Cooperative Jahn-Teller transitions with tripling of the period: CaCuCl₃

D. I. Khomskiĭ

P. N. Lebedev Physics Institute, USSR Academy of Sciences

It is shown that the cooperative Jahn-Teller effect can be accompanied by a structural transition with tripling of the period, similar to the transition observed in CsCuCl₃. The absence of softening of the phonons with $q = 2\pi/3c$ at $T > T_c$ is explained. It is shown that uniaxial pressure can alter the period of the low-temperature phase.

A first-order transition due to the cooperative Jahn-Tell effect (CJTE) was observed in CsCuCl₃ at 423 K. [1] The high-temperature phase has a hexagonal structure of the CsNiCl₃ type (one-dimensional chains of octahedra of CuCl₆ along the c axis, with a common face and two octahedra in the unit cell); at $T < T_c$ the period along the c axis is tripled. This is not a typical situation of substances with CJTE, in which one usually observes a deformation of either the "ferro" or "antiferro" (with doubling of the period) type. CsCuCl₃ is at present the only known example in which the distortion has a more complicated form. In this paper we explain the mechanism that leads to the observed structure.

Describing, as usual[2,3] the ordering in a system with a doubly degenerate e_g level on the Cu²⁺ ion by means of a pseudospin value $\sigma_i = 1/2$ or by the coordinates of the oscillations (Q_2, Q_3), we can characterize the ordering by means of the modulus of the order parameter $|\Delta| = |\langle \sigma_i \rangle|$ and the phase ϕ_i in the (σ^x, σ^z) or (Q_2, Q_3) plane. The interaction of the degenerate orbitals on the centers i and j is given by

$$H = \frac{1}{2} \sum_{ij} J_{ij} \vec{\sigma_i} \vec{\sigma_j} . \tag{1}$$

In principle, the interaction (1) could itself lead to a tripling of the period, if the Fourier transform of the exchange constant $J(q)$ were to have a maximum at $q = 2\pi/3c$. This, however, seems accidental and not very probable. We shall show that a transition with a tripling of the period is possible also in an interaction (1) of the "antiferro" type when simultaneous account is taken of the effect of the anharmonicity that stabilizes the hole orbitals of the type $d_{x^2-y^2}$ on the Cu²⁺ ions.

Allowance for the local anharmonicity leads to the appearance in the energy of terms of the type[3] $-g|\Delta|^3 \sum_i \cos 3\phi_i$. As a result, the determination of the type of order reduces to linearization, with respect to the phases ϕ_i of the free energy

$$F = -\tilde{g} \sum_i \cos 3\phi_i + \tilde{J}_1 \sum_i \cos(\phi_i - \phi_{i+1}) + \tilde{J}_2 \sum_i \cos(\phi_i - \phi_{i+2}),$$

$$\tilde{g} = g|\Delta|^3, \qquad \tilde{J}_a = J_a|\Delta|^2. \tag{2}$$

We have retained here, by virtue of the quasi-one-dimensional character of $CsCuCl_3$, only the interaction along the c axis and have confined ourselves to an approximation that takes the nearest neighbors and the next-nearest neighbors into account. In this case J_1 and J_2 are positive, as follows from an analysis of the crystal structure; the anharmonicity constant for the Cu^{2+} ion is also positive, and the elongated octahedra become stabilized in all cases without exception. [4, 8]

An exactly similar situation, which reduces to minimization of expression (2) with respect to the phases ϕ_i, is encountered in the analysis of three-dimensional ordering of charge-density waves in layered dichalcogenides of transition metals. [5-7] As shown in[7], depending on the ratio of the constants, two types of solution exist, with doubling and with tripling of the period. We present here the results that can explain the singularities of the transition in $CsCuCl_3$.

We consider first the case of strong anharmonicity, $\tilde{g} > \tilde{J}$. In this case the phases ϕ_i take on values near 0 and $\pm 2\pi/3$. Taking into account the interaction between the centers (1), two solutions are possible. The first solution of (a) is a two-sublattice structure, in which, for example, the phases $\pm(2\pi/3 - \delta)$ alternate (canted pseudospins). For layered compounds this solution was obtained by McMillan[6]; in substances with CJTE it was obtained by Kanamori, [3] who has shown that it is realized in perovskites of the type MnF_3 and $LaMnO_3$. The value of δ is determined by minimization of the energy (2); the energy obtained by perturbation theory in $\tilde{J}/\tilde{g}$ is of the form

$$F_{(a)} = -N(\tilde{g} + \tilde{J}_1/2 - \tilde{J}_2 + \tilde{J}_1^2/6\tilde{g}). \tag{3}$$

In this case $\delta = \tilde{J}_1\sqrt{3/9\tilde{g}}$. With decreasing anisotropy, δ increases and the phases $\phi_i \to \pm\pi/2$ as $\tilde{g} \to 0$.

