Structural Phase Transition Induced by the Jahn-Teller Effect. Antiferrodistortive Ordering

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We study the phase transitions induced by the Jahn-Teller effect of E-doublet ions in a cubic crystal with antiferrodistortive interactions. An S=1 pseudospin model is constructed which takes the three lowest vibronic levels of the Jahn-Teller complexes into account. We find a second-order phase transition to a tetragonal phase with two inequivalent sublattices. The transitions between the vibronic levels give rise to bands of collective vibronic excitations with strongly temperature-dependent frequencies. The nature of the various modes is analyzed in detail. We also study the coupling to the elastic displacement field of the crystal. For a sufficiently large coupling constant, this coupling stabilizes a different low-temperature tetragonal phase with two equivalent sublattices. In a certain region of coupling constants, a transition occurs between the two tetragonal phases by second-order transitions to an intermediate phase of lower symmetry. The influence of the coupling on the dynamic behaviour is discussed.

I. Introduction

The Jahn-Teller (JT) effect in crystals containing ions with orbital degeneracy has a destabilizing influence on the ionic structure, and may thus induce structural phase transitions in a crystal which would be stable in the absence of electron-lattice interaction (cooperative JT effect). We present here a theoretical treatment of such a transition with particular emphasis on the dynamic behaviour of the system. The dynamical properties have their origin in the transitions between the low-lying vibronic levels of the JT-complexes. Because of the lattice-dynamical coupling, these transitions give rise to bands of collective vibronic excitations with a characteristic temperature dependence associated with the transition. Surveys of both experimental and theoretical work on the JT effect can be found in the review articles of Sturge [1] and Gebhardt [2] and in the books of Ham [3] and Englman [4]. In the present paper, we consider phase transitions in ionic crystals induced by the cooperative JT effect of transition-metal ions with E-doublet ground state in octahedral environment. Transitions of this type have been observed in perovskites and spinels containing Ni\(^{2+}\), Cu\(^{2+}\), Sc\(^{2+}\), Cr\(^{2+}\), or Mn\(^{3+}\) ions. References to various examples can be found in [5–10]. In particular, the work of Reinen and Friebel [11–13] and of Kroese and Maaskant [14] on the JT ion Cu\(^{2+}\) in different compounds is of special interest for us.

The case of JT and pseudo-JT-induced transitions in crystals containing rare earth ions, on the other hand, has been studied by a number of authors. Reviews of this work are given by Elliott et al. [15] and by Gehring and Gehring [16]. Our discussion is further limited to the case of ionic crystals. Phase transitions induced in metals by a “band JT effect” have recently been discussed [17, 18].

The JT effect as a mechanism for structural phase transitions was first considered by Dunitz and Orgel [5]. The theory of such JT-induced transitions has been treated in a number of papers [6–10, 16, 19–21]. A discussion of the general mechanism and a classification of the various types of transition can be found particularly in [9, 16, 20]. While the role of the strong correlation between the ionic and the electronic motion of a JT complex is emphasized in the treatments [9, 10, 20], this correlation is neglected and is
replaced by an interaction between the mean ionic and electronic motion (random phase approximation on the same site) in [7, 8, 19]. As a consequence, the local JT distortion becomes temperature dependent and is zero above the transition, and for the transition temperature one obtains the unphysical result that it is finite for non-interacting JT complexes and decreases with increasing interaction strength. The shortcoming of this approach has also been pointed out by Halperin [23].

The theory of JT-induced cubic-to-tetragonal transitions in crystals with E-doublet ions was developed for the case of ferrodistortive interactions in [10]. In the present paper, we extend the theory to the experimentally important case of antiferrodistortive ordering, with particular emphasis on the dynamic aspects.

The purely static antiferrodistortive order-disorder case is presented in [21]. The theoretical model is developed in Section II. We start with the JT effect of a single octahedral complex and introduce an $S=1$ pseudospin representation for the case of strong localization in configuration space. The single complexes are then coupled by an antiferrodistortive lattice-dynamical interaction. The static properties of the model are discussed in mean-field approximation (MFA) in Section III, the dynamic properties are studied in random-phase approximation (RPA) in Section IV. In Section V, the influence of the coupling to the elastic displacement field on the static and dynamic properties is investigated.

