

Mössbauer-Effect Study of the Ferroelectric Transitions in Potassium Ferrocyanide Trihydrate and Ferric Ammonium Sulfate Dodecahydrate*

T. G. GLEASON† AND J. C. WALKER‡

The Johns Hopkins University, Baltimore, Maryland 21218

(Received 13 December 1968; revised manuscript received 31 July 1969)

The Mössbauer effect has been used to study the ferroelectric transitions in potassium ferrocyanide trihydrate (KFCT) and ferric ammonium sulfate dodecahydrate (FAS). The recoilless fraction and isomer shift of these materials have been observed as a function of temperature. For FAS, the absorption linewidth was also observed. For FAS, the recoilless fraction f and absorption linewidth w were found to behave anomalously at the ferroelectric transition temperature T_c ; f exhibits a minimum at T_c , and w has a maximum there. No change in the isomer shift was detected at the FAS transition. The behavior of f is consistent with a description of the transition in FAS in terms of a "soft" transverse optical (TO) lattice mode of zero wave vector ($\omega_{TO} \rightarrow 0$ at $T = T_c$). For KFCT, no anomalous behavior of any Mössbauer-effect parameter was detected. This is contrary to a previous report by other workers of a maximum in f near T_c for KFCT. The lack of any anomaly in KFCT is consistent with an order-disorder model of the KFCT transition, but does not preclude one particular type of displacive transition.

I. INTRODUCTION

THE Mössbauer-effect recoilless fraction, isomer shift and absorption linewidth have been measured as a function of temperature at and near the ferroelectric transition in two ferroelectric crystals. Results have been obtained which are consistent with a widely used lattice dynamic model of ferroelectric transitions¹ which predicts a minimum in the recoilless fraction at the transition temperature.

Several workers have previously reported Mössbauer-effect studies of ferroelectric systems²⁻⁵; these workers used ferroelectric materials that do not normally contain any Mössbauer nuclei. The nuclei actually studied were, therefore, present either as impurities or, in one case,⁵ as part of a nonferroelectric compound which was in solid solution with the ferroelectric compound.

Despite acknowledged difficulties in doping the samples without changing their ferroelectric properties,² these experiments demonstrated the existence of a minimum in the Mössbauer fraction at the transition. In addition, isomer shift discontinuities have been reported,²⁻⁴ and the quadrupole splitting of the Mössbauer absorption spectrum has been reported to be proportional to the square of the spontaneous polarization of the ferroelectric crystal.^{2,4}

At the time the present work was begun, no report has been made of any Mössbauer studies of the ferroelectric

transition in either of the two known ferroelectrics which contain iron as a normal constituent. These materials are potassium ferrocyanide trihydrate ($K_4Fe(CN)_6 \cdot 3H_2O$) (KFCT), and ferric ammonium sulfate dodecahydrate ($NH_4Fe(SO_4)_2 \cdot 12H_2O$) (FAS). FAS has a first-order ferroelectric transition at about 88°K,⁶ and KFCT has a second-order transition at about 250°K.⁷ Since Fe⁵⁷ is the most convenient of all the nuclei used in the Mössbauer effect, these two materials offer an opportunity to observe the transition, using pure undoped samples. In addition, some uncertainty exists with regard to the nature of the transition in KFCT which Mössbauer-effect measurement might be able to clarify.

While the present work was in progress, Hazony and co-workers⁸ published a Mössbauer-effect study of KFCT in which they reported a maximum in the recoilless fraction slightly above the transition temperature. They suggest a method of reconciling the maximum with the theoretically predicted minimum, and claim to have determined the microscopic nature of the KFCT transition.

In the present work no Mössbauer-effect anomaly of any kind was observed at the ferroelectric transition in KFCT. For FAS, a minimum in the Mössbauer fraction and anomalous behavior by the absorption linewidth were observed.

II. EXPERIMENTAL CONSIDERATIONS

Polycrystalline samples of FAS and KFCT were prepared by growing small single crystals in an aqueous solution, and then powdering them coarsely and potting them in relatively soft compounds. For KFCT, rubber cement was used, for FAS, a soft shellac. Dielectric-constant measurement on such samples indicated that a

* Work supported by the U. S. Atomic Energy Commission.

† Present address: U. S. Army Harry Diamond Laboratories, Washington, D. C. 20438.

‡ Alfred P. Sloan Foundation Fellow.

