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Electron paramagnetic resonance of the incommensurate cooperative Jahn-Teller compound $Tl_2PbCu(NO_2)_6$

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Electron-paramagnetic-resonance experiments, in the temperature range $4.5 < T < 375$ K, are reported for the cooperative Jahn-Teller compound $Tl_2PbCu(NO_2)_6$ which exhibits both incommensurate and commensurate phase transitions. A theory is presented which provides a unified explanation for the resonance and the structural data, and correctly predicts the relative magnitudes of the incommensurate and the commensurate phase-transition temperatures.

I. INTRODUCTION

The compounds $R_2PbCu(NO_2)_6$ ($R \equiv$K,Rb,Tl) with the elpasloite structure have recently been of interest due to their incommensurate cooperative Jahn-Teller (JT) phase transitions.[1–5] At high temperatures, they have cubic lattices with space group $Fm3$—T_h^3 (phase I).[6] As the temperature is lowered, there is a transition into an incommensurate phase (phase II) followed by another transition into a commensurate phase (phase III). Various theoretical explanations have been proposed[1–5] to elucidate the nature of these transitions, a common feature being that the JT properties of Cu^{2+} ions are involved.

In this paper we report electron-paramagnetic-resonance (EPR) experiments in the temperature range $4.5 < T < 375$ K on $Tl_2PbCu(NO_2)_6$ and propose a new theory to explain the various observations.

We have chosen $R =$Tl, rather than K or Rb, because its compound has the widest incommensurate region $247 < T < 291$ K and the crystals are closest to being monodomain. EPR has previously been reported on powder[7] and single crystals[8] of this compound in a narrower temperature range. These results[7,8] were reported before the incommensurate nature of phase II had been recognized. Our experiments extend the temperature range to very low and high temperatures. Furthermore, in all three phases there are some differences between the previous results and ours.

II. EXPERIMENTAL RESULTS

The EPR experiments were performed at ~9 GHz on single crystals of $Tl_2PbCu(NO_2)_6$ grown by slow cooling of the saturated aqueous solution. The crystal structure is shown in Fig. 1. The octahedrally coordinated Cu^{2+} ions produce both the JT effect and the EPR signals (shown in Fig. 2).

The theory of single Cu^{2+}-ion EPR spectra is well developed.[9] The free ionic orbital quintuplet, spin doublet $(3d^9,{}^2D)$ state breaks up into a lower $\Gamma_3(E_g)$ orbital doublet and a higher $\Gamma_5(T_{2g})$ orbital triplet under the influence of the octahedral crystal field. The static JT distortion splits the ground Γ_3 levels into two Kramers doublets:[10]

$$|2^s\rangle \equiv \frac{1}{\sqrt{2}}(\,|+2\rangle + |-2\rangle) \equiv |x^2-y^2\rangle\ ,$$

$$|0\rangle \equiv |3z^2-r^2\rangle\ ,$$

where OZ has been chosen as the axis of quantization. Due to the admixture of the excited Γ_5 states (also split by the static JT effect), through the spin-orbit interaction, the Γ_3 levels acquire anisotropic g tensors whose formulas to second order have been given by Bleaney *et al.*[9] for rhombic distortions. These formulas are modified when dynamic effects due to zero-point vibrations are taken into account.[9,10]

In the concentrated crystals, the hyperfine and dipolar broadenings are narrowed by the exchange interactions and only a single line is observed for single domain crystals. The temperature variations of the g values and the linewidths with the external magnetic field applied along the three cubic $\langle 100 \rangle$ directions are shown in Figs. 3—8. In these figures the c axis refers to the pseudotetragonal axis along which the crystal is contracted as a result of the cooperative JT effect.

At very low temperatures, in phase III, linewidths rapidly broaden and two of the three g values become tem-

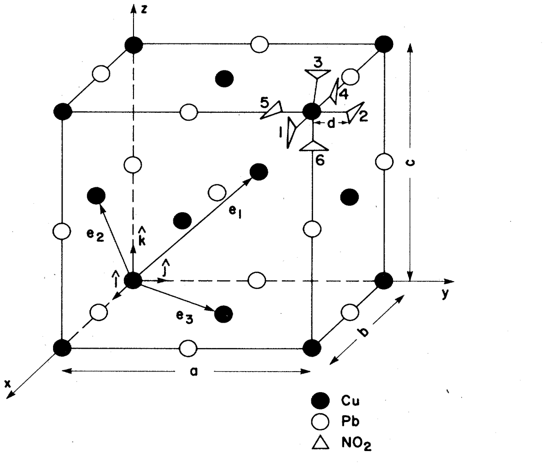

FIG. 1. Crystal structure of $Tl_2PbCu(NO_2)_6$. For clarity the Tl ions are omitted and the six NO_2 neighbors are shown only for one Cu^{2+} ion.

