Critical behavior at the incommensurate structural phase transition in K_2SeO_4

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K_2SeO_4 has a second-order incommensurate structural phase transformation with a two-component order parameter of continuous symmetry. Its critical behavior should therefore be that of a $d=3$ XY model. We have measured the critical exponents associated with the growth of primary and secondary diffraction satellites and find them to be $2\beta=0.75(\pm0.05)$ and $2\tilde{\beta}=1.57(\pm0.07)$, respectively. These values are in reasonable agreement with the theoretical estimates $2\beta=0.70(\pm0.04)$ and $2\tilde{\beta}=1.69(\pm0.09)$ obtained by series expansions. The theoretical value of $2\tilde{\beta}$ is appreciably different from the naive Landau prediction $2\tilde{\beta}=4\beta$, and is given by $2\tilde{\beta}=2(2-\alpha-\phi)$ where ϕ is a crossover exponent associated with a uniaxial perturbation.

I. INTRODUCTION

K_2SeO_4 undergoes a continuous structural phase transformation at a critical temperature $T_c \approx 128$ K. The low-temperature phase is incommensurate and may be viewed as a result of the condensation of two high-temperature-phase modes with wave vector $\pm\vec{q}_\delta = \pm\frac{1}{3}(1-\delta)a^*$.[1] This paper describes a neutron scattering study of the critical behavior occurring close to this phase transformation. Specifically, we report measurements of the temperature dependence of the intensity of the primary satellite (located at $\vec{q}_\delta$) and that of the secondary satellite [located at $\vec{q}_{2\delta}=\frac{1}{3}(1+2\delta)a^*$]. These experiments are described in Sec. II. We devote Sec. III to an analysis of the data, from which we have determined values for the two exponents characterizing the rates at which the primary and secondary satellites vanish as $T\rightarrow T_c^-$. In Sec. IV, we develop the relevant theory, the key features of which it will be helpful to summarize at this point.

Like any other phase transition associated with a twofold degenerate soft mode, the transformation in K_2SeO_4 may be modeled by an $n=2$-component Landau-Ginzburg-Wilson (LGW) Hamiltonian. The distinctive feature of this transformation (indeed, of all such transformations to incommensurate phases) lies in the fact that the appropriate LGW model possesses a continuous symmetry, expressing the invariance of the free energy of the incommensurate phase against changes in the phase of the distortion profile.[2,3] In consequence, the theoretical predictions are free from the ambiguities which result from the symmetry-breaking perturbations generally present in solid-state realizations of this model: the universal features of the critical behavior should be those of the XY model of ferromagnetism, for which relatively precise series expansion results are available. In particular, elementary theory shows that the intensity of the primary satellite should have the asymptotic temperature dependence

$$I_1(T)\approx B_1(T_c-T)^{2\beta} , \quad (1)$$

where, employing the series results reported by Pfeuty *et al.*[4] and Ferer *et al.*[5] and making use of a scaling relation,

$$2\beta=2-\alpha-\gamma=0.70\pm0.04 . \quad (2)$$

The theory of the intensity of the secondary satellite is not quite so straightforward. We will show that

$$I_2(T)\approx B_2(T_c-T)^{2\tilde{\beta}} , \quad (3)$$

where

$$2\tilde{\beta}=2(2-\alpha-\phi)=1.69\pm0.09 , \quad (4)$$

with ϕ the crossover exponent associated with a uniaxial symmetry-breaking perturbation.[4] We will see that these predictions are in fair accord with experiment.

II. MEASUREMENT OF SATELLITE INTENSITY

The single crystal, kindly provided by the Kyushu University group, was grown from the saturated aqueous solution by slow evaporation at 323 K. The volume of the crystal was approximately 4 cm^3. The crystal was mounted in an aluminum can filled with He gas and placed in a Displex refrigerator. The temperature was controlled to within ±0.01 K.

