ON THE JAHN–TELLER-DISTORTED HELICAL STRUCTURE OF CsCuBr$_3$

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Abstract. The previously determined structure of CsCuBr$_3$ is rationalized and can be understood as a combination of a Jahn–Teller effect and magnetic exchange interactions. Its *hc* structure is a consequence of a spin-Peierls effect. The unusual occurrence of this effect arises because of alternating stretched and bent Cu–Br–Cu superexchange paths.

Key words: Jahn–Teller effect, magnetic superexchange, spin-Peierls effect, hexagonal perovskites.

INTRODUCTION

This compound has been investigated by Ting-i Li and Stucky [1]. The structure is orthorhombic with the axes $a = 12.776$, $b = 7.666$, and $c = 12.653$ Å. Its space group is a subgroup of P6$_3$/mmc, with a 4L (*hc*) stacking of layers. So far this is the only exception since the Jahn–Teller (JT) compounds CsCuCl$_3$ [2], CsCrCl$_3$ [3], RbCrCl$_3$ [4, 5], CsCrI$_3$ [3], and RbCuCl$_3$ [6] all have superstructures with an *h* stacking (2L). The *hc* stacking can be described as consisting of structural dimers of face-sharing CuCl$_6$ octahedra corner-connected with three similar dimers above and three dimers below.

4L (*hc*) stacking occurs e.g. in HT-BaMnO$_3$ and BaRuO$_3$ and is intermediate between the cubic (3L) and the hexagonal (2L) arrangement of the layers AX$_3$ of compounds with a composition ABX$_3$ (e.g. Wells [7], Megaw [8], Goodenough and Longo [9]). Goldschmidt [10] defined a tolerance factor depending on the empirical radii of the respective ions. However, an explanation of the stacking in CsCuBr$_3$ as a result of the radii of the ions is not likely since CsNiBr$_3$ [11], CsMgBr$_3$ [12], CsCdBr$_3$ [12],

CsMnBr$_3$ [13, 14, 15], and CsCrBr$_3$ [16] have all an h stacking and belong to the aristotype of hexagonal perovskites.

A question arises then why CsCuBr$_3$ has a different layer stacking?

Ting-i Li and Stucky [1] have also investigated the magnetic susceptibility of this compound. They have found completely coupled spins up to 300 K. They ascribe this to a relatively strong superexchange of the approximately 180° interaction in the superexchange path between two corner-connected CuBr$_6$ octahedra. These two corner-connected CuBr$_6$ octahedra, which are magnetically coupled, are said to form a magnetic dimer, which differs from the structural dimers defined before.

In the following we give an explanation for a 4L stacking based on the Jahn–Teller effect (JTE) and magnetic interactions. Besides, it is shown that this compound is similar to CsCuCl$_3$ having an optically active superstructure.

MAGNETIC EXCHANGE PATHS

For a long time already it has been recognized that the JTE has an important role in determining the magnetic superexchange path between transition metal ions. E.g. for Cu^{2+} octahedral halides there is only one orbital for each Cu ion which carries a magnetic moment. And only through the ligand which connects those two orbitals for the neighbouring sites an appreciable magnetic interaction arises, depending still on the angle of intersection. A nice example of this phenomenon has been found in the one-dimensional magnetic chains in KCuF$_3$ [17].

When one sketches the exchange paths for CsCuCl$_3$ and for CsCuBr$_3$ by selecting the anions which have short distances to both neighbouring Cu ions, one finds that these constitute chains which are not interconnected. In CsCuCl$_3$, all Cu–Cl–Cu parts are equivalent both in distance and in angle. The angle is 81.12° in CsCuCl$_3$, so the magnetic interaction between two Cu^{2+} ions is relatively weak. Each column of face-sharing octahedra contains one magnetic chain, which winds itself around that column. In CsCuBr$_3$, however, these chains have alternately Cu–Br–Cu angles of 82.02° and 171.46°, so that each Cu ion contributes to one weak and one strong magnetic interaction. Ting-i Li and Stucky [1] have measured the magnetic susceptibility of this compound. This turns out not to be experimentally different from zero, which has led them to the conclusion that the unpaired electrons of the copper ions are completely coupled. Conceptually one might say that a spin-Peierls transition has taken place, when comparing CsCuBr$_3$ to CsCuCl$_3$. Whereas usually one thinks of a spin-Peierls transition as the one changing distances [18], here the essence is the change in the angle of the superexchange path from almost 90° to almost 180°, which leads from a small magnetic interaction at the acute angle to a strong antiferromagnetism in magnetically isolated dimers.

A JAHN–TELLER-INDUCED $h \to hc$ TRANSITION

Although at the first instant one would regard the structure of $CsCuBr_3$ as a superstructure of an hc stacking, there are two reasons which make it more probable to think in this case of a transition from an h packing. As shown above, $CsBBr_3$ with B a non-Jahn–Teller ion has invariably an h structure. Secondly, when comparing the magnetic path in $CsCuBr_3$ with the one in $CsCuCl_3$, one can see exactly which face-sharing dimers belonged to the same h stack before transforming. It is therefore plausible to imagine a conceptual displacive phase transition between the h and the hc stacking. Since the c-axis is doubled with respect to the original hexagonal perovskite, the q vector belongs to the A point in the 1st BZ.