¹ W. Cochran, *Advan. Phys.* **9**, 387 (1960).

² V. G. Bhide and M. S. Multani, *Phys. Rev.* **139**, A1983 (1965).

³ L. M. Krizhanskii, B. I. Rogozev, and G. V. Popov, *Zh. Eksperim. i Teor. Fiz. Pis'ma v Redaktsiyu* **3**, 248 (1966) [English transl.: *Soviet Phys.—JETP Letters* **3**, 248 (1966)].

⁴ V. V. Sklyarevskii, I. I. Lukashevich, V. P. Romanov, N. I. Filippov, Yu. N. Venevtsev, and A. S. Viskov, *Zh. Eksperim. i Teor. Fiz. Pis'ma v Redaktsiyu* **3**, 135 (1966) [English transl.: *Soviet Phys.—JETP Letters* **3**, 135 (1966)].

⁵ P. Z. Hien, A. S. Viskov, V. S. Shpinel, and Yu. N. Venevtsev, *Zh. Eksperim. i Teor. Fiz.* **44**, 2182L (1963) [English transl.: *Soviet Phys.—JETP* **17**, 1465L (1963)].

⁶ F. Jona and G. Shirane, in *Ferroelectric Crystals* (Macmillan Co., New York, 1962), p. 325.

⁷ S. Waku, H. Hirabayashi, H. Toyoda, and H. Iwasaki, *J. Phys. Soc. Japan* **14**, 973 (1959).

⁸ Y. Hazony, D. E. Earls, and I. Lefkowitz, *Phys. Rev.* **166**, 507 (1968).

dielectric anomaly of the correct form was present at the ferroelectric transition, indicating that the macroscopic ferroelectric properties of these materials had not been seriously affected by the powdering and potting procedures used. The ferroelectric samples were used as absorbers with a source consisting of 5 mc. of Co^{57} diffused into a Pd foil. The absorber was mounted in a variable gas flow cryostat. The absorbers were thin enough to insure that saturation effects were not significant, being slightly less than one resonant absorption length for FAS and approximately $\frac{2}{3}$ of a resonant absorption length for KFCT. Temperature control to within $\pm 0.010^\circ\text{K}$ was achieved by manually setting the gas flow rate and automatically controlling a set of small heaters surrounding the absorber. The source was held at $(296 \pm 1)^\circ\text{K}$.

Data were taken on several different samples of each material, and several temperature scans were made on each sample. All results were completely reproducible. FAS was studied over the temperature range 20–295°K; KFCT was studied in the 225–295°K range. The Mössbauer absorption spectra were fit to Lorentzian (Breit–Wigner) line shapes on a digital computer, using an iterative least-square-fitting program. Quoted errors in the Mössbauer parameters are the standard deviations in the fits, as determined by the fitting program.

III. GENERAL DISCUSSION

Ferroelectric transitions can be divided into two major classes, depending on the microscopic mechanism which gives rise to spontaneous polarization of the crystal—*order-disorder* transitions and *displacive* transitions. In an order-disorder transition, permanent electric dipoles which are present above the transition temperature become ordered at the transition. Such a transition is similar to a ferromagnetic transition and can be treated with the same types of ordering theories as are used in the magnetic case. On the other hand, a displacive ferroelectric transition is very different from a magnetic transition in that no electric dipoles exist above the transition temperature. The dipoles only come into existence at the transition, when the unit cell distorts in such a way that an ordered set of electric dipoles is created. The process leading to such a distortion of the crystal can be described in terms of a cancellation of long-range Coulomb forces by short-range forces between the ions.⁹ The cancellation of these forces leads to an anomaly in the frequency of a transverse optical (TO) vibrational mode of the crystal. The particular mode involved has wave vector q equal to zero, which corresponds to entire Bravais sublattices moving as rigid units relative to each other (a so-called breathing mode of the crystal). If ω_T is the frequency of the TO mode with $q=0$, we have

$$\omega_T^2 = G(T - T_0), \quad (1)$$

⁹ W. Cochran, Phys. Rev. **166**, 507 (1968), p. 391.

where T_0 is a temperature near the transition temperature T_c . Equation (1), along with the Lyddane–Sachs–Teller relation¹

$$\omega_L^2 / \omega_T^2 = \epsilon_s / \epsilon_e, \quad (2)$$

leads to the experimentally determined Curie-law temperature dependence of the static dielectric constant ϵ_s . (ω_L is the frequency of the longitudinal mode with $\mathbf{q}=0$, and ϵ_e is the high-frequency dielectric constant.)