The neutron-diffraction measurements were performed on a triple-axis spectrometer in the elastic scattering mode at the Brookhaven High Flux Beam Reactor. Incident neutron energies of 4.71 and 4.91 meV were chosen to minimize multiple-scattering effects as discussed below. A pyrolytic graphite monochromator and analyzer were used in conjunction with a polycrystalline Be filter to eliminate higher-order neutron contamination.

The scattering plane coincides with the [010] zone, shown in Fig. 1. Reflections and vectors in reciprocal space are represented by reference to an orthorhombic cell with $a^* \equiv 2\pi/a$ and $c^* \equiv 2\pi/c$ where $a = 7.588$ Å and $c = 5.973$ Å at 130 K in the high-temperature phase. In the incommensurate phase a^* is replaced by $a_L^* \equiv \frac{1}{3}a^*$. Thus, the $(h,0,l)$ reflection in the high-temperature phase corresponds to the $(3h,0,l)$ reflection in the incommensurate phase. The value of δ associated with the incommensurate wave vectors $\vec{q}_\delta$ and $\vec{q}_{2\delta}$ is 0.07 at 123 K. δ decreases with decreasing temperature. At 93 K, a second transition to a commensurate ferroelectric state occurs where the spontaneous polarization is directed along the c axis. The crystallography of the various phases is discussed in detail in Ref. 1. Briefly the high-temperature paraelectric phase belongs to the orthorhombic space group *Pnam*. Although no direct structure determination has been attempted in the ferroelectric phase, it can be inferred from the symmetry of the soft mode with the wave vector $\vec{q} = \frac{1}{3}\vec{a}^*$ which condenses to form the ferroelectric phase that the crystal must assume a c_{2v}^9 low-temperature structure. The displacement pattern of the atoms in the incommensurate phase closely resembles that of the ferroelectric phase.

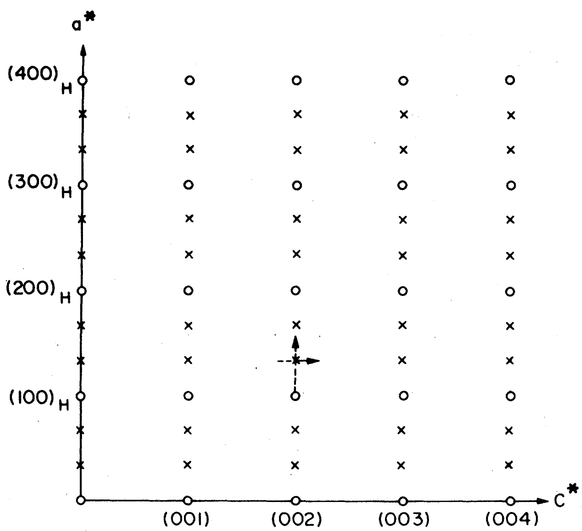

FIG. 1. [010]-zone scattering plane in the reciprocal lattice of K_2SeO_4. Open circles indicate the reciprocal-lattice points in the high-temperature (H) paraelectric phase and ×'s locate the commensurate positions of the superlattice reflections found in the low-temperature ferroelectric phase. The $(h,0,l)$ reflection using the high-temperature basis vectors corresponds to the $(3h,0,l)$ reflection using the low-temperature basis vectors.

In measuring the intensities of the primary and secondary satellite reflections, it is necessary to avoid multiple-scattering processes which can add to or subtract from the fundamental diffracted intensity. Multiple scattering occurs whenever two or more reciprocal-lattice points lie simultaneously on the Ewald sphere. It is especially important to ensure that the much weaker secondary satellite intensities are not contaminated by two separate scattering events both involving primary satellites. This would result in a doubly scattered beam parallel to that actually scattered from the secondary satellite. Since this spurious intensity is proportional to the product of the two primary satellite intensities involved, it is proportional to $|T_c - T|^{2(2\beta)}$.