In Fig. 1 a wave of a shift in the x direction is depicted, which describes the cutting of the Cu stack in face-sharing dimers.
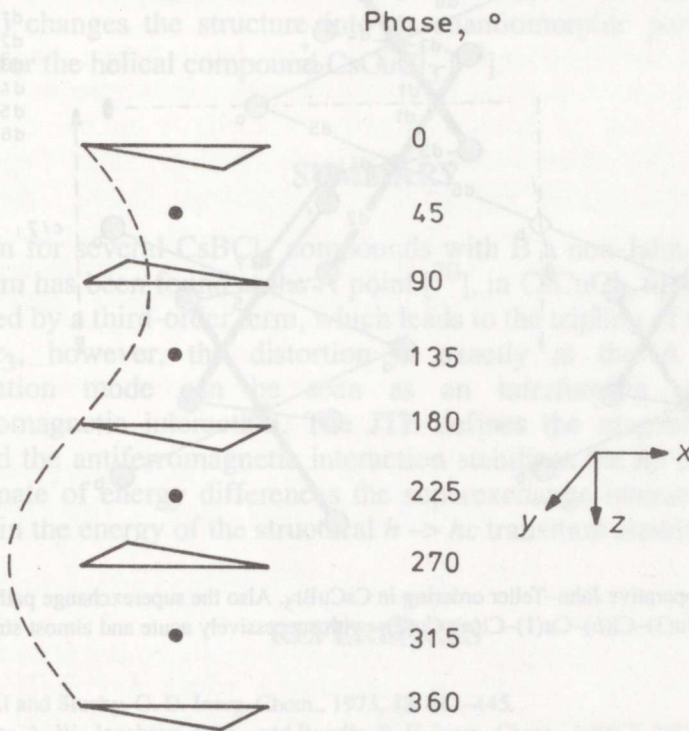

Fig. 1. Shift of layers such that h stacking is converted into hc stacking. This shift belongs to a wave at the A point ($q = 0,0,\pi/c$) with respect to the h lattice.

This can also be expressed as follows:

$$m_{xq} = -(1/2N)^{-1/2} \sum_n (-1)^n m_{n0x} \cos(\pi z_n/c). \tag{1}$$

It would be a mistake to draw long axes from the Jahn–Teller effect in Fig. 1, since the observed arrangement is fully adapted to the hc structure. In Fig. 2 a slightly idealized picture of the observed structure is given. The

structure consists of layers of equally oriented structural Cu dimers. Each dimer is connected to three dimers in the upper slab and three dimers in the layer below. Dimers of successive layers are differently oriented. A 2-fold axis through Br(b), practically perpendicular to the plane of the paper, connects these dimers. There is also a 2_1-axis, parallel to z, which passes close to Br(b) and which connects these two dimers. Each dimer has also a 2-fold axis through Br(a), as indicated in one case. A third dimer in the lower slab, which is also connected to the upper dimer and which contains Cu ion nr. 7, is not drawn for reasons of clarity. Br(a) and Br(b) correspond to Br(1) and Br(3) of the structure determination [1]. Note the difference between the magnetic dimers and the structural dimers.
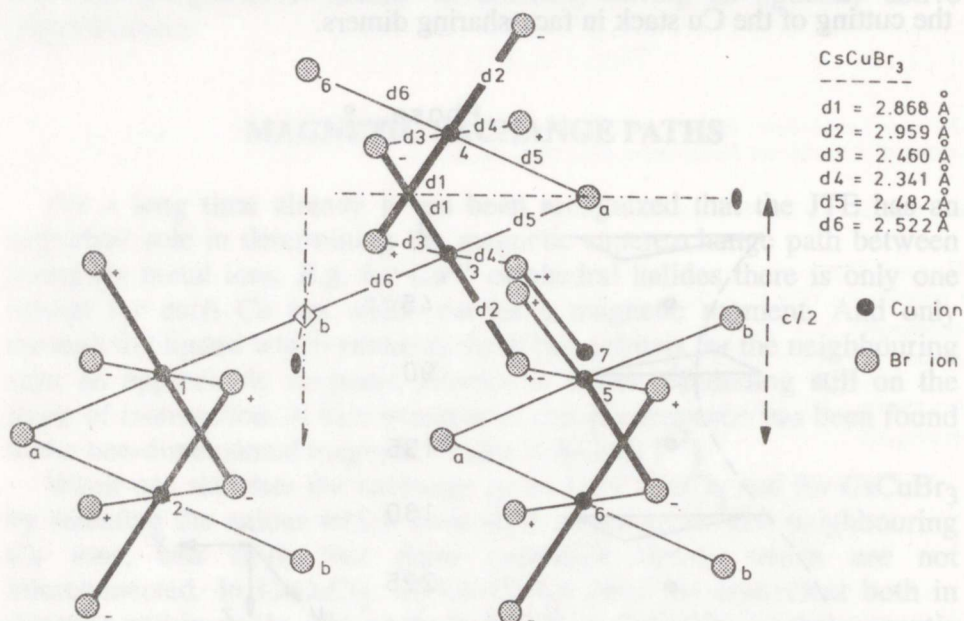