It was suggested in 1963,¹⁰ that the anomalous behavior of ω_T^2 should lead to a minimum in the Mössbauer-effect recoilless fraction f . We can express f as a sum over the normal modes of the crystal lattice¹¹

$$f \approx \exp \sum_s [- (2n_s + 1) | (hK)^2 / 2Mh\omega_s | a_s^2], \quad (3)$$

where n_s is the occupation number for the mode, K is the wave vector of the emitted or absorbed γ ray, M is the nuclear mass, and a_s^2 is a coefficient in the expansion of K in terms of the normal coordinates of the lattice. The coefficients a_s^2 are normalized by the requirement

$$\sum_{\text{all } s} a_s^2 = 1.$$

If we assume that removing one term from the sum in Eq. (3) does not materially affect the sum as a whole, then we can remove the anomalous mode (say, $s=a$) and treat the remainder of the sum using the Debye model of a solid, giving

$$\begin{aligned} f &\approx \exp \left\{ \frac{(hK)^2}{2M} \frac{6}{k_B \Theta_D} \left[\frac{1}{4} + \left(\frac{T}{\Theta_D} \right)^2 \int_0^{x_m} \frac{x dx}{e^x - 1} \right] \right\} \\ &\quad \times \exp \left\{ - (2n_a + 1) \left[\frac{(hK)^2}{2Mh\omega_a} \right] a_a^2 \right\} \\ &\approx f_D(T) \exp \left\{ - (2n + 1) \left[\frac{(hK)^2}{2Mh\omega_a} \right] a_a^2 \right\}, \quad (4) \end{aligned}$$

where $x_m = \Theta_D/T$, Θ_D is the Debye temperature of the crystal and k_B is the Boltzmann constant; $f_D(T)$ is the normal Debye model temperature dependence of f . Using Bose-Einstein statistics for n_a and Eq. (1) to give ω_a , we have

$$\begin{aligned} f(T) &= f_D(T) \exp \left\{ - \left(\frac{2}{e^y - 1} + 1 \right) \right. \\ &\quad \left. \times \left[\frac{(hK)^2}{2Mh} a_a^2 \right] \frac{h}{k_B T y} \right\}, \quad (5) \end{aligned}$$

$$y = (h/k_B T) [G(T - T_0)]^{1/2}.$$

For a second-order ferroelectric transition $T_0 = T_c$ and at $T = T_c$, we have $y = 0$ and $f(T = T_c) = 0$; for a first-

¹⁰ C. Muzikar, V. Janovec, and V. Dvorak, Phys. Status Solidi **3**, K9 (1963).

¹¹ H. J. Lipkin, Ann. Phys. (N. Y.) **9**, 332 (1960).

order transition $T_0 \neq T_c$, so that y never equals zero, but y does have a minimum at $T = T_c$ and, therefore, $f(T)$ has a minimum there. In addition to the temperature dependence of y , the coefficient a_a might be expected to change near T_c when the frequency ω_a is anomalous. The unknown temperature dependence of a_a complicates the problem of comparing Eq. (5) to the experimental data.

The simple theory outlined above predicts a minimum in f at the ferroelectric transition. However, in a triatomic crystal, or any crystal whose structure consists of three or more interpenetrating Bravais lattices, it is possible that f may be unaffected by the lattice-mode anomaly at T_c . If the Mössbauer nuclei are restricted to one sublattice, f will be sensitive only to changes in the vibrational spectrum of that sublattice. No more than two sublattices need be involved in the $\omega_T \rightarrow 0$ mode, so that if there are three or more sublattices, the one containing the Mössbauer nuclei may experience no anomaly at T_c .

Hazon and his co-workers suggest that it is possible for the $q=0$ TO mode for the Mössbauer active sublattice to exhibit an anomaly of the opposite kind, that is $\omega_T' \rightarrow \infty$ at T_c , which would correspond to this lattice being at a node of the anomalous vibrational mode. They suggest that such an anomaly in ω_T' would lead to a maximum in f ; however, examination of Eq. (3) indicates that as long as the $s=a$ term in the sum is not singular, and the coefficient a_a^2 remains small, no significant change in f would be expected. A maximum in f is not predicted by this model, as a maximum due to $\omega_T' \rightarrow \infty$ can only occur if a_a^2 is large enough that the a th term in the sum in Eq. (3) is a significant fraction of the entire sum. It is unlikely that a_a^2 would be large, in light of the normalization requirement for the sum of the coefficients a_s^2 and the large number of normal modes present in the crystal.