Because of the relatively large lattice spacings in K_2SeO_4, the density of points in reciprocal space is high. In an effort to find satisfactory scattering geometries, data were obtained as a function of incident neutron energy and as a function of angle about an axis parallel to the scattering vector for many satellites in the scattering zone. Several particularly unfavorable configurations were also predicted by a numerical analysis. As an additional check for multiple scattering, the intensities of the reflections $(h-\delta,0,l)$ and $(\overline{h-\delta},0,l)$ were compared: the intensities of the otherwise symmetrical reflections present different possibilities for multiple scattering since the origin of the Ewald sphere in reciprocal space is in general not symmetric for the two cases. At incident neutron energies of the order of 14 meV, none of the satellites examined was found to be completely unaffected by multiple scattering over the range of temperatures of interest (δ and the lattice constants are temperature dependent so that points in reciprocal space have different positions relative to the Ewald sphere at different temperatures). It was therefore necessary to use a shorter incident wave vector corresponding to a neutron energy of about 5 meV. However, even at such a relatively low energy, the number of reflections within resolution distance of the Ewald sphere can still be substantial. In fact, only one of the secondary satellite reflections, $(8-2\delta,0,0)$, was found to be suitably free of multiple scattering and at the same time sufficiently intense to follow as $T \rightarrow T_c$.

Extinction effects can significantly reduce the diffracted intensity in the large crystals if the reflectivity is sufficiently high. However, the fact that satellite reflections whose intensities differed by a factor of $\simeq 20$ were found to show the same temperature dependence was taken as evidence that extinction effects were negligible for $(T_c - T) \lesssim 10$ K. [For $10 \lesssim (T_c - T) \lesssim 30$ K, the strong primary satellites showed some decrease in intensity characteristic of extinction whereas the weak primary satellites did not.]

III. ANALYSIS OF THE DATA

The basic problem posed by the analysis of the results presented in Sec. III lies in the existence of critical inelastic scattering which masks the anticipated sharp onset of the Bragg satellites. This scattering results in two difficulties, common to all neutron scattering investigations of order-parameter behavior. First, it evidently limits the utility of the data obtained in the regime close to T_c, where the inelastic scattering ultimately dominates the Bragg contribution. Its effects also extend, however, even to the regime where the Bragg scattering is dominant, since it may introduce significant uncertainty into the value of the transition temperature to be employed in fitting data to expressions such as Eqs. (1) and (3).

The latter difficulty is less acute in circumstances in which an independent measurement of T_c is available. We performed two experiments with this objective.

First, we examined the linewidth of the total scattering (Bragg plus critical) as a function of temperature. The width of the Bragg peak is essentially the resolution width of the instrument, the mosaic spread being negligible in the present sample. At $T = T_c$, the width of the total scattering is a minimum since the width of the critical scattering vanishes. The fitted linewidths indicated a value of 128.3 $(+0.2, -0.5)$ K for T_c.

Another method for determining T_c is to identify it with the temperature corresponding to the maximum rate of change of the total scattering at a primary satellite position. It can be shown that dI_{tot}/dT is proportional to the anomalous contribution to the heat capacity which should have a cusp at T_c. A plot of I_{tot} vs T is shown in Fig. 2, from which we estimate $T_c = 127.8 \pm 0.3$ K. Neither study resulted in an extremely precise estimate of T_c. Accordingly, we have treated T_c as an adjustable though sharply defined parameter. We have also considered the possibility of an inhomogeneity in T_c. Assuming a distribution of transition temperatures about a mean value, we calculated that an inhomogeneity greater than 0.1 K would result in a measurable "S"-shaped distortion of the $\ln I$ vs $\ln t$ plot which cannot be reproduced by a simple adjustment of T_c and/or β. Such a characteristic distortion was not observed in our data (Fig. 3).