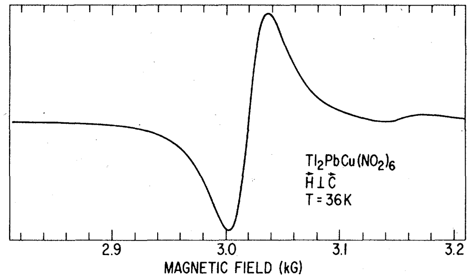

FIG. 2. EPR spectrum of $Tl_2PbCu(NO_2)_6$ with the magnetic field perpendicular to the c axis in the commensurate distorted phase.

perature dependent. These variations are probably caused by the incipient antiferromagnetic effects caused by the Kramers degeneracy of the Cu^{2+} ions. Magnetic susceptibility measurements down to 4.5 K indicate a negative Curie-Weiss $\Theta \cong -8$ K. At high temperatures in phase I, the linewidth is a rapidly increasing function of temperature. Unlike the previously reported single-crystal work,[8] in both phases II and III, we observe rhombic rather than tetragonal signals although the degree of rhombicity is small. In the incommensurate phase II the g factors for $\mathbf{H} \perp \mathbf{c}$ decrease and the g factor for $\mathbf{H} || \mathbf{c}$ increases as functions of temperature, whereas all three linewidths are temperature independent within experimental uncertainties. An interesting feature of the experiments is that the c axis along which a given crystal chooses to contract varies from run to run, showing the complete equivalence of the three $\langle 100 \rangle$ axes.

III. THEORY

A. Introductory remarks

The first question to consider is why, as the temperature is lowered, should there be a transition into an incommensurate phase? One explanation[1] is that, if one considers the vibrational modes of a lattice which correspond to a high symmetry point on the surface of the Brillouin zone (BZ), it is possible to have two families of modes of differing symmetries but similar frequencies. If now, due to anharmonic effects, one of the frequencies is temperature dependent, it should be possible for the modes to cross without interference. On the other hand, at a small distance into the BZ the symmetries will be lowered, and it may happen that there are now two modes of the same (but lower) symmetries, which will not cross but will repel each other as the temperature is lowered. Therefore, the initial softening of one mode on the zone boundary may cause the other mode to soften even more just within the BZ, opening the possibility of an incommensurate phase transition with a wave vector close to that of a high symmetry point on the BZ. In other words, the frequency of a mode just inside the zone may fall to zero before that of a mode on the boundary, due to the repulsion between modes of the same symmetry.

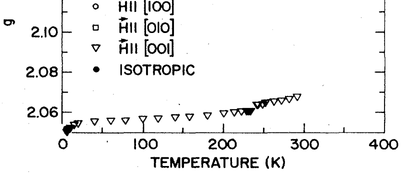

FIG. 3. Temperature dependence of the g values with the magnetic field applied along the cubic $\langle 100 \rangle$ axes.

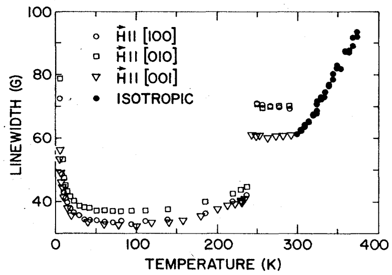

FIG. 4. Temperature dependence of the EPR linewidths with the magnetic field applied along the cubic $\langle 100 \rangle$ axes.

There is, however, one major problem with this explanation; the wave vector associated with the incommensurate phase is far from a zone boundary.[1] According to Yamada *et al.*,[2] the wave vector is (0.425,0.425,0). The structure of phase I belongs to the space group $Fm3$, which means that the crystal is face-centered cubic as far as translations are concerned, but that it does not have all the rotation, reflection, etc., symmetries of a cube. It has threefold rotational symmetries about $\langle 111 \rangle$ axes, but only a very limited number of reflection planes. The point on the BZ in the [110] direction is at $(3\pi/2a, 3\pi/2a, 0)$, and even so it does not have particularly high symmetry. (For a face-centered-cubic lattice with cubic unit cell side a, the reciprocal lattice is body centered with cube edge $4\pi/a$. Unfortunately, Yamada *et al.*[2] do not give the units of their reciprocal-lattice vector). So the explanation along these lines is not particularly convincing, even when the JT effect is brought in to assist.

The explanation that we wish to put forward goes along the following lines: We suppose that, for some unknown reason, there is a lattice mode, in phase I, which has wave vector (0.425,0.425,0) and is particularly low in frequency, but that its frequency is not zero. As it vibrates, it in-

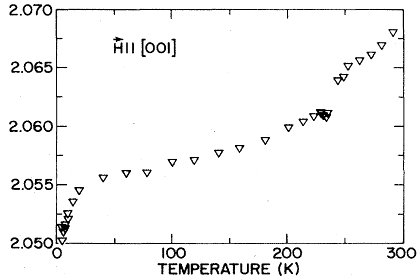

FIG. 5. Temperature dependence of the g factor in the distorted phases with the magnetic field applied along the c axis.

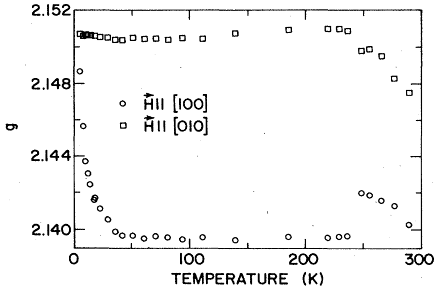

FIG. 6. Temperature dependence of the g factors in the distorted phases with the magnetic field applied perpendicular to the c axis.