In addition to the minimum in f due to the anomalous lattice mode, f might change at T_c because of a change in the Debye temperature of the crystal at the transition. Such a change is not unreasonable due to the distortion of the crystal structure which occurs when the crystal changes from a polar to nonpolar state. The Debye temperature may have a strong temperature dependence near T_c . To further complicate matters, the constants G and T_0 appearing in Eq. (5) should have different values above and below T_c . The coefficient a_a^2 will almost certainly change when the crystal structure changes, and may have a complicated temperature dependence near the transition. Despite these complications, Eq. (5) is in qualitative agreement with the behavior of f near T_c , as reported by other workers, and as observed for FAS in the present experiment.

It is more difficult to say what f might be expected to do at an order-disorder ferroelectric transition. If the transition is first order, we might expect the Debye temperature to change when the crystal structure

changes. In a second-order order-disorder transition, there is no reason to expect any change in f at T_c . The absence of any anomaly in the temperature dependence of f thus either could indicate a displacive transition in which the Bravais lattice bearing the Mössbauer nuclei does not participate in the $\omega_T \rightarrow 0$ lattice mode, or it could indicate an order-disorder type of transition.

In addition to the recoilless fraction, other Mössbauer-effect parameters may provide information about a ferroelectric transition. If the crystal bonding is distorted or changes its degree of ionicity at the transition, the isomer shift will reflect the resulting change in the s -electron density at the nucleus. A discontinuity in the isomer shift at the ferroelectric transition temperature has been reported by several workers.²⁻⁴ No such discontinuities were observed in this experiment. If the absorption spectrum is split by quadrupole interactions, the splitting will allow measurement of the changes in the electric field gradient at the Mössbauer nucleus resulting from the spontaneous polarization of the crystal below T_c . The quadrupole splitting of the spectrum may also reflect change in the crystal symmetry which are connected with the ferroelectric transition.

In Secs. IV and V, the results of a study of the Mössbauer effect in FAS and KFCT are described and compared with the predictions outlined above.

IV. RESULTS—FAS

FAS is one of several alums which are ferroelectric. It has a first-order ferroelectric transition at about 88°K.⁶ Its crystal structure is cubic and it can become spontaneously polarized along any one of its three cubic axes. Three different samples of polycrystalline FAS were studied over the temperature range 20–295°K, with increments between data points varying from 25°K far from the transition down to 0.5°K near T_c . A total of 73 Mössbauer spectra were taken on the three samples.

The normalized area of the Mössbauer absorption line for one of the three samples is shown as a function of temperature in Fig. 1. For the thin absorbers used in this experiment, with the source held at constant temperature and the experimental geometry fixed, the normalized area is connected to f by a simple constant proportionality. A minimum in f is present at T_c and was observed for all three samples, although the depth of the minimum was not entirely reproducible. An attempt was made to fit the temperature dependence of f with Eq. (5), but, while reasonable qualitative agreement was obtained, no exact quantitative fit was possible. It is not surprising that the simple theory fails to account for the details of the experimental results, in light of the oversimplifications involved in ignoring the temperature dependence of a_a^2 and the Debye temperature. The large number of parameters in Eq. (5) also complicated the problem of fitting the theory to the

experimental results. The qualitative agreement between the data and theory indicates that a model in which the Bravais lattice containing the iron nuclei participates in a $\omega_T \rightarrow 0$ anomaly is capable of explaining the observed features of the ferroelectric transition in FAS.

The observed absorption line for FAS was observed to vary in width as a function of temperature. The half-width at half-maximum of the FAS line is plotted versus temperature in Fig. 2. The temperature variation of the linewidth is complementary to the variation in f : the line becomes broader and shallower at T_c . The depth of the line thus shows an even more pronounced minimum at T_c than the area shown in Fig. 1. Besides showing a temperature variation, the FAS line was broadened at all temperatures to nearly ten times the minimum observable linewidth as calculated from twice the

uncertainty principle linewidth. [At 275°K, the observed linewidth was (1.93 ± 0.14) mm/sec.]