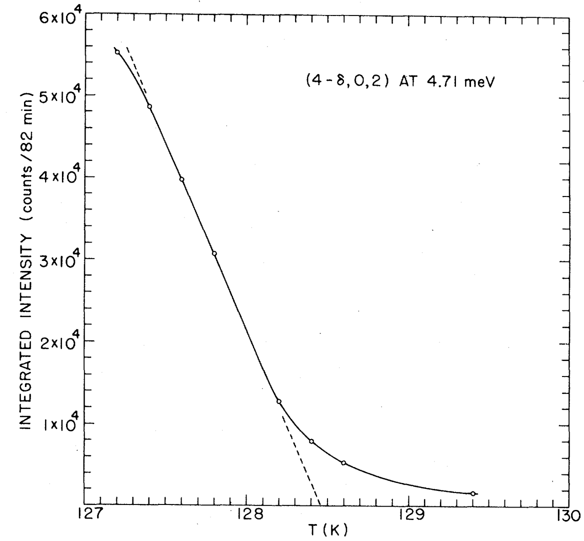

FIG. 2. Intensity of the $(4-\delta,0,2)$ primary satellite in the neighborhood of T_c. Only a temperature-independent background has been subtracted.

To utilize the data close to T_c, it is essential first to estimate and then to subtract out the contribution made by the inelastic scattering. There is no wholly satisfactory way of carrying out this procedure, since the intensity of the inelastic scattering contribution depends in a complicated way upon the frequency and wave-vector resolution of the experiment. We have adopted the traditional expedient[6] of estimating the temperature dependence of the critical scattering

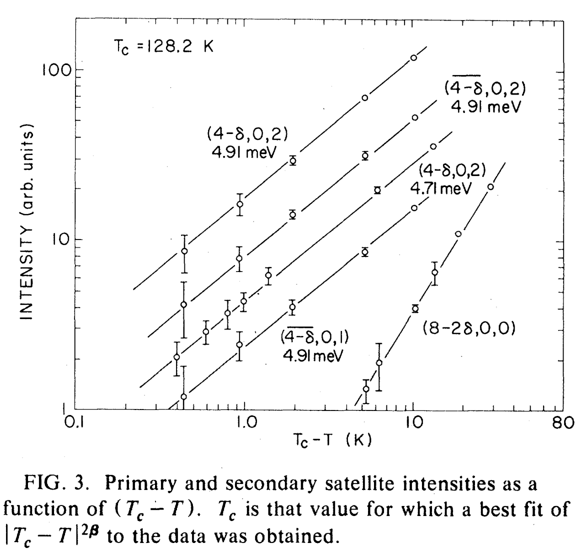

FIG. 3. Primary and secondary satellite intensities as a function of $(T_c - T)$. T_c is that value for which a best fit of $|T_c - T|^{2\beta}$ to the data was obtained.

occurring below T_c from the temperature dependence of the scattering actually observed above T_c. In doing so, we have made the assumption that the fluctuation spectrum may be treated within the framework of a classical quasiharmonic theory.[2] In this approximation, the soft phonons at $\pm \vec{q}_\delta$ (degenerate for $T > T_c$) are the progenitors of two incommensurate phase excitations: a temperature-independent "phason" mode, and an amplitude mode whose frequency hardens, according to a Curie-law form, with increasing $T_c - T$. This picture is clearly oversimplified since it fails to take account of the nonclassical character of the fluctuation spectrum (which, we shall see, is clearly revealed by the "observed" values of β and $\tilde{\beta}$). A more refined treatment of the fluctuation spectrum is possible[7] but seems unwarranted here, in view of the uncertainties associated with the experimental resolution. Within the framework, then, the form of the critical scattering is easily determined and we can write [defining $t \equiv (T - T_c)/T_c$]

$$I(-t) = \tfrac{1}{2} I(0) + \tfrac{1}{2} I(2t) \ , \qquad (5)$$

which is valid (within the quasiharmonic theory) for the inelastic scattering near both satellites.

In Fig. 3, we show log-log plots of the corrected intensities, for a number of different primary and secondary satellite reflections, versus $|T_c - T|$, with T_c taken as 128.2 K. The intensity scale is arbitrary. The measured intensities, $I_{\rm obs}$, of the various reflections are in approximately the following ratios to one another: $I_{\rm obs}[(4-\delta,0,2),(\overline{4-\delta},0,2)]/I_{\rm obs}[(\overline{4-\delta},0,1)]/I_{\rm obs}[(8-2\delta,0,0)] \simeq 2000/100/4$. The slopes of the linear plots are equal to the values of the critical-point exponents 2β and $2\tilde{\beta}$.