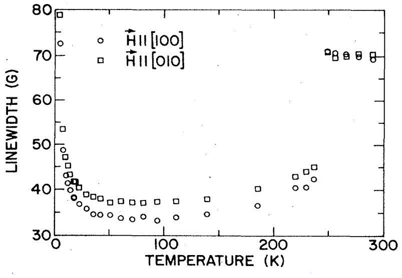

FIG. 8. Temperature dependence of the EPR linewidths in the distorted phases with the magnetic field applied perpendicular to the c axis.

duces lattice strains, which the Cu^{2+} ions experience. In the absence of such strains, the Cu^{2+} ions will have low-lying Γ_3 orbital states. The vibrations will cause dynamic splittings of the energy levels. If, however, the temperature is so high that on the whole the split energy levels remain approximately equally populated, the Cu^{2+} ions will not be contributing much of physical interest. But as the temperature is lowered, the levels will not remain equally populated, and so a "magnetic" (or crystal-field) energy term begins to enter, which must be taken into account in examining the equilibrium of the lattice. Indeed, it is just this kind of effect which gives rise to cooperative JT phase transitions.

The transition to an incommensurate phase then occurs from a combination of circumstances, a suitable low-frequency mode and a temperature-dependent magnetic energy. Of course, such features can be expected for most of the lattice modes; so it is necessary to show that any such mode can have its effective frequency reduced to zero by the interactions with the Cu^{2+} ions. It can then be assumed that, as the temperature is lowered, it is the first mode to have its effective frequency reduced to zero which determines the structure of phase II. Once the frequency has fallen to zero, the crystal-field splittings of the Cu^{2+} ions become static splittings and the crystal structure changes. There will be vibrational modes associated with the new structure, but there is no reason to suppose that it will then be unstable against further modes having zero frequencies, except possibly at lower temperatures.

In this respect one can notice a very interesting feature that, with an incommensurate lattice, the Cu^{2+} ions do not all have the same crystal-field splitting, and in fact there will be a continuous range of splittings. Therefore at some Cu^{2+} sites the splittings will be less than kT, and both levels will be approximately equally populated. In other words, although a phase transition has occurred, it has not removed all the entropy associated with the orbital doublets of the Cu^{2+} ions. The free energy of any system in thermal equilibrium at temperature T contains a term $-TS$, which acts, if the entropy S is large, to reduce the importance of the other energy terms—but only if T is high. As the temperature is lowered, the entropy contribution becomes less and less important, and it happens, not infrequently, that a phase with lower entropy will actually have a lower total free energy. It, therefore, seems plausible that at lower temperatures a lower free energy may be found with a phase in which all the Cu^{2+} ions have equal splittings—which is precisely a property that can be anticipated will occur in the phase-III structure.

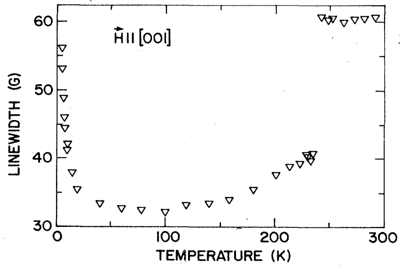

FIG. 7. Temperature dependence of the EPR linewidths in the distorted phases with the magnetic field applied along the c axis.

B. Properties of the cubic phase

To examine the interaction of an elastic wave with Cu^{2+} ions, it is necessary to determine some details of the strain field near each ion. A given Cu^{2+} ion (see Fig. 1) can be regarded as at (λ,μ,ν) where λ,μ,ν assume integer values. The Cu^{2+} position vector $\mathbf{R}$ is

$$\mathbf{R}=\lambda\mathbf{e}_1+\mu\mathbf{e}_2+\nu\mathbf{e}_3=\frac{a}{2}[(\mu+\nu)\hat{\mathbf{i}}+(\nu+\lambda)\hat{\mathbf{j}}+(\lambda+\mu)\hat{\mathbf{k}}] \tag{1}$$

with

$$\mathbf{e}_1=\frac{a}{2}(\hat{\mathbf{j}}+\hat{\mathbf{k}})\ ,$$

$$\mathbf{e}_2=\frac{a}{2}(\hat{\mathbf{k}}+\hat{\mathbf{i}})\ ,$$

$$\mathbf{e}_3=\frac{a}{2}(\hat{\mathbf{i}}+\hat{\mathbf{j}})\ ,$$

where the cubic unit cell has sides of length a, and $\hat{\mathbf{i}},\hat{\mathbf{j}},\hat{\mathbf{k}}$ are unit vectors along the x,y,z axes.

A Cu^{2+} ion at $\mathbf{R}$ has six nearest N neighbors octahedrally arranged at

$$(\mathbf{R}_1,\mathbf{R}_2,\mathbf{R}_3,\mathbf{R}_4,\mathbf{R}_5,\mathbf{R}_6)=\mathbf{R}+d(\hat{\mathbf{i}},\hat{\mathbf{j}},\hat{\mathbf{k}},-\hat{\mathbf{i}},-\hat{\mathbf{j}},-\hat{\mathbf{k}})\ . \tag{2}$$

Suppose now that a distortion is imposed on the lattice, which corresponds to that which would be found for a standing vibrational wave in the lattice if its time dependence is ignored. Such a wave ϵ will have a direction $\mathbf{q}$, a polarization $\mathbf{A}$, and a phase constant α associated with it. Thus

$$\epsilon=\mathbf{A}\sin(\mathbf{q}\cdot\mathbf{R}+\alpha)\ . \tag{3}$$

The mode which starts to soften in phase I corresponds to $\mathbf{q}=(\xi,\xi,0)$, so we particularize to such a direction.