Previous studies of FAS indicate that the linewidth is due to spin-spin relaxation.¹² Such a relaxation mechanism is not temperature-dependent, in general, but no studies have been made near critical points. Our results, shown in Fig. 2, show a temperature variation in the linewidth which implies a temperature variation in the spin-spin relaxation time. Such a variation is expected when the average distance between iron ions increases at T_c . The increased linewidth is thus correlated with the decrease in f at T_c .

The FAS isomer shift was relatively poorly determined due to the broad line and small effect observed. Within the precision of the experiment, no change in the isomer shift was observed at T_c . This indicated that

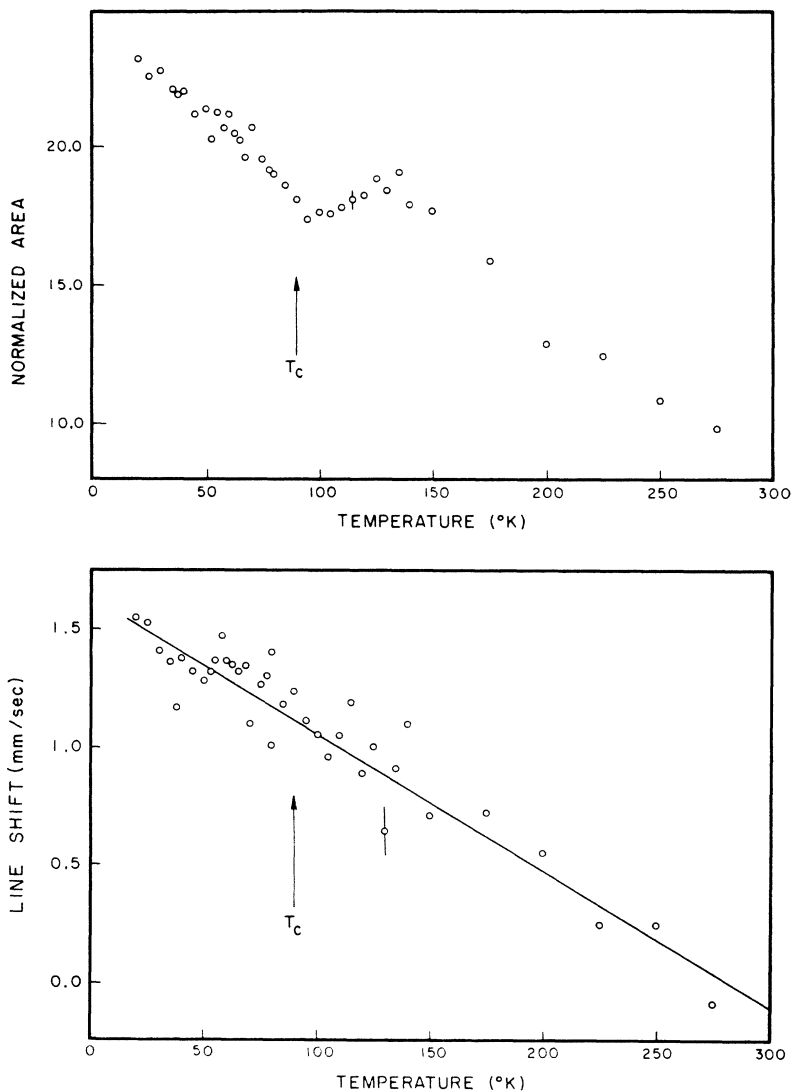


FIG. 1. Normalized area and line shift of the FAS absorption line as a function of temperature. The minimum in the normalized area at T_c is qualitatively consistent with theoretical predictions.

¹² J. W. G. Wignall, *J. Chem. Phys.* **44**, 2462 (1966).

whatever crystal structure change takes place at T_c either does not distort the iron bonds or distorts them in such a way that there is fortuitously no change in the s -electron density at the iron nucleus, at least to within the precision of this experiment.

V. RESULTS—KFCT

The normalized area and isomer shift observed for KFCT at and near T_c are shown in Fig. 3. No change in either parameter was observed at the transition temperature. A total of 193 absorption spectra on three different KFCT samples gave completely negative results, with all temperature scans fully reproducing the one scan shown in Fig. 3. These results indicate that the second-order ferroelectric transition in KFCT is either an order-disorder transition or a displacive transition for which the Bravais lattice of iron atoms does not share in the $\omega_T \rightarrow 0$ lattice mode. Interpreted in this manner, the data are completely consistent with the theory presented earlier.

