## Jahn-Teller-like model for the 208-K phase transition in the solid electrolyte $RbAg_4I_5^{\dagger}$

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Because the optical birefringence in  $RbAg_4I_5$  has been found to depend linearly on the order parameter near the 208-K phase transition, it is necessary to consider a model in which the order parameter couples linearly to the static strain. In this paper, such a model is developed in which coupling to lattice strains lifts the degeneracy of nearest-neighbor pairs of Ag ions and leads to a Hamiltonian which is very similar to that for cooperative Jahn-Teller systems. The large number of such pairs (12) requires the use of group-theoretical methods in choosing the appropriate combinations. This Hamiltonian is treated in the Landau theory, and is shown to predict the occupancy of Ag sites in the rhombohedral lower-temperature phase, to explain the softening of the  $C_{44}$  elastic constant, and to lead to the observed linear dependence of the birefringence on the order parameter.

## I. INTRODUCTION

A number of highly ionic-conductive materials are characterized by an excess of crystallographic sites for the mobile species.<sup>1</sup> In some of these materials, a partial ordering of the mobile ion into a portion of these sites occurs, accompanied by the behavior generally associated with a secondorder phase transition.<sup>2,3</sup> A model for such transitions has been proposed by Pardee and Mahan,<sup>4</sup> based on an effective interaction between ions mediated by optical phonons and giving rise to an Ising-like phase transition. In the original calculation, an idealized alternating site model was assumed. It is our purpose here to describe a somewhat modified model as applied to a specific example of such a material RbAg<sub>4</sub>I<sub>5</sub>.

We have already reported<sup>3</sup> that the specific heat and optical birefringence of  $RbAg_4I_5$  behave, in the vicinity of the 208-K phase transition, as they would for a three-dimensional Ising system. Unlike an Ising magnet,<sup>5</sup> however, the birefringence varies linearly rather than quadratically with the order parameter, as noted in Table I. This forces us to consider a model in which the order parameter can couple directly to the lattice distortion, in a manner similar to the cooperative Jahn-Teller effect.<sup>6</sup> Such a model was suggested for RbAg<sub>4</sub>I<sub>5</sub> in Ref. 3, and will now be described in detail.

 $RbAg_4I_5$  crystallizes into a cubic phase with space group  $P4_132$  with four formula units per unit cell.<sup>7</sup> The 20 iodide ions are so arranged as to produce 56 tetrahedral sites for the 16 silver ions. These sites are composed of two sets of 24 general positions, labeled Ag(II) and Ag(III), and one set of eight special positions, labeled Ag(c). The coordinates and room-temperature occupancies are listed in Table II. Recently, Geller has succeeded<sup>8</sup> in solving the structure of this material in the

intermediate phase  $(120 \le T \le 208 \text{ K})$  and in the lowtemperature phase. The intermediate phase is rhombohedral R32, a subgroup of  $P4_132$ , and is characterized by having only small distortions and shifts of site coordinates. The previously equivalent 24 Ag(II) sites are, of course, split into four groups of six equivalent sites, but the occupancies of the new sets are quite different, one set being empty within experimental error. A considerable shift in occupancy among the Ag(III) sites occurs a as well. In the cubic phase<sup>8</sup> of  $RbAg_4I_5$ , the Ag(II)sites play a unique role: every second diffusive step must involve an  $Ag(\Pi)$  site. What is more, these sites occur in pairs and therefore represent a degeneracy in the system which could be lifted by a suitable lattice distortion, thereby giving us the Jahn-Teller-type interaction required to explain the observed linear birefringence.

In Sec. II we describe the location and symmetry properties of the Ag(II) sites and define a set of pseudospin operators for use in the Jahn-Teller Hamiltonian. This operator is combined in Sec. III with local distortions and an effective cooperative Jahn-Teller Hamiltonian is derived. This is discussed in mean-field theory and found to agree qualitatively with experiments, although a weakly first order transition is expected, which has not been observed.

TABLE I. Comparison of experimental specific-heat critical parameters and the birefringence exponent with Ising-model values (Ref. 3).