The next question is what direction to choose for $\mathbf{A}$. In lattice dynamics, it is usually assumed that the modes have either longitudinal or transverse polarizations. However, in the present crystal, and for propagation along [110], it is not obvious that these distinctions can be made. On symmetry grounds, it can be seen that there will be one transverse mode, with $\mathbf{A}$ in the z direction. In the xy plane, there is no symmetry operator which leaves the direction of propagation unaltered and which distinguishes between longitudinal and transverse modes. We shall, therefore, assume that the modes with displacements in this plane are mixtures of the two. There are thus three possibilities for $\mathbf{A}$, the first being the transverse mode:

$$\mathbf{A}_1=A_1\hat{\mathbf{k}}\ , \tag{4a}$$

and the other two:

$$\mathbf{A}_2=\frac{A_2}{\sqrt{2}}[(\cos\beta+\sin\beta)\hat{\mathbf{i}}+(\sin\beta-\cos\beta)\hat{\mathbf{j}}]\ , \tag{4b}$$

$$\mathbf{A}_3=\frac{A_3}{\sqrt{2}}[(-\sin\beta+\cos\beta)\hat{\mathbf{i}}+(\cos\beta+\sin\beta)\hat{\mathbf{j}}]\ , \tag{4c}$$

where β is an arbitrary parameter.

The Γ_3 ground doublet of Cu^{2+} ion is only sensitive to local strains:[9]

$$Q_2=\tfrac{1}{2}[(X_1-X_4)-(Y_2-Y_5)]\ , \tag{5a}$$

$$Q_3=\frac{1}{\sqrt{12}}[2(Z_3-Z_6)-(X_1-X_4)-(Y_2-Y_5)]\ , \tag{5b}$$

where (X,Y,Z) are the Cartesian components of ϵ at the positions of the six neighbors (i.e., the changes in the coordinates of the N neighbors).

For the polarization $A_1\hat{\mathbf{k}}$, the X and Y of all six neighbors are zero, so $Q_2=0$, and Q_3 is also zero because $Z_3=Z_6$ when there is a strain in the $\hat{\mathbf{k}}$ direction. This polarization, therefore, does not couple to the Cu^{2+} ions and will not be further considered.

Coming now to the second polarization given by Eq. (4b) from Eqs. (1)—(3):

$$\begin{bmatrix}X_1\\X_4\end{bmatrix}=\frac{A_2}{\sqrt{2}}(\cos\beta+\sin\beta)\sin(\theta\pm\xi d)\ , \tag{6a}$$

$$\begin{bmatrix}Y_2\\Y_5\end{bmatrix}=\frac{A_2}{\sqrt{2}}(\sin\beta-\cos\beta)\sin(\theta\pm\xi d)\ , \tag{6b}$$

$$\begin{bmatrix}Z_3\\Z_6\end{bmatrix}=0\ , \tag{6c}$$

where

$$\theta\equiv\frac{a\xi}{2}(\lambda+\mu+2\nu)+\alpha\ .$$

There is a question over the value to be chosen for α, the phase angle of the wave. Since $(\xi,\xi,0)$ is assumed to give rise to an incommensurate phase, there is no loss in generality in taking it to be zero, for there will be some Cu^{2+} sites at which the associated displacements are zero. The point which then arises is what determines which Cu^{2+} ions have this property, or can the strain wave be freely displaced by arbitrary lattice vectors? We shall assume that the wave is pinned, perhaps by the presence of defects, by the existence of surfaces, or by a domain structure.

From Eqs. (5) and (6):

$$Q_2=\sqrt{2}A_2\cos\beta\cos\theta\sin(\xi d)\ , \tag{7a}$$

$$Q_3=-\sqrt{2/3}A_2\sin\beta\cos\theta\sin(\xi d)\ . \tag{7b}$$

The corresponding expressions for the third polarization $\mathbf{A}_3$ may be obtained by letting $\beta\rightarrow\beta+\pi/2$.

C. The incommensurate phase transition

Continuing with the polarization $\mathbf{A}_2$, the splitting of the Γ_3 doublet of the Cu^{2+} ion at $\mathbf{R}$ will be proportional $(Q_2^2+Q_3^2)^{1/2}$, with proportionality factor Δ. To create such a splitting, it is necessary to strain the crystal, and this requires a strain energy of $\frac{1}{2}\eta_2A_2^2$ per Cu^{2+} ion. The magnetic free energy of the Cu^{2+} ion at $\mathbf{R}$ will be

$$F_m=-kT\ln[\exp(-\delta/kT)+\exp(\delta/kT)]\ , \tag{8}$$

which is even in δ.