In a previous report⁸ of Mössbauer-effect studies of KFCT, Hazony, Earls, and Lefkowitz have stated that a *maximum* in f was observed approximately 4–6°K above T_c . Examination of the data presented in

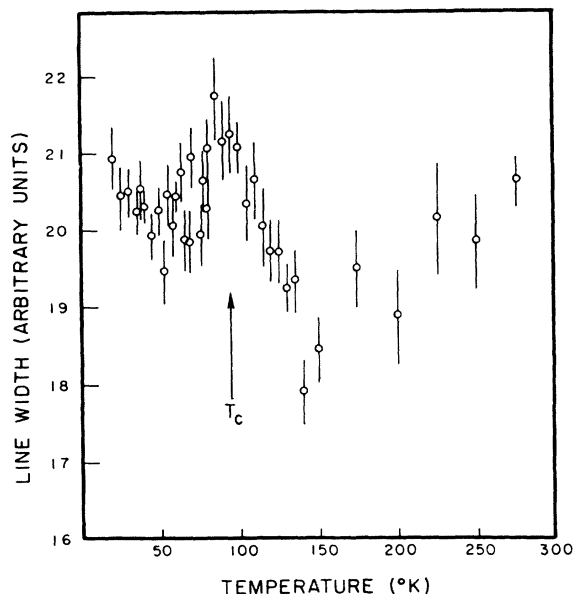


FIG. 2. The half-width at half-maximum (HWHM) of the FAS absorption line (in channels, one channel equals 0.094 mm/sec, or approximately one uncertainty width for the 14.4 keV line of Fe^{57}) as a function of temperature. In addition to the maximum at T_c , the HWHM of FAS exhibits an anomalous increase with increasing temperature in the region well above T_c .

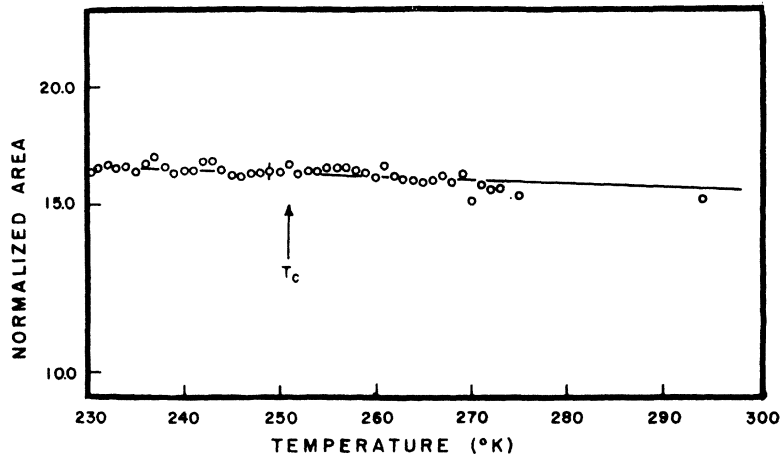
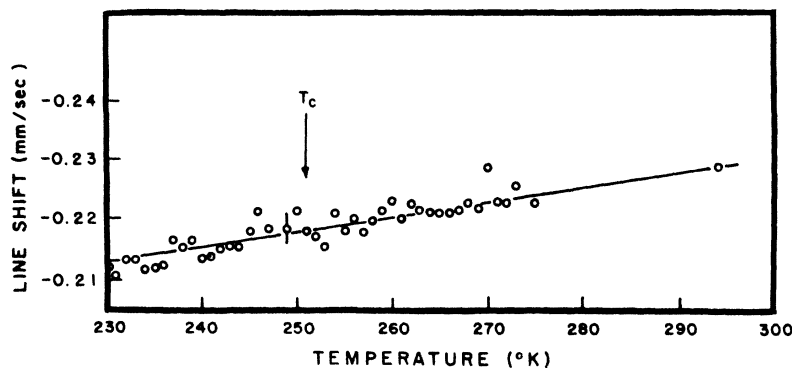


FIG. 3. The normalized area and line shift of KFCT as a function of temperature. Neither quantity exhibits any unusual behavior at or near the ferroelectric transition.



that report suggests that the data itself is not inconsistent with the results of the present experiment. The fluctuation in f , which they