Figure 4 displays the values of 2β obtained by fitting $|T_c - T|^{2\beta}$ to the corrected (and combined) primary satellite intensities (for a variety of choices of T_c), along with the estimated uncertainties. Also shown are the values of $2\tilde{\beta}$ obtained by fitting $|T_c - T|^{2\tilde{\beta}}$ to the secondary satellite intensities. However, a critical scattering correction was not applied to the secondary satellite intensities for two reasons. First, no critical scattering about the secondary satellite position could be observed above T_c. Second, the temperatures at which secondary satellite peaks could be observed below T_c were far enough away from the transition temperature that the ratios of critical scattering intensity to Bragg intensity, based on the primary satellite intensities, were negligibly small. It is important to emphasize that we are making, nonetheless, the explicit assumption that the data are taken close enough to T_c to be representative of the critical region. This assumption is open to some question particularly for the secondary reflections where data collection nearer T_c was impossible due to lack of intensity. It may be pointed out that away from the critical region, the temperature dependence

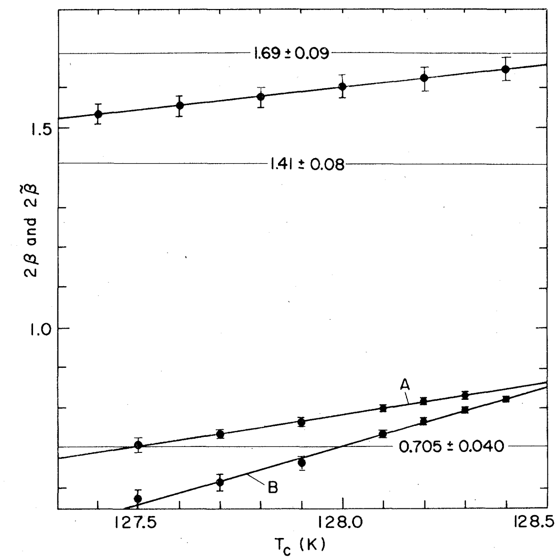

FIG. 4. Experimental and theoretical values for the exponents 2β (lower part of figure) and $2\tilde{\beta}$ (upper part of figure). The experimental results (Φ) were obtained by fitting the appropriate power law [Eqs. (1) and (3)] to the primary and secondary satellite intensities, for a number of choices of T_c lying within the range prescribed by independent studies. The best experimental estimate is $T_c = 127.8$ K (see text). The theoretical predictions (and uncertainties) $2\beta = 0.70$ [Eq. (2)] $2\tilde{\beta} = 1.69$ [Eq. (4)] and the naively modified Landau result $2\tilde{\beta} = 4\beta = 1.41$ are indicated. The values of 2β denoted by "A" are obtained when the data leading to the values of 2β indicated by "B" are corrected for critical scattering.

of incommensurate satellite intensities is complicated by anomalous Debye-Waller factors.[8]

Figure 4 also shows the theoretical predictions for 2β [Eq. (2)] and $2\tilde{\beta}$ [Eq. (4)]; the theoretical value of 4β is included for comparison.

Finally, it should be pointed out that although extinction effects are believed to be negligible, as discussed above, failure to correct for any intensity loss due to extinction would result in values of 2β and $2\tilde{\beta}$ that are too low. Our analysis of the data indicates $2\beta = 0.75(\pm 0.05)$ which is consistent with, and more precise than, the value of $2\beta = 0.8(\pm 0.1)$ given in Ref. 1. For $2\tilde{\beta}$, we find a value of $1.57(\pm 0.07)$. The uncertainties quoted for both 2β and $2\tilde{\beta}$ were arrived at by taking ± 0.3 K as the uncertainty in T_c.