The splitting 2δ for mode $\mathbf{A}_2$ from Eq. (7) is

$$2\delta=\Delta(Q_2^2+Q_3^2)^{1/2}=\sqrt{2}\Delta A_2(\tfrac{1}{3}\sin^2\beta+\cos^2\beta)^{1/2}\times\sin(\xi d)\cos\theta\ . \tag{9}$$

The total free energy per unit volume will consist of the elastic energy and the magnetic free energies of the Cu^{2+} ions, which vary with δ. The unit volume should, therefore, be large enough to contain the whole range of values for δ. We shall suppose that it contains N Cu^{2+} ions. The free energy for this unit volume will then be

$$F=\tfrac{1}{2}\eta_2A_2^2N-\sum_{\lambda,\mu,\nu}F_m\ . \tag{10}$$

The summation over $\lambda\mu\nu$ will be converted into an integral, but before doing so it is convenient to examine the variation of the free energy with A_2 and to determine what value of A_2 produces the minimum free energy. This is obtained from the solution of

$$\frac{\partial F}{\partial A_2}=0=\eta_2A_2N-\frac{\Delta}{\sqrt{2}}(\tfrac{1}{3}\sin^2\beta+\cos^2\beta)^{1/2}\times\sin(\xi d)\sum_{\lambda,\mu,\nu}\cos\theta\tanh\left[\frac{\delta}{kT}\right]\ . \tag{11}$$

Since δ and Δ are linear in A_2, it is readily seen that $A_2=0$ is a solution for all T. In fact, at high T it is the only solution, so there is no reason to expect that a spontaneous deformation to an incommensurate lattice will occur. However, as T is reduced, another solution enters, at a critical value of T_c obtained by replacing $\tanh(\delta/kT_c)$ by δ/kT_c. From Eqs. (9) and (11) T_c is determined by

$$\eta_2 N k T_c = \tfrac{1}{2}\Delta^2(\tfrac{1}{3}\sin^2\beta+\cos^2\beta)\sin^2(\xi d)\sum_{\lambda,\mu,\nu}\cos^2\theta \ . \tag{12}$$

On further reduction of temperature $\tanh(\delta/kT)$, at least for most of the Cu^{2+} ions, tends rapidly to unity, in which case A_2 tends to A_2^0 given by

$$\eta_2 N A_2^0 = \frac{1}{\sqrt{2}}\Delta(\tfrac{1}{3}\sin^2\beta+\cos^2\beta)^{1/2}\sin(\xi d)\sum_{\lambda,\mu,\nu}|\cos\theta| \ . \tag{13}$$

A more detailed theory would treat λ,μ,ν as continuous variables. (See the Appendix.) The N factors then disappear from the Eqs. (12) and (13) for T_c and A_2^0, giving

$$\eta_2 k T_c = (\Delta/2)^2(\tfrac{1}{3}\sin^2\beta+\cos^2\beta)\sin^2(\xi d) \ , \tag{14}$$

$$\eta_2 A_2^0 = \frac{\sqrt{2}}{\pi}\Delta(\tfrac{1}{3}\sin^2\beta+\cos^2\beta)^{1/2}\sin(\xi d) \ . \tag{15}$$

These are useful relations, because they show that the values to which A_2 tends, as T is reduced, is simply related to T_c, thus

$$8kT_c = \pi^2\eta_2(A_2^0)^2 \ . \tag{16}$$

From Eqs. (8)—(16), the minimum free energy tends to

$$F_{\min} = -\tfrac{1}{2}N\eta_2(A_2^0)^2 = -\frac{4}{\pi^2}NkT_c \ , \tag{17}$$

which implies that, as the temperature is reduced from a high value, it can be expected that if the first lattice mode to soften is along [110] say at $(\xi,\xi,0)$, then as the temperature is lowered there is no other mode, for this direction, that will possess an even lower free energy. Once the mode with the highest T_c is chosen it will be stable as T is decreased. It does not, as will be seen in Sec. III D, exclude the possibility that there is another mode, for some other direction, which has a lower critical temperature T_c' and a lower free energy. All that is required is a larger numerical factor than $4/\pi^2$ in the expression relating the minimum free energy to T_c'—a factor which arises from the summations (integrations) over the strain distributions at the lattice sites.

D. The commensurate phase transition

In the light of the remarks in Sec. III C, an obvious distortion mode to study is one which removes the Cu^{2+} orbital degeneracy equally at every site, and which, significantly, corresponds to that found at low temperatures[2] (i.e., the [111] distortion).

The strain field for this direction can be written as

$$\boldsymbol{\epsilon}' = \mathbf{A}'\sin(\mathbf{q}'\cdot\mathbf{R}+\alpha') \tag{18}$$

with $\mathbf{q}'=(\pi/a)(1,1,1)$. Since [111] is a threefold symmetry axis, the polarizations separate into longitudinal and symmetry-related transverse modes. For the longitudinal mode, the polarization is

$$\mathbf{A}_1' = \frac{A_1'}{\sqrt{3}}(\hat{\mathbf{i}}+\hat{\mathbf{j}}+\hat{\mathbf{k}}) \ . \tag{19}$$

Then from Eqs. (1) and (18),

$$\begin{bmatrix} X_1' \\ X_4' \end{bmatrix} = \begin{bmatrix} Y_2' \\ Y_5' \end{bmatrix} = \begin{bmatrix} Z_3' \\ Z_6' \end{bmatrix} = \frac{A_1'}{\sqrt{3}}\sin(\phi\pm d) \ , \tag{20}$$

where

$$\phi \equiv \pi(\lambda+\mu+\nu)+\alpha' \ ,$$

so

$$Q_2' = Q_3' = 0 \ ,$$

and the longitudinal mode does not couple to the Cu^{2+} ions.

