to orbital states p_x, p_y, and p_z. The other kind are the four trigonal distortions such as $Q_4 = Q_5 = Q_6 = Q_{111}/\sqrt{3}$ with the associated orbital state $p_\zeta = (p_x + p_y + p_z)/\sqrt{3}$. If one assumes that the E_g and T_{2g} modes have the same effective mass and frequency and taking k_E and k_T as linear Jahn-Teller coupling coefficients, then the energies of these stationary points are[7] $-\frac{1}{4}k_E^2$ and $-\frac{1}{4}k_T^2$ when the configuration coordinates $Q_2, \ldots,$ and Q_6 are expressed in unit of $(\hbar\omega)^{1/2}$. Öpik and Pryce showed that for $k_E^2 > k_T^2$ the tetragonal stationary points are true minima in the five-dimensional space $(Q_2, \ldots, Q_6)$. For the reverse situation, it is the trigonal stationary points which are the minima. A very interesting situation is the one encountered when $k_E^2 = k_T^2$.[8,9] Then there is a continuum of minima which allows one to go at constant energy from the tetragonal distortion $Q_3 = Q_D$ and the corresponding orbital state p_z to, say, the trigonal distortion $Q_{111} = Q_D$ and the corresponding orbital state p_ζ. Now, as suggested by hydrostatic pressure experiments,[1,10] we shall assume that the coupling coefficients k_E and k_T are some linear functions of the totally symmetrical coordinate Q_1. Then one understands that, depending on the value of Q_1, one may have either $k_E^2 > k_T^2$ or $k_E^2 < k_T^2$ and correspondingly one gets tetragonal or trigonal minima. Minimizing their energies with respect to Q_1, one gets the actual coordinates Q_{1E} and Q_{1T} of the RES's. There is also a value of $Q_1 = Q_{1D}$ for which the condition $k_E^2 = k_T^2$ is realized. One then understands the small value of the activation energy to go from A_T to A_X RES's. One does not need to get over some potential barrier comparable to the Jahn-Teller energy E_{JT}. Instead, one first moves in Q_1 space to get to $Q_1 = Q_{1D}$ (which does not need much energy if Q_{1E} is not very different from Q_{1D}). Then one goes at constant energy from the tetragonal to the trigonal distortion, and finally Q_1 relaxes to its equilibrium Q_{1T} value corresponding to a trigonal minimum. This description is obviously schematic since some of the described vibrational relaxations may take at the same time. Moreover, a true description of the dynamic of the system would involve vibronic states and not APES.

Keeping the same simplified model, we shall now make it more quantitative. For the simplicity of the calculations we take k_E^2 and k_T^2 as linear functions of Q_1. For the quantities to be calculated this is equivalent to the usual assumption which is to take k_E and k_T as linear functions of Q_1.[1] Then the energies of the tetragonal and trigonal stationary points are

$$\langle z|\mathcal{H}|z\rangle = -\tfrac{1}{4}k_E{}^2 + W_1$$

$$= -\tfrac{1}{4}k_D{}^2 - a_E(Q_1 - Q_{1D}) + W_1, \qquad (3)$$

$$\langle \zeta|\mathcal{H}|\zeta\rangle = -\tfrac{1}{4}k_T{}^2 + W_1$$

$$= -\tfrac{1}{4}k_D{}^2 - a_T(Q_1 - Q_{1D}) + W_1, \qquad (4)$$

which are written in a way which makes clear that for $Q_1 = Q_{1D}$ the two Jahn-Teller energies are equal, and where we have added the potential energy associated with Q_1: $W_1 = Q_1{}^2 - k_1Q_1$. The origin of Q_1 is chosen at the equilibrium position when the ion is in its ground state; and for simplicity the lattice potential $Q_1{}^2$ will be assumed to be the same in the excited and ground states. Minimizing (3) and (4) one obtains the two values Q_{1E} and Q_{1T} for which the tetragonal A_T and trigonal A_X minima occur. The corresponding Jahn-Teller energy for A_T is given by

$$E_{\mathrm{JT}}(A_T) = \tfrac{1}{4}k_D{}^2 + \tfrac{1}{2}a_E(k_1 + a_E - 2Q_{1D}). \qquad (5)$$

Then the Stokes shift (SS) and the activation energy B required to move from the A_T minimum to the saddle point are given respectively by

$$\mathcal{S}(A_T) = 2E_{\mathrm{JT}}(A_T) + \tfrac{1}{2}k_1(k_1 + a_E), \qquad (6)$$

$$B = \tfrac{1}{4}(k_1 + a_E - 2Q_{1D})^2. \qquad (7)$$

Similar expressions are obtained for A_X.

We have five parameters k_1, k_D, a_E, a_T, and Q_{1D} to fit the data. By considering k_1 as an adjustable parameter, it is easy to calculate the quantities of interest, and one realizes that there is a narrow range of values of k_1 which allow a general fit. A plausible set of the parameters is the following: $k_1 = 60$, $k_D = 151$, $a_E = -86.4$, $a_T = 47$, and $Q_{1D} = 10.3$ (all expressed in $\mathrm{cm}^{-1/2}$). This leads to $E_{\mathrm{JT}} = 7700\ \mathrm{cm}^{-1}$ and $\Delta E = 1320\ \mathrm{cm}^{-1}$ (see Fig. 2). The sign of a_E was chosen so that A_T is a more compact state than A_X as evidenced by pressure measurements.[1,10] Presently we do not see clearly why A_T is preferentially populated in the nonradiative process; it is true that the slope of the APES is larger for Q_3 than it is for Q_4, Q_5, and Q_6 at the origin (i.e., $Q_i = 0$, for $i = 1, \ldots, 6$) but the difference does not seem to be large enough. A crucial test of the model will be the measurement of the temperature dependence of A_T and A_X emissions under hydrostatic pressure.