IV. THEORY

As with any universal characteristic of the critical region, the exponents governing the critical singularities displayed by the incommensurate phase satellites do not depend upon the microscopic details of the system under consideration: the character of the critical behavior may, as always, be established by studying the simplest system representative of the universality class of interest. In this spirit, then, we consider a crystal with a single atom in the primitive unit cell. We denote by $\{\vec{x}\}$ the set of lattice sites of the high-temperature phase. The completely elastic scattering at wave-vector transfer $\vec{Q}$ is then proportional to

$$S(\vec{Q}) = \sum_{\vec{x},\vec{x}'} \exp[-i\vec{Q}\cdot(\vec{x}-\vec{x}')]\, d_Q(\vec{x})\, d_{Q^*}(\vec{x}') \ , \tag{6}$$

where

$$d_Q(\vec{x}) = \langle e^{-i\vec{Q}\cdot\vec{u}(\vec{x})}\rangle \ , \tag{7}$$

while $\vec{u}(\vec{x})$ describes the instantaneous displacement of the atom at site $\vec{x}$, with respect to its high-symmetry site.

We suppose that the system concerned undergoes a structural instability associated with the softening of the modes at $\pm\vec{q}_\delta$ (each of which is taken to be nondegenerate). In the immediate vicinity of the critical point, the essential fluctuations will have Fourier components with wave vectors in the neighborhood of $\pm\vec{q}_\delta$. Accordingly, we may write

$$\vec{u}(\vec{x}) = \vec{e}(\vec{q}_\delta)\int_{|\vec{k}|<\Lambda} \times\{Q(\vec{q}_\delta+\vec{k})\exp[-i(\vec{q}_\delta+\vec{k})\cdot\vec{x}] + Q(-\vec{q}_\delta+\vec{k})\exp[i(\vec{q}_\delta-\vec{k})\cdot\vec{x}]\}\, d\vec{k} \ , \tag{8}$$

where $\vec{e}(\vec{q}_\delta)$ is a unit vector giving the polarization of the critical mode, Λ is some small but otherwise arbitrary cutoff, and $Q(\vec{q})$ is the classical mode amplitude of wave vector $\vec{q}$. It proves convenient to introduce two new local coordinates $P_1(\vec{x})$ and $P_2(\vec{x})$ defined by

$$P_1(\vec{x}) = \int_{|\vec{k}|<\Lambda} [Q(\vec{q}_\delta+\vec{k}) + Q(-\vec{q}_\delta+\vec{k})] \times e^{-i\vec{k}\cdot\vec{x}}\, d\vec{k} \ ,$$
$$P_2(\vec{x}) = -i\int_{|\vec{k}|<\Lambda} [Q(\vec{q}_\delta+\vec{k}) - Q(-\vec{q}_\delta+\vec{k})] \times e^{-i\vec{k}\cdot\vec{x}}\, d\vec{k} \ . \tag{9}$$

In this representation, the displacement field (8) assumes the form

$$\vec{u}(\vec{x}) = \vec{e}(\vec{q}_\delta)[P_1(\vec{x})\cos(\vec{q}_\delta\cdot\vec{x}) + P_2(\vec{x})\sin(\vec{q}_\delta\cdot\vec{x})] \ . \tag{10}$$

This result may be reexpressed in a still simpler form by introducing two further local coordinates $A(\vec{x})$ and $\phi(\vec{x})$ such that

$$P_1(\vec{x}) = A(\vec{x})\cos\phi(\vec{x}) \ , \tag{11}$$
$$P_2(\vec{x}) = A(\vec{x})\sin\phi(\vec{x}) \ .$$

Evidently,

$$\vec{u}(\vec{x}) = \vec{e}(\vec{q}_\delta)A(\vec{x})\cos[\vec{q}_\delta\cdot\vec{x}+\phi(\vec{x})] \tag{12}$$

so that $A(\vec{x})$ and $\phi(\vec{x})$ describe, respectively, the amplitude and the phase of the local fluctuations.

Making use of the representation (12), it is easy to recast Eq. (7) in the form

$$d_Q(\vec{x}) = 1 + \sum_{m=1}^{\infty}(-i)^m \times\langle \exp\{-im[\vec{q}_\delta\cdot\vec{x}+\phi(\vec{x})]\}J_m(QA(\vec{x})) + \exp\{im[\vec{q}_\delta\cdot\vec{x}+\phi(\vec{x})]\}J_m(QA(\vec{x}))\rangle \ , \tag{13}$$

where we have made use of a Bessel-function expansion[9] and have written $Q \equiv \vec{Q}\cdot\vec{e}(\vec{q}_\delta)$. The form of the dominant singular term contributing to each Bragg satellite may be determined by expanding the Bessel functions to leading order,

$$J_m(QA(\vec{x})) \approx \frac{1}{2^m m!}[QA(\vec{x})]^m \ . \tag{14}$$

Combining Eqs. (11), (13), and (14) one finds that the nontrivial contributions to Eq. (6) may be expressed in the form

$$S(\vec{Q}) = \frac{N^{(2\pi)^3}}{v} \times \sum_{\{\vec{\tau}\}}\sum_{m=1}^{\infty}[\delta(\vec{Q}+\vec{\tau}+m\vec{q}_\delta)+\delta(\vec{Q}+\vec{\tau}-m\vec{q}_\delta)] \times \left|\frac{Q^m\langle[P_1(\vec{x})+iP_2(\vec{x})]^m\rangle}{2^m m!}\right|^2 \ , \tag{15}$$

where $\{\vec{\tau}\}$ denotes the set of reciprocal-lattice vectors of the high-temperature phase. In particular, the intensity of the primary ($m=1$) and secondary ($m=2$) satellites will be proportional to

$$I_1(T) = \langle P_1(\vec{x})\rangle^2 + \langle P_2(\vec{x})\rangle^2 \tag{16}$$

and

$$I_2(T) = [\langle P_1^2(\vec{x})\rangle - \langle P_2^2(\vec{x})\rangle]^2 + 4\langle P_1(\vec{x})P_2(\vec{x})\rangle^2 \ . \tag{17}$$

The argument is completed by noting that in the representation defined by the coordinates P_1 and P_2 the effective Hamiltonian for the system is precisely that of an $n=2$-component LGW model [see, e.g., Cowley and Bruce, Eq. (2.9)].[3] One concludes immediately that, as usual, the primary satellite intensity, Eq. (16), follows the square of the order parameter, and thus gives a measure of the conventional order parameter exponent β [Eq. (1)]. The behavior of the secondary satellite intensity, however, is more subtle. The operator $P_1^2-P_2^2$ has the form of a perturbation produced by a uniaxial anisotropy, as does the operator P_1P_2 (the two operators transform into one another under a "rotation" of the coordinate space). A scaling argument (cf. Fisher and Nelson[10]) then readily establishes the prediction (3). The intensity of the secondary satellite vanishes with exponent $2\tilde{\beta}\approx 1.69$, and not the exponent $(4\beta\approx 1.41)$ which a cavalier modification of Landau theory would suggest. This discussion is, in fact, not quite complete since, in addition to the "diffraction harmonics" described by Eq. (13), there exists additional Bragg scattering associated with the harmonics of the displacement field. It is possible to show, however,[3] that the associated contribution to the secondary satellite intensity follows precisely the same power law [Eq. (4)] as the contribution we have considered explicitly here.

V. SUMMARY AND CONCLUSIONS

We have studied the critical behavior occurring at the 128-K phase transition in K_2SeO_4. The temperature dependence of the intensities of both primary and secondary satellites has been determined, particular care having been taken to avoid contamination of the secondary peaks by multiple-scattering effects. The precision of the exponents 2β and $2\tilde{\beta}$ obtained is limited by the accuracy with which we have been able to locate the transition temperature. Accordingly, the experimental results do not provide an extremely stringent test of the theoretical predictions we have presented on the basis of the system's isomorphism with the three-dimensional XY model. As summarized in Fig. 4, however, the results are at the least consistent with the theoretical predictions, and provide clear evidence favoring our prediction [Eq. (4)] for $2\tilde{\beta}$ as compared with the prediction $(2\tilde{\beta}=4\beta)$ of naively modified Landau theory.

ACKNOWLEDGMENT

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