	<i>α</i> = <i>α</i> ′	$A^+/A^-$	β
Experiment	$0.14 \pm 0.02$	$0.46 \pm 0.01$	$0.36 \pm 0.03$
Ising, series Ising, -expansion	$\begin{array}{c} 0.125 \\ 0.08 \end{array}$	$0.62 \pm 0.03$ 0.53	$\begin{array}{c} 0.31 \\ 0.33 \end{array}$

15

2236

TABLE II. Positions and occupancies of Ag sites in the cubic phase of  $RbAg_4I_5$ . Data from Ref. 7 and the lattice parameter a=11.24 Å.

	$\operatorname{Ag}(c)$	Ag(II)	Ag(III)
x/a	0.1739	0.5299	0.9964
y/a	=x/a	0.2713	0.8506
z /a	=x/a	0.7980	0.2154
Occupancy	$0.88 \pm 0.30$	$9.38 \pm 0.87$	$5.50 \pm 0.83$
Fractional occupancy	0.11	0.39	0.23

## II. PAIRING OF Ag(II) SITES

The 24 sites labeled Ag(II) are derived from the general position (x, y, z) by application of the 24 elements of the crystallographic space group. For these sites x = 0.5299a, y = 0.2713a, and z = 0.798a, and a = 11.24 Å. One of the sites so generated  $(\frac{3}{4} - y, \frac{3}{4} - x, \frac{3}{4} - z) = (0.4787, 0.2201, 0.952)$  lies in an adjacent iodine tetrahedron across a shared face. In the set of 24 Ag(II) sites there are 12 suchpairs. The members of the pairs which may be generated from (x, y, z) by the eight threefold rotations and the three twofold rotations along the cube axes are denoted  $\alpha$ , while those generated by the six fourfold and six twofold group elements are denoted  $\beta$ . Owing to the proximity of these sites, it is highly unlikely that both members of a pair would be simultaneously occupied by Ag<sup>+</sup> ions, but on the average each would be equally occupied. The room-temperature determination by Geller

showed that 9.4 of the 16 ions are on these sites, on the average.

Consider now the first pair (x, y, z) and  $(\frac{3}{4} - y, \frac{3}{4} - z, \frac{3}{4} - z)$ . The point midway between these sites is at  $(\overline{x}', \frac{3}{4} + x', \frac{3}{8})$  where x' = 0.5043, a site of twofold point symmetry. This enables us to define a pseudospin operator for the pair as the difference between the occupancy of the  $\alpha$ -site  $n_{ij}^{\alpha}$  and the  $\beta$ site  $n_{ij}^{\beta}$  of the *i*th pair, in the *j*th cell which is

$$S_{ij}^{z} = n_{ij}^{\alpha} - n_{ij}^{\beta} , \qquad (1)$$

and which takes on the values  $S_{ij}^{z} = \pm 1$ . This pseudospin is taken to occupy the 12 sites of twofold point symmetry located at the midpoints of the pair sites. It is clearly odd under the twofold rotation which interchanges  $\alpha$  and  $\beta$ .

It is convenient to introduce the Fourier lattice sums of these pseudospin operators as follows:

$$S_{i}^{z}(\vec{k}) = \frac{1}{\sqrt{N}} \sum_{j} S_{ij}^{z} e^{-i\vec{k}\cdot\vec{R}_{j}} , \qquad (2)$$

where  $\vec{k}_j$  is the coordinate of the origin of the *j*th cell. These 12 functions transform among themselves under the operations of the space group and therefore form a 12-dimensional (reducible) representation of the little group of  $\vec{k}$ . In particular, at  $\vec{k} = 0$ , the space group is isomorphous with the point group 432, and the 12-dimensional representation decomposes into

$$\Gamma(S_i(0)) = A_2 + E + 2T_1 + T_2 . \tag{3}$$

As we have noted above, the lower-temperature phase of this material is rhombohedral which in-

TABLE III. Definitions of pair sites for the pseudospin operators in the *j*th cell and the coefficients for symmetrized combinations which transform according to the  $T_2$  representation at k=0. The coordinates x, y, and z are given in Table II for Ag(II) sites; the present coordinates are in units of a=11.24 Å. The  $C_{T_2,q}^i$  are defined in Eq. (7).