These results and others on F^+ centers in CaO[11] and KCl:Au$^-$ [12] illustrate a qualitative difference in the Jahn-Teller couplings in triplet states originating from a d or p states in octahedral symmetry. The former are most of the time coupled primarily to E_g modes.[13] For the latter, the coupling to E_g and T_{2g} modes is approximately the same, and when it is small the vibronic states retain a "spherical" symmetry.[8] When it is large, an additional bilinear coupling to the totally symmetrical mode Q_1 allows the coexistence of tetragonal minima in the six-dimensional configuration-coordinate space.

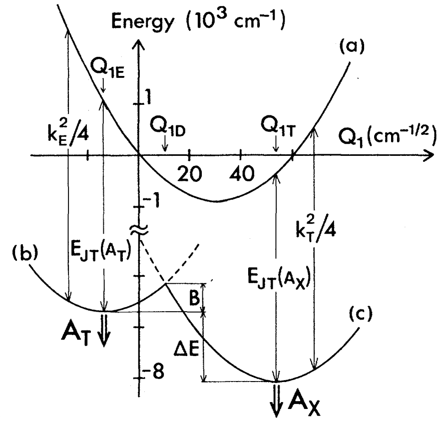

FIG. 2. Energy of the excited state A as a function of the Q_1 coordinate before (curve a) and after coupling to E_g modes (curve b) or to T_{2g} modes (curve c) has been included. Curve (b) represents the energy of the tetragonal minima [Eq. (3)], while curve (c) represents the trigonal minima [Eq. (4)]. Dashed line represents stationary points which are not minima. Intersection of curves b and c is actually a two-dimensional space at constant energy (see Ref. 8).

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Electronic Structures of GaAs-Ga$_{1-x}$Al$_x$As Repeated Monolayer Heterostructure

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We present the first pseudopotential calculation of the fundamental band gaps for heterostructures consisting of alternating monolayers of GaAs and Ga$_{1-x}$Al$_x$As ($0 \leq x \leq 1$). Significant differences are found between the GaAs-AlAs gaps and those of the Ga$_{0.5}$Al$_{0.5}$As random alloy. The imaginary part of the dielectric function has been calculated for GaAs-AlAs and appears consistent with the experimentally reported optical absorption edge.

With molecular beam epitaxial techniques (MBE) it is possible to grow repeated heterostructures made up of very thin layers of semiconducting materials.[1,2] One of the most interesting features of these materials is that they add a periodic potential along the heterostructure axis to the usual lattice periodic potential. By changing the layers' composition and thickness basically new devices are produced with energy bands and electronic properties artificially varied over wider limits than exist in "naturally occurring materials." Recently Gossard and co-workers have reported producing the GaAs-AlAs monolayer heterostructure.[3] This requires depositing alternate single monolayers of Ga, As, Al, and As on the (001) GaAss substrate. In this Letter we report the first theoretical study of the energy spectrum of the monolayer material using the semi-empirical pseudopotential method. The motivation for this study is twofold. First, unlike heterostructures whose layers are between a few tens and a few hundreds of angstroms thick and whose potential in the z direction can be represented by a series of rectangular wells capable of trapping carriers in two-dimensional quantum states, the properties of much thinner heterostructures cannot be calculated from the effective-mass approximation in the Kronig-Penney model. As the layers become thinner the quantum states extend through the barriers and couple,[4] eventually losing all two-dimensional character. Thus in the monolayer case, a three-dimensional band structure calculation is needed; a pseudopotential method is capable of serving this purpose well. Second, because self-diffusion constants usually quoted for high quality III-V crystals are from 10^{-11} to 10^{-14} cm^2/sec,[5] it might be expected that such thin layers would completely blend together producing a Ga$_{2-x}$Al$_x$As$_2$ random alloy. However, Dingle has inferred $D < 10^{-22}$ cm^2/sec for multilayer heterostructures grown at 600°C.[6] But this implies similarly small diffusion in the monolayer structure only if the small D results from the MBE method and not from the multilayer structure itself. This prompted us to calculate the composition dependence of the band structures of both the repeated monolayer material and the usual random alloy. We have also calculated ϵ_2 for GaAs-AlAs in order to provide a basis for comparison with optical experiments. Full energy bands and details of the calculation will appear in a later paper.

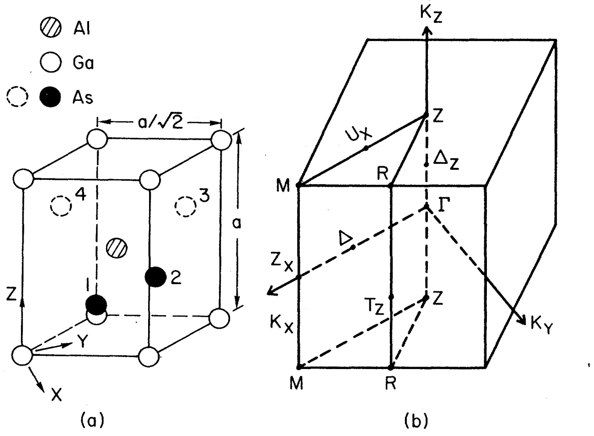

FIG. 1. (a) Tetragonal unit cell of GaAs-AlAs monolayer. (b) Brillouin zone of the monolayer structures.