If the anharmonicity is strong, another solution (b) with tripling of the period (phases $\phi_i = 2\pi/3$) becomes possible. The energy of this configuration is

$$F_{(b)} = -N(\tilde{g} + \tilde{J}_1/2 + \tilde{J}_2/2). \tag{4}$$

Comparison of (3) and (4) shows that the solution (b) is more likely upon satisfaction of the condition[7] $\tilde{J}_2 > \tilde{J}_1^2/9\tilde{g}$ or $J_2 > J_1^2/9g|\Delta|$. This is apparently the case realized in $CsCuCl_3$.[1] In view of the absence of cubic terms in the free energy, the corresponding phase transitions should be of first order, as is indeed observed in experiment.

The foregoing approach provides a natural explanation for the absence of softening of phonons with $q = 2\pi/3c$ at $T > T_c$[9]: the distortion with this value of q becomes stabilized on account of the terms $g|\Delta|^3\cos3\phi$, and above T_c these terms play no role whatever. The mode that is more likely to be softened at $T > T_c$ is the one corresponding to doubling of the period (or here, when account is taken of the presence of two layers per unit cell, one of the optical modes with $q = 0$).

In principle it is possible to alter the character of the low-temperature phase by applying external action. Thus, uniaxial compression in the basal plane, directed along the projection of one of the local axes of the octahedra of $CuCl_6$, increases the energy of one of the admissible states (for example, with $\phi \approx 0$—an octahedron elongated along the compression axis), and lowers the energy of the two others. The energy then acquires a term of the type $F_p = \lambda P |\Delta| \Sigma_i \cos\phi_i$ (we consider only the influence of the pressure on the phase of the order parameter). By adding the corresponding contribution to (3) and (4) we find that the solution (a) becomes more favored than (b) at $\lambda P > 3 |\Delta| (J_2 - J_1^2/9g |\Delta|)$ (in this case we still have $\lambda P \ll J_1 \sim kT_c$). We see that the realignment of the structure becomes easier at small values of Δ (for example, near T_c). To the contrary, uniaxial compression in the basal plane, directed at an angle 30° to the projections of the axis of the octahedra, corresponds to a change in the sign of the expression for F_p, and leads to stabilization of the phase with the tripled period.

Inasmuch as realization of one type of lattice distortion or another depends on the numerical values of the parameters, it would be of interest also to investigate other analogous compounds containing Jahn-Teller ions, for example, a compound of the TMMC type with Cu^{2+} in place of Mn^{2+}. We note that the period of the $CsCuF_3$ lattice, according to the data of[10] is not tripled but doubled in comparison with the period of the undistorted structure.

[1] The solution (a) in substances of the type $CsNiCl_3$, which have two octahedra per unit cell, would correspond not to a doubling of the period along the c axis, but to no change in the period, $c' = c$.

[1] C. J. Kroese, J. C. M. Tindemans-van Eyndhoven, and W. J. A. Maackant, Solid State Commun. **9**, 1707 (1971).
[2] G. A. Gehring and K. A. Gehring, Rep. Prog. Phys. **38**, 1 (1975).
[3] J. Kanamori, J. Appl. Phys. Suppl. **31**, 14S (1960).
[4] D. I. Khomskii and I. I. Kugel, Solid State Commun. **13**, 763 (1973).
[5] L. N. Bulaevskiĭ and D. I. Khomskiĭ, Pis'ma Zh. Eksp. Teor. Fiz. **23**, 581 (1976) [JETP Lett. **23**, 532 (1976)].
[6] W. L. McMillan, Phys. Rev. **B14**, 1496 (1976).
[7] L. N. Bulaevskiĭ and D. I. Khomskiĭ, Zh. Eksp. Teor. Fiz. **73**, No. 9 (1977) [Sov. Phys. JETP **46**, No. 3 (1977)].
[8] C. Friebel and D. Reinen, Z. Anorg. Allg. Chem. **407**, 193 (1974).
[9] S. Hirotsu, J. Phys. C **8**, 212 (1975).
[10] D. Babel, Z. Naturforsch. Teil A **20**, 165 (1965).