	Site	Site	$C^i_{T_2,4}$	C <sup>i</sup> <sub>T2,5</sub>	$C_{T_{2},6}^{i}$	
$S_{1j}$	(x, y, z)	$(\frac{3}{4}-y, \frac{3}{4}-x, \frac{3}{4}-z)$	1	-1	0	
S <sub>2j</sub>	$(x-\tfrac{1}{2},\tfrac{1}{2}-y,\overline{z})$	$(\frac{1}{4} - y, x - \frac{1}{4}, \frac{1}{4} + z)$	1	1	0	
$S_{3j}$	$(\overline{x}, \frac{1}{2} + y, \frac{1}{2} - z)$	$(\frac{1}{4}+y, \frac{1}{4}-x, \frac{3}{4}+z)$	-1	-1	0	
$S_{4j}$	$(\frac{1}{2}-x,\overline{y},\frac{1}{2}+z)$	$(\frac{3}{4}+y,\frac{1}{4}+x,\frac{1}{4}-z)$	-1	1	0	
$S_{5j}$	$(\boldsymbol{z}, \boldsymbol{x}, \boldsymbol{y})$	$(\frac{3}{4}-z,\frac{3}{4}-y,\frac{3}{4}-x)$	0	1	-1	
$S_{6j}$	$(\overline{z},x{-}\tfrac{1}{2},\tfrac{1}{2}{-}y)$	$(\frac{1}{4} + z, \frac{1}{4} - y, x - \frac{1}{4})$	0	1	1	
$S_{\gamma j}$	$(\frac{1}{2}-z,\overline{x},\frac{1}{2}+y)$	$(\frac{3}{4}+z,\frac{1}{4}+y,\frac{1}{4}-x)$	0	-1	-1	
$S_{8j}$	$(\frac{1}{2} + z, \frac{1}{2} - x, \overline{y})$	$(\frac{1}{4} - z, \frac{3}{4} + y, \frac{1}{4} + x)$	0	-1	1	
$S_{9j}$	(y,z,x)	$(\frac{3}{4} - x, \frac{3}{4} - z, \frac{3}{4} - y)$	-1	0	1	
$S_{10,j}$	$(\frac{1}{2} - y, \overline{z}, x - \frac{1}{2})$	$(\frac{3}{4} + x, \frac{3}{4} - z, \frac{3}{4} - y)$	1	0	1	
$S_{11,j}$	$(\frac{1}{2} + y, \frac{1}{2} - z, \vec{x})$	$(\frac{1}{4}-x,\frac{3}{4}+z,\frac{1}{4}+y)$	-1	0	-1	
S <sub>12,j</sub>	$(\overline{y}, \frac{1}{2}+z, \frac{1}{2}-x)$	$(\frac{1}{4}+x, \frac{1}{4}-z, \frac{3}{4}+y)$	1	0	-1	

dicates the presence of a static strain of  $T_2$  symmetry. Since we will eventually wish to include coupling terms between the static strain and the symmetric combinations of the pseudospins at k = 0, we have written the definitions of the sites  $S_{ij}^z$  and the combinations of them which transform according to  $T_2$  in Table III.

## **III. JAHN-TELLER-LIKE INTERACTION**

In the cubic phase, with all ions at their equilibrium positions, the Ag(II) sites are equivalent. If, however, the iodine lattice is displaced from equilibrium, there will be a difference in energy between the  $\alpha$  and  $\beta$  sites when the local strain at the *i*th site in the *j*th cell is odd under the twofold rotation symmetry of this site. Such strains lift the twofold degeneracy of the occupancy of this pair of Ag(II) sites, which effect may be described in terms of an interaction energy<sup>6</sup>

$$H_{\rm int} = \sum_{i, j} V_B S_{ij}^z Q_{ij}^B , \qquad (4)$$

where  $V_B$  is a coupling constant,  $Q_{ij}^B$  is the local strain at site *i* in cell *j*, and *B* refers to the nontrivial representation of the point group  $2(C_2)$ . This is precisely the Hamiltonian for a cooperative Jahn-Teller system, but with one important difference. In the Jahn-Teller system, the spacegroup operations do not affect the state of the pseudospin operators while in the present situation certain group elements interchange  $\alpha$  and  $\beta$ sites, thus reversing the spin. This requires more careful consideration of the symmetry properties of the pseudospin operators here than is necessary in the Jahn-Teller problem.