The amplitude of the corresponding transverse mode, with arbitrary polarization, in the plane (111) is

$$\mathbf{A}_2' = A_2'\left[\frac{\cos\gamma}{\sqrt{2}}(\hat{\mathbf{i}}-\hat{\mathbf{j}})+\frac{\sin\gamma}{\sqrt{6}}(\hat{\mathbf{i}}+\hat{\mathbf{j}}-2\hat{\mathbf{k}})\right] \tag{21}$$

with γ an arbitrary parameter. Then

$$\begin{bmatrix} X_1' \\ X_4' \end{bmatrix} = A_2'\left[\frac{\cos\gamma}{\sqrt{2}}+\frac{\sin\gamma}{\sqrt{6}}\right]\sin(\phi\pm d) \ , \tag{22a}$$

$$\begin{bmatrix} Y_2' \\ Y_5' \end{bmatrix} = A_2'\left[\frac{-\cos\gamma}{\sqrt{2}}+\frac{\sin\gamma}{\sqrt{6}}\right]\sin(\phi\pm d) \ , \tag{22b}$$

$$\begin{bmatrix} Z_3' \\ Z_6' \end{bmatrix} = A_2'\left[\frac{-2\sin\gamma}{\sqrt{6}}\right]\sin(\phi\pm d) \ . \tag{22c}$$

Substitution of Eq. (22) into Eq. (5) gives

$$Q_2' = \sqrt{2}A_2'\cos\gamma\cos\phi\sin d \ , \tag{23a}$$

$$Q_3' = -\sqrt{2}A_2'\sin\gamma\cos\phi\sin d \ . \tag{23b}$$

It follows that the splitting $2\delta'$, which is proportional to $[(Q_2')^2+(Q_3')^2]^{1/2}$ with the proportionality factor Δ, is independent of the polarization direction, and that the choice of the phase angle $\alpha'=0$ optimizes it at every Cu^{2+} site. The free energy per unit volume then becomes

$$F' = \tfrac{1}{2}\eta'(A_2')^2N - kT\ln[\exp(-\delta'/kT)+\exp(\delta'/kT)] \ , \tag{24}$$

where

$$2\delta' = \Delta[(Q_2')^2+(Q_3')^2]^{1/2} = \sqrt{2}\Delta A_2'\sin d \ . \tag{25}$$

Minimizing the free energy with respect to A_2' gives

$$\frac{\partial F'}{\partial A_2'} = 0 = \eta' A_2' N - N\frac{\Delta}{\sqrt{2}}\sin d\tanh(\delta'/kT) \ , \tag{26}$$

and a phase transition if it occurs, will be at T_c', where

$$2\eta' kT_c' = (\Delta\sin d)^2 \ . \tag{27}$$

The maximum value of A_2', $(A_2')^0$ can be obtained by letting $\tanh(\delta'/kT)\rightarrow 1$ in Eq. (26):

$$\eta'(A_2')^0 = \frac{\Delta}{\sqrt{2}}\sin d \ . \tag{28}$$

The relationship between the critical temperature T_c' and the maximum distortion amplitude $(A_2')^0$ from Eqs. (27) and (28) is

$$kT_c' = \eta'[(A_2')^0]^2 . \tag{29}$$

The minimum free energy at low temperatures from Eqs. (24)–(29) is

$$F'_{\min} = -\tfrac{1}{2}NkT_c' . \tag{30}$$

A comparison of Eqs. (17) and (30) shows that the factor multiplying the critical temperature for the [111] distortion is greater in magnitude than the factor multiplying the critical temperature for the $[\xi\xi 0]$ distortion. It follows that if the $[\xi\xi 0]$ mode is that chosen for the high-temperature transition, the low-temperature mode [111] will play no part unless its transition temperature is within $(4/\pi^2)/\frac{1}{2} \sim 80\%$ of that of the high-temperature transition. That is, if the transition T_c to the incommensurate phase occurs at ~291 K as in $Tl_2PbCu(NO_2)_6$, and there is a second phase transition to the commensurate phase at T_c', the latter transition cannot be below ~236 K. The measured T_c' is[7,8] ~247 K. Figure 9 shows the competition between the incommensurate and the commensurate modes schematically.

E. The uniform strain

The theory up to this point suggests that, in the incommensurate phase the Cu^{2+} Γ_3 doublets will be split with the sign of the splitting varying with position in the crystal. Some sites can be expected to have the orbital electronic state $|0\rangle$ and others to have the state $|2^s\rangle$ as the ground state. There are, however, several experimental observations which seem to be at variance with this picture. The first is that there is ample structural evidence[2–4] that in phases II and III the crystal lattice is approximately tetragonal, compressed along the c axis, and the model contains no feature of this kind. The second series of observations are those related to the EPR results of Sec. II and those of Refs. 3, 4, 7, and 8. In both phases II and III, a single resonance line appears which shows a pseudotetragonal (slightly orthorhombic) behavior with $g_{\parallel} \sim 2.06$ and $g_{\perp} \sim 2.15$. This behavior is also in agreement with the picture of a simple structural phase transition to a pseudotetragonal lattice compressed along the c axis with all the Cu^{2+} ions being in the $|0\rangle$ state. From the resonance point of view, the incommensurate nature of phase II is hardly noticeable. So the question arises as to how to reconcile these observations which are in apparent conflict with those reported in Ref. 2.