CsCuBr₃

d1 = 2.868 Å
d2 = 2.959 Å
d3 = 2.460 Å
d4 = 2.341 Å
d5 = 2.482 Å
d6 = 2.522 Å

● Cu ion
◉ Br ion

Fig. 2. The cooperative Jahn–Teller ordering in CsCuBr₃. Also the superexchange path of –Cu(b)–Cu(4)–Cl(a)–Cu(3)–Cl(b)–Cu(1)–Cl(a)–Cu(2)– with successively acute and almost straight angles is shown.

Figure 2 has been drawn in order to show the superexchange path (Br(b)–Cu(4)–Br(a)–Cu(3)–Br(b)–Cu(1)–) and the cooperative JT ordering. The + and – signs indicate whether Br ions are in front or behind Cu(5). The long bonds, due to the JTE, are denoted by a thicker line. Once the exchange path is chosen, there are two possible orientations for the JTE in a dimer. If one of them is chosen, the ordering in successive layers is also fixed, when it is assumed that all dimers in the a,b plane are equally oriented and that two long axes attached to one Br ion is not allowed.

The displacements of the Br ions in each octahedron can be described in a first approximation by the quadrupoles situated on the Cu ions by the following equations:

$$Q_{qxz} = - (\tfrac{1}{2}N)^{-\frac{1}{2}} \Sigma_n (-1)^n Q_{n0xz} \sin(\pi z_n/c), \qquad (2)$$

$$Q_{qyz} = - (\tfrac{1}{2}N)^{-\frac{1}{2}} \Sigma_n (-1)^n Q_{n0yz} \cos(\pi z_n/c), \qquad (3)$$

where Q_{n0xz} and Q_{n0yz} are unit quadrupoles attached to Cu(n), all oriented in the same way.

All these deformations belong to the A point in the 1st BZ of the h cell. In the harmonic theory the amplitudes Q_{0xz} and Q_{0yz} are related. However, the amplitude of the displacement mode with respect to the h cell is so large that anharmonicity is expected. So the quadrupole amplitudes adjust themselves independently, such that in each octahedron the long axes can be placed in accordance with the local minima in the JT trough. Nevertheless the occurrence of these two quadrupole amplitudes reminds us of a helical structure. The space group of this structure is $C222_1$ (D_2^5), which is enantiomorphic. The changing of the sign of the expression Q_{qyz} (Eq. (3)) changes the structure into its enantiomorphic partner. This is similar for the helical compound $CsCuCl_3$ [19].

SUMMARY

When for several $CsBCl_3$ compounds with B a non-Jahn–Teller ion a minimum has been found at the A point [20], in $CsCuCl_3$ this minimum is overruled by a third-order term, which leads to the tripling of the c-axis. In $CsCuBr_3$, however, the distortion is exactly at the A point. The deformation mode can be seen as an interference of JTE and antiferromagnetic interaction. The JTE defines the magnetic exchange path and the antiferromagnetic interaction stabilizes the hc structure. For an estimate of energy differences the superexchange interaction and the change in the energy of the structural $h \rightarrow hc$ transition should be known.

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CsCuBr₃ JAHNI–TELLERI MOONUTUSEGA SPIRAALSTRUKTUURIST

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Mitmetel CsBCl₃-ühenditel, kus B ei ole Jahni–Telleri tüüpi ioon, on energiamiinimum A-punktis. CsCuCl₃-l prevaleerib kolmandat järku liige, mille tõttu c-telg on kolmandat järku. CsCuBr₃-l on moonutus siiski täpselt A-punktis. Deformatsioonimood on käsitletav Jahni–Telleri efekti ja antiferromagnetilise interaktsiooni interferentsi kaudu. Jahni–Telleri efekt määrab magnetilise vahetuse trajektoori ja antiferromagnetiline interaktsioon stabiliseerib hc-struktuuri. Energiadiferentside hinnanguks on vaja teada supervahetusinteraktsiooni ja struktuurse siirde $h \rightarrow hc$ energiamuutust.

О СПИРАЛЬНОЙ СТРУКТУРЕ CsCuBr₃ С ЯН–ТЕЛЛЕРОВСКИМ ИСКАЖЕНИЕМ

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Некоторые соединения CsBCl₃ с ионом B, не являющимся ян-теллеровским, имеют минимум энергии в точке А [20]. В CsCuCl₃ превалирует член третьего порядка, что приводит к c-оси третьего порядка, однако в CsCuBr₃ искажение точно в точке А. Деформационная мода рассматривается через интерференцию эффекта Яна–Теллера (ЭЯТ) и антиферромагнитного взаимодействия. ЭЯТ определяет магнитную обменную траекторию и антиферромагнитное взаимодействие стабилизирует hc-структуру. Для оценки разностей энергий нужно знать суперобменное взаимодействие и изменение энергии структурного перехода $h \rightarrow hc$.