Hamiltonian (4) has been treated for the Jahn-Teller problem by Gehring.<sup>9</sup> The sum over cells is eliminated by converting to a lattice sum similar to (2),

$$H_{\rm int} = \sum_{i, \vec{k}} V_B S_i^{\#}(\vec{k}) Q_i^B(-\vec{k}) , \qquad (5)$$

where

$$Q_i^B(-\vec{k}) = \frac{1}{\sqrt{N}} \sum_j Q_{ij}^B e^{i\vec{k}\cdot\vec{R}_j}$$

The  $Q_i^B(-\vec{k})$  may be written as an expansion in the phonon mode operators  $a_{pq}(\vec{k})$  which belong to the *q*th row of the *p*th representation (or *q*th polarization of the *p*th branch) at wave vector  $\vec{k}$ . Only those representations *p* which are compatible with the *B* representation of  $2(C_2)$  will appear.<sup>6</sup> After shifting the phonon coordinates in the usual manner, Gehring obtains a new interaction Hamiltonian

$$H_{\rm int} = \sum_{i,i'} J_{ii'}(\vec{k}) S_i^{a}(\vec{k}) S_i^{a'}(-\vec{k}) , \qquad (6)$$

where  $J_{ii'}(\vec{k})$  is a sum of the contributions of all compatible phonon modes with wave vector  $\vec{k}$ . At  $\vec{k} = 0$ , all phonon modes except those of  $A_1$  symmetry contribute to the exchange interactions. Thus it appears unlikely that one of these modes will be driven soft by the interactions. Even without actually calculating these pseudoexchange constants, we can use the symmetry properties of the crystal to determine which terms are nonzero.

As noted above, the  $S_i^{\epsilon}(\vec{k})$  form the basis of a 12dimensional (reducible) representation of the group of  $\vec{k}$ . This representation may, in general, be brought into block form by a matrix  $C_{pq}^{i}(\vec{k})$  in which  $i=1,\ldots,12$  and p and q take on the labels p of the irreducible representations with rows q into which this representation decomposes.<sup>10</sup> This matrix also defines the combinations of the reducible basis functions which form bases for the irreducible representations through

$$S_{pq}^{z}(\vec{\mathbf{k}}) = \sum_{i} C_{pq}^{i}(\vec{\mathbf{k}}) S_{i}^{z}(\vec{\mathbf{k}}) .$$

$$\tag{7}$$

In the same way, the  $S_i^z(-\vec{k})$ 's form a conjugate representation to the first, and may be expanded in terms of the irreducible conjugate representations. Then, using a well-known theorem,<sup>10</sup> we can form invariant products of the basis functions of the irreducible representations, obtaining

$$H_{\text{int}} = \sum_{pq} J_{p}(\vec{\mathbf{k}}) S_{pq}^{z}(\vec{\mathbf{k}}) S_{pq}^{z}(\vec{\mathbf{k}}) , \qquad (8)$$

where only those

$$J_{p}(\vec{k}) = \sum_{i,i'} J_{ii'}(\vec{k}) (C^{-1})_{pq}^{i} (C^{-1})_{pq}^{*i}$$

which are independent of q will appear.

Clearly, (8) has the form of a multisublattice Ising system. However, we have considered only the interaction with  $k \neq 0$  acoustic modes and with optic modes. As is usual, we consider the coupling to the uniform strain separately.<sup>6</sup> Since x-ray studies have now shown the intermediate temperature phase to be rhombohedral, we expect the uniform strain to have  $T_2$  symmetry. Using the notation 4 = yz, 5 = xz, and 6 = xy, we can write the strain-pseudospin coupling as

$$H_{\text{strain}} = \frac{1}{2} N\Omega C_{44} (e_4^2 + e_5^2 + e_6^2) + \eta (N)^{1/2} [e_5 S_{T_2,5}^z (0) + e_4 S_{T_2,4}^z (0) + e_6 S_{T_2,6}^z (0)] , \qquad (9)$$

where the  $e_q$  are the usual strain components and the  $S_{T_2,q}^z$  are symmetrized combinations of pseudospins which transform according to the  $T_2$  representation of  $P4_132$  at  $\Gamma(k=0)$  and which are given in Table III.