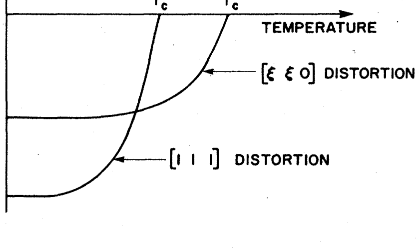

FIG. 9. Schematic diagram of the temperature variation of the free energies associated with the incommensurate phase transition at T_c and the commensurate phase transition at T_c'.

We shall, therefore, now explore the possibility that in phase II, *two* modes become soft simultaneously. The extra mode which we shall introduce is that which describes a transition to a tetragonal lattice. This mode only produces a Q_3 component at a Cu^{2+} site and we take its amplitude as A'', with elastic constant η'', and examine the total free energy E in phase II associated with modes A_2 and A'':

$$E = \tfrac{1}{2}[\eta_2 A_2^2 + \eta''(A'')^2]N - kT \sum_{\lambda,\mu,\nu} \ln \left[\exp\left[-\frac{\delta''}{kT} \right] + \exp\left[\frac{\delta''}{kT} \right] \right] , \tag{31}$$

where the splitting $2\delta''$ is

$$2\delta'' = \Delta\{[-\sqrt{2/3}A_2 \sin\beta \cos\theta \sin(\xi d) + A'']^2 + 2A_2^2 \cos^2\beta \cos^2\theta \sin^2(\xi d)\}^{1/2} \tag{32}$$

and so varies with the site indices λ,μ,ν. The requirement is to choose A_2 and A'' so that E is as small as possible. As usual, at high temperatures the condition is $A_2 = A'' = 0$, so that $E = 0$. We have already seen that with $A'' = 0$, another solution enters at a critical temperature, and the question is whether or not there is a further solution in which neither A_2 nor A'' are zero. It can be expected that if such a solution exists and that T_c is the temperature at which it first appears, then A_2/kT_c and A''/kT_c will be small, in which case up to second order:

$$\frac{\partial E}{\partial A_2} \sim \eta_2 A_2 N - \frac{1}{kT}\frac{\partial}{\partial A_2} \sum_{\lambda,\mu,\nu} (\delta'')^2 , \tag{33a}$$

$$\frac{\partial E}{\partial A''} \sim \eta'' A'' N - \frac{1}{kT}\frac{\partial}{\partial A''} \sum_{\lambda,\mu,\nu} (\delta'')^2 . \tag{33b}$$

The interesting point which now emerges is that the cross term of type $A_2 A''$ in $(\delta'')^2$ disappears in the summation over sites, so the conditions on T_c reduce to two:

$$\left[\eta_2 kT_c N - \frac{\Delta^2}{2}(\tfrac{1}{3}\sin^2\beta + \cos^2\beta) \times \sin^2(\xi d) \sum_{\lambda,\mu,\nu} \cos^2\theta \right] A_2 = 0 , \tag{34a}$$

$$\left[\eta'' kT_c - \frac{\Delta^2}{4} \right] A'' = 0 . \tag{34b}$$

The obvious solutions to Eqs. (34) are either $A_2 = 0$ and $A'' \neq 0$, or vice versa. However, there may be a special solution in which neither is zero, as can be seen as follows. It is not obvious, assuming there is an incommensurate phase, how the value of ξ is determined. It is just possible that the explanation is that the major effect is due to a nonzero A'', so that phase II is basically that of a ferrodistortive JT phase, in which each Cu^{2+} ion has the same ground state $|0\rangle$. Thus T_c is determined by Eq. (34b). It can then happen that there is some value of ξ (and β) for which the equation (34a) is also satisfied without the requirement that A_2 be zero. There would then be a superposition of an incommensurate wave of distortions on the presumably larger ferrodistortion. There seems little doubt that if the above effect occurs the value of E with $A_2=0$ will be greater than that for some nonzero $|A_2|$, so the onset of the ferrodistortion will be accompanied by an incommensurate distortion.

The attraction of the above explanation is that the crystallographic and resonance results can be reconciled. In the first place, the crystallographic data[2] show the effect we are describing. Secondly, the resonance data are typical of a strongly exchange-narrowed line for Cu^{2+} ions in the $|0\rangle$ state. If $A'' \gg A_2$, the uniform strain component dominates in Q_3, while contributing nothing to Q_2. So Q_3 reflects the uniform strain with Q_2 reflecting the incommensurate strain. The EPR spectrum in this approximation would be tetragonal since for any ion with a given Q_2, one can find another ion with the reversed value. This means that the crystal field for one ion is that for the other rotated about the z axis by $\pi/2$. Since there is, in fact, a slight variation in $g_\perp$ in the (001) plane (Fig. 6), evidence is provided for an incommensurate component of Q_3.