II. Model of a Jahn-Teller Crystal

II.1. Jahn-Teller Effect of a Single Complex

We consider an $E$-doublet JT ion in octahedral environment with electronic ground-state wave-functions $\psi_1$ and $\psi_2$ transforming as

$$\psi_1(r) = \frac{1}{\sqrt{2}}(x^2 - y^2), \quad \psi_2(r) = (x^2 + y^2).$$

(1)

The electronic motion of the JT ion is coupled to the ionic motion of the ligands of the surrounding octahedral complex. Linear JT coupling occurs with the local normal coordinates $Q_3$ and $Q_2$ of the octahedral complex which transform also according to the $E$-representation (Fig. 1). In the $(Q_3, Q_2)$-plane, we introduce polar coordinates

$$Q_3 = \rho \cos \theta, \quad Q_2 = \rho \sin \theta.$$ 

(2)

Cubic crystal symmetry induces $C_{3v}$-symmetry in the $(Q_3, Q_2)$-plane.

We assume that the system is well described by taking only the electronic states $\psi_1$ and $\psi_2$ and the ionic coordinates $Q_3$ and $Q_2$ into account. This approach is valid, if all other electronic states have much higher excitation energies and if there is only weak coupling to other ionic coordinates. The vibronic state of the complex is then given by a wave function

$$\Psi(Q, r) = \Phi_1(Q) \psi_1(r) + \Phi_2(Q) \psi_2(r).$$

(3)

The Hamiltonian describing the coupled ionic and electronic motion is represented with respect to the electronic basis ($\psi_1, \psi_2$) by the matrix

$$H = (P^2/2 + V_1(Q)) + V_3(Q) \sigma_3 + V_2(Q) \sigma_1.$$ 

(4)

$P = (P_3, P_2)$ are the momenta conjugated to $Q = (Q_3, Q_2)$ and $\sigma_1, \sigma_3$ are the Pauli matrices. By means of the Wigner-Eckart theorem we can see that $V_1$ must be invariant against the operations of the cubic symmetry group, and $V_3, V_2$ have to transform as $Q_3, Q_2$.

According to the same theorem, the Taylor series of the potential with respect to $Q$ starts with the terms

$$V_1(Q) = \omega^2_0 (Q_3^2 + Q_2^2)/2 + B_3 (Q_3^3 - 3Q_3 Q_2^2)$$

$$+ B_4 (Q_3^4 + 2Q_2^4 - 3Q_3^2 Q_2^2)$$

$$V_3(Q) = A_3 Q_3 + A_5 (Q_3^3 - Q_2^2) = A_3 \rho \cos \theta + A_5 \rho^2 \cos 2\theta$$

$$V_2(Q) = -A_4 Q_2 + 2A_5 Q_3 Q_2 = -A_4 \rho \sin \theta + A_5 \rho^2 \sin 2\theta.$$ 

(5)

The potential $V_1$ gives rise to a twodimensional Einstein oscillator with harmonic frequency $\omega_0$ and third and fourth order anharmonicities $B_3$ and $B_4$, the eigenstates of which are all electronically doubly degenerate. The JT terms $V_1$, $V_3$, and $V_2$ describe the coupling between the ionic and electronic motion. For fixed ionic configuration, the harmonic part of $V_1$ and the linear JT coupling terms produce the "Mexican hat" energy surface

$$E = \frac{1}{4} A \rho + \frac{\omega_0^2}{2} \rho^2/2,$$ 

(6)

associated with the electronic states

$$\psi_1(r, Q) = \psi_1(r) \sin \theta/2 + \psi_2(r) \cos \theta/2 = (\sin \theta/2, \cos \theta/2)$$

$$\psi_2(r, Q) = \psi_1(r) \cos \theta/2 - \psi_2(r) \sin \theta/2 = (\cos \theta/2, -\sin \theta/2).$$ 

(7)

Characteristic quantities are the depth of the potential $E_0$ at its minimum and the coordinate $\rho_0$ of the minimum,

$$E = -E_0 = -A \rho_0/2 = -\omega_0^2 \rho_0^2/2; \quad \rho_0 = A/\omega_0^2.$$ 

(8)

The destabilisation energy $E_0$ favours the distorted configuration of the complex, and therefore provides the energetic mechanism for the JT-induced phase transition. The dynamic behaviour of the complex is governed by the ratio of vibrational zero point energy $\hbar \omega_0/2$ to