Because we expect the strain to couple to the

order parameter we need consider only the term  $p = T_2$  and k = 0 in (8). It is then possible to return to the more standard interaction Hamiltonian (6), where, now

$$J_{ii'}(0) = J_{T_2}(0) \sum_{q} C^{i}_{T_2q} C^{*i'}_{T_2q} ,$$

and where the  $C_{T_{2q}}^{i}$  are given in Table III. Without detailed knowledge of the lattice dynamics of RbAg<sub>4</sub>I<sub>5</sub>, it is not possible to determine the  $J_{b}(\mathbf{k})$ , and a solution of the problem is not possible. We note that, in general, the presence of lattice coupling in the Ising model leads to first-order behavior sufficiently close to  $T_c$ .<sup>11</sup> The strength of the first-order component will depend in general on the size of  $dT_c/dV$ . For RbAg<sub>4</sub>I<sub>5</sub> the transition temperature has been found to vary guadratically with pressure,<sup>12</sup> with  $dT_c/dP$  very small near zero pressure. Thus, the observation of Ising-like critical behavior even very close to  $T_c$  may not be inconsistent with the addition of terms such as (9)to the interaction (8). Despite the clear evidence of Ising-like behavior in this system (see Table I), we ignore this and treat the system in terms of a Landau model which should at least reveal the qualitative features of the phase transition.

### **IV. LANDAU THEORY**

In the Landau theory,<sup>10</sup> the free energy of a system undergoing a phase transition is assumed to be expandable in powers of a physical density which vanishes in the high-temperature phase and has finite value in the low-temperature phase. In the high-temperature phase, this density, the order parameter, transforms according to some irreducible representation other than the identity representation of the space group of the system at a point  $\vec{k}$ ; in the low-temperature phase, the order parameter transforms according to the identity representation of the smaller space group. The transformation from P4,32 to R32 involves a reduction in the number of group elements from 24 to 6, and thus does not violate the rule<sup>10</sup> that the number of elements cannot be reduced by a factor of 3. In  $RbAg_4I_5$  the phase transition is accompanied by only a small change in the rhombohedral angle (to  $90.1 \pm 0.05^{\circ}$ ), and lattice parameter (from 11.24 to 11.19 Å), and no change in the cell dimensions.<sup>8</sup> Thus, the transition is characterized by zero wave vector and the order parameter must transform according to some irreducible representation of P4,32 at  $\Gamma(k=0)$ , at which point the space group is isomorphic with the point group 432. In view of the coupling terms (9) we expand the free energy in powers of the densities  $\phi_q = N^{-1/2} S_{T_2,q}^z(k=0)$ , q = 4, 5, 6, and 4 = yz, 5 = xz, and 6 = xy as above.

Keeping terms to fourth order in the densities, but only quadratic in the strains, we obtain

$$F = \frac{V}{2} \sum_{q} (a\phi_{q}^{2} + b\phi_{q}^{4} + 2C_{44}e_{q}^{2} + \eta e_{q}\phi_{q}) + c(\phi_{4}^{2}\phi_{5}^{2} + \phi_{5}^{2}\phi_{6}^{2} + \phi_{6}^{2}\phi_{4}^{2}) - d\phi_{4}\phi_{5}\phi_{6} , \qquad (10)$$

where  $a = a_0(T - T_c)$ , b, c, and d are temperatureindependent positive constants, and  $C_{44}$  and  $\eta$  have the same meaning as above. The form of the free energy is such that upon minimizing with respect to the  $\phi_a$  and  $e_a$ , the amplitudes of the  $\phi_a$  and of the  $e_a$  are equal but not necessarily the phases. In the low-temperature phase, there are four possible states, representing rhombohedral distortions along the four threefold axes. In each of these the phases of the distortions are different. Thus, for example, if the  $e_a$  are equal in both amplitude and phase, the distortion is along the [111] axis and the combination  $\phi_4 + \phi_5 + \phi_6$  is invariant under the operations of the space group of the low-temperature phase; for a distortion along  $[\overline{1}\overline{1}1]$  the proper combination would be  $\phi_4 + \phi_5 - \phi_6$ .

If we now write (10) in terms of the amplitude  $\phi_0 = |\phi_q|$  of the order parameter and the amplitude  $e_0 = |e_q|$  of the distortion we have

$$F = (\frac{3}{2}V)[a\phi_0^2 + b\phi_0^4 + 2C_{44}e_0^2 + \eta e_0\phi_0 + c\phi_0^4 - (\frac{1}{3}d)\phi_0^3] .$$
(11)

Upon minimizing with respect to the amplitudes we find that

$$e_0 = (-\eta/4C_{44})\phi_0 , \qquad (12)$$

which shows that the distortion follows the amplitude of the order parameter. The presence of a cubic term in (11) causes the transition to be first order with a transition temperature of

$$T_c^* = T_c + \eta^2 / 8a_0 C_{44} + d^2 / 32a_0 (b+c) .$$
 (13)

If  $d^2/32a_0(b+c)$  is small, the transition is only weakly first order. In view of the failure to observe a first-order component experimentally, we shall take d=0.

We may now add a stress term  $-Se_0$  to (11) and, considering only terms quadratic in the density  $\phi_0$ , calculate the effective elastic constant  $C'_{44}$  $=\frac{1}{2}\partial S/\partial e_0$ . The result is that, above  $T'_c$  $= T_c + \eta^2 / 8C_{44}a_0$ 

$$C'_{44} = C_{44} \left[ 1 + \eta^2 / 8a_0 C_{44} (T - T'_c) \right]^{-1} .$$
 (14)

This softening of the  $C_{44}$  elastic constant has been observed by Graham and Chang.<sup>13</sup> At  $T - T'_c \cong 10$ K, the elastic constant has decreased by 5%, and we may estimate  $\eta^2 \cong 8a_0C_{44}(5 \text{ K})$ . From the rhombohedral distortion of  $\delta \theta = 0.1^{\circ}$ , we estimate  $a_0 T_c \cong C_{44}(\delta \theta)^2 \cong 10^{-6} C_{44}$ . This gives an estimate

of  $\eta \approx 10^{-4}C_{44}$ , the small value of which may explain the absence of observable first order effects produced by (9).

In the absence of the cubic term (d=0), the order parameter increases as  $(T_c - T)^{1/2}$  and the specific heat has a step discontinuity, as usual in Landau models. The true behavior of the system, as noted in Table I, is Ising-like and the Hamiltonian (8) + (9) should be used. We shall, nonetheless, proceed to discuss the nature of the intermediate temperature phase in Landau theory terms, with the understanding that this is a qualitative description only.

# V. NATURE OF THE INTERMEDIATE TEMPERATURE PHASE

The intermediate temperature phase of  $\text{RbAg}_4 I_5$ is rhombohedral, with one of the threefold axes compressed.<sup>8</sup> In a normal crystal, all four possible distortions are observed,<sup>3,8</sup> making interpretation of experimental results in this phase difficult. We shall assume that the [111] axis of our idealized crystal remains a threefold axis in the rhombohedral phase. Quite clearly, the combination  $\phi_{[111]} = \phi_4 + \phi_5 + \phi_6$  is invariant under a threefold rotation about [111] and defines the order parameter in the rhombohedral phase. Referring to Table III, one can easily show that the combination of pseudospins corresponding to this symmetrized order parameter is

$$\phi_{[111]} \propto (S_{2j} - S_{3j} + S_{6j} - S_{7j} + S_{10,j} - S_{11,j})$$
.

When the order parameter takes on its maximum value, pairs labeled 2, 6, and 10 will have the  $\alpha$ -site occupied and the  $\beta$ -site empty, while pair sites 3, 7, and 11 will be oppositely occupied. The reverse is also obviously possible. The remaining pairs 1, 4, 5, 8, 9, and 12 will not be affected. Should we have chosen a different direction for the rhombohedral axis, the combination would be different and these other sites ordered. Thus, the ordering described above represents one of four possible domains.

Geller has succeeded<sup>8</sup> in deconvolving the domain structure of  $\text{RbAg}_4I_5$  and has determined the occupancies based on the setting of the crystal in which [111] is the rhombohedral axis. In this setting, the 24 equivalent Ag(II) sites are split into four sets of six equivalent sites, with both members of the pairs 1, 5, and 7 belonging to one set, which we label  $6f_1$ ; both members of pairs 4, 8, and 12 belonging to another set,  $6f_4$ ; the  $\alpha$ -site members of 2, 6, and 10 and the  $\beta$ -site members of 3, 7, and 11 belonging to  $6f_2$ ; and the remaining sites belonging to  $6f_3$ . Thus, the ordering described above occurs with either set  $6f_2$  or  $6f_3$  becoming full and the other empty. Sets  $6f_1$  and  $6f_4$  do not participate in the ordering in a single domain sample. In Table IV we have listed the coordinates of the various equivalent sets in the rhombohedral phase assuming the positions to be unshifted along with the actual positions and occupancies found by Geller<sup>8</sup> at 125 K.

## VI. DISCUSSION

It is clear from Table IV that our Jahn-Tellerlike model, treated in mean-field theory, has been successful in explaining the partial ordering of Ag ions in the intermediate temperature phase. Despite this success, the picture has been greatly oversimplified. Geller's data<sup>8</sup> also show ordering in the Ag(III) sites, though to a lesser degree. Nearly a third of the Ag ions are located on the  $6f_3$ sites, and this occupancy has come at the expense of both the  $6f_2 \operatorname{Ag}(\Pi)$  sites, and some of the  $\operatorname{Ag}(\Pi I)$ sites. In the cubic phase, each Ag(III) site has two Ag(II) neighbors.<sup>7</sup> Thus we might expect that ordering of the Ag(II) sites will affect the occupancies of the neighboring Ag(III). In fact we find that those Ag(III) sites having both neighbors taking part in the ordering process are reported empty by Geller; those having only one ordered neighbor contain 1.2 ions among the six sites; while those having no ordered neighbors contain 3.0 ions, approximately the same as their disordered Ag(II) neighbors. This would seem to indicate that our consideration of only pairs of  $Ag(\Pi)$  ions is too simplified a picture, despite its complexity, and that a complex of Ag(II) pairs and their Ag(III) neighbors is the proper unit for consideration.

The model we have presented is capable of explaining, in at least a qualitative manner, the Ising-like nature of the phase transition in  $RbAg_4I_5$ .

TABLE IV. Coordinates of equivalent Ag(II) sites in the intermediate temperature phase. Cubic coordinates are referred to an origin shifted by  $(\frac{3}{8}, \frac{3}{8}, \frac{3}{8})$  relative to the original cell. The rhombohedral values were obtained by Geller. Here  $a_c = 11.24$  Å and  $a_{th} = 11.19$  Å.

	6f <sub>1</sub>	6 <i>f</i> <sub>2</sub>	6 <i>f</i> 3	$6f_4$	
$x_{\text{cubic}} / a_c$	0.160	0.66	0.395	0.92	
$x_{\rm rh} / a_{\rm rh}$	0.160	• • •	0.397	0.92	
$y_{\rm cubic} / a_c$	0.895	0.86	0.325	0.595	
$y_{\rm rh}/a_{\rm rh}$	0.886	•••	0.327	0.601	
$z_{\rm cubic}/a_c$	0.42	0.825	0.095	0.355	
$z_{\rm rh}/a_{\rm rh}$	0.428	•••	0.096	0.344	
Occ. theor.	•••	6 or 0	0 or 6	• • •	
Occ. expt.	3.0	0	4.8	2.7	

We have not included the dielectric constant explicitly, but by analogy with other systems,<sup>14</sup> we expect the birefringence to follow the strain through the elasto-optic coupling. Thus, the linear dependence of the strain on the order parameter given by (12) is directly responsible for the linear dependence of the birefringence on the order parameter.

In the Landau model we have also been able to demonstrate the softening of the  $C_{44}$  lattice constant accompanying the partial ordering of Ag ions, such as has been observed.<sup>13</sup> This softening is relatively weak, and indicates that the order parameter is coupled only weakly to strain modes. This was to be expected on the basis of the persistence of second-order-like critical behavior to

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small values of reduced temperature.<sup>11</sup>

Having determined the nature of the ordering process in  $\operatorname{RbAg}_4I_5$ , we must next determine its effect on the ionic conductivity. The relationship between the known correlations in this system which accompany the partial ordering transition and the activation energy for ionic conductivity will be the subject of a subsequent publication.

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