In the transition from phase II to phase III, there is no question of A'' being anything but finite throughout; so the role of the [111] distortion is simply to provide an extra process to lower the overall energy, at some appropriate temperature. In other words, the condition for this change to occur is obtained by taking the derivative of the free energy with just the one variable A', the amplitude of the [111] mode, at some definite nonzero A'' and A_2. We have examined the free-energy expressions in more detail than is needed to determine onsets of phase transitions and confirmed our conclusions. This leads to a unique expression for the critical temperature, although as already demonstrated, no phase transition will occur unless the resulting free energy is less than that of phase II. The fact that such a transition occurs suggests that this condition is satisfied. There will be little change in the position of the resonances on going through the transition from phase II to phase III, because there is little change in the ground state of the Cu^{2+} ion. On the other hand, there is a distinct reduction in the resonance linewidths, which suggests that the exchange interactions have increased. These interactions do not depend solely on the ground states of the Cu^{2+} ions, for they also involve the nature and positions of intervening diamagnetic ions. While the nature of these is not affected by the II→III transition, their positions are, and we therefore suppose that it is this which accounts for the change in the magnitude of the exchange interactions.

IV. CONCLUSIONS

We have presented EPR results for the incommensurate cooperative JT system $Tl_2PbCu(NO_2)_6$ and proposed a theory which provides a unified explanation for our measurements and the structural results, and correctly predicts the relative magnitudes of the incommensurate and commensurate phase-transition temperatures.

There have been a number of papers giving explanations of the properties of crystals similar to the ones we have used, and some controversy has been generated.[3,4] It therefore seems appropriate to try and place our model against some of the previous work. We feel that a certain amount of confusion has been caused by ignoring the coupling to the uniform strain in phases II and III, which we believe must be regarded as ferrodistortive in both phases. What has happened is that, for phase II, by concentrating on the strain field due to the incommensurate mode, several authors[3] have been led to describe this as antiferrodistortive in nature. (This was before the incommensurate nature had been fully established). In a sense, it may be so described, but only with the caveat that there is also present an accompanying ferrodistortion, which in phase II still leaves some sites with splitting $< kT$. Associated with these descriptions, there have been different opinions about the nature of the Cu^{2+} ground state. We believe that there can be no question that in both phases II and III it must be close to being almost pure $|0\rangle$. There seems to be no other way of explaining the resonance g values, and again the controversy surrounding this assignment seems to have been caused by ignoring the overall tetragonal strain. Such a strain was not ignored by Heine and McConnell and Yamada *et al.*[2] The latter suggested that in phase II there is a "fan spin" structure, which in phase III becomes a "canted spin" structure. This explanation has similarities with ours, the main difference being that $Q_2^2+Q_3^2$ was supposed to have the same magnitude for all Cu^{2+} ions, with $\tan^{-1}(Q_2/Q_3)$ being distributed over a range of values in phase II and having just two values in phase III. This seems to us to be an unnecessary restriction, and in both phases we suppose that the magnitude of $Q_2^2+Q_3^2$ does not have to be the same for all sites. Provided, as we have supposed, that A'' dominates, this ensures that to a good approximation each Cu^{2+} ion has the same state.

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APPENDIX

To go from Eqs. (12) and (13) to Eqs. (14) and (15) the summation over (λ,μ,ν), which are points in a cubic lattice, should be replaced by a volume integral. We make an orthonormal transformation to new coordinates (u,v,w):

$$u=(\lambda-\mu)/\sqrt{2}\ ,$$

$$v=(\lambda+\mu-\nu)/\sqrt{3}\ ,$$

$$w=(\lambda+\mu+2\nu)/\sqrt{6}\ .$$

Then in Eq. (11),

$$\sum_{\lambda,\mu,\nu}\cos\theta\tanh\left[\frac{\delta}{kT}\right]\to\sum_{u,v,w}\{\cos(\tfrac{1}{2}a\xi w)\times\tanh[B_2\cos(\tfrac{1}{2}a\xi w)]\}\ ,$$

where

$$B_2=\frac{\Delta}{\sqrt{2}}\frac{A_2}{kT}(\tfrac{1}{3}\sin^2\beta+\cos^2\beta)^{1/2}\sin(\xi d)\ .$$

The sum over (u,v,w) may be approximated by an integral:

$$\sum_{u,v,w}\{\cos(\tfrac{1}{2}a\xi w)\tanh[B_2\cos(\tfrac{1}{2}a\xi w)]\}\to\frac{N}{\int du\,dv\,dw}\int\cos(\tfrac{1}{2}a\xi w)\tanh[B_2\cos(\tfrac{1}{2}a\xi w)]du\,dv\,dw\ .$$

$$=\frac{N}{\int dw}\int\cos(\tfrac{1}{2}a\xi w)\tanh[B_2\cos(\tfrac{1}{2}a\xi w)]dw\ ,$$

where in both integrals in the range of integration for w should include all values of $\cos(\tfrac{1}{2}a\xi w)$. It is sufficient to integrate from $w=0$ to $w=\pi/a\xi$. Setting $\tfrac{1}{2}a\xi w\to W$:

$$\sum_{u,v,w}\{\cos(\tfrac{1}{2}a\xi w)\tanh[B_2\cos(\tfrac{1}{2}a\xi w)]\}\to N\frac{2}{\pi}\int_0^{\pi/2}\cos W\tanh(B_2\cos W)dW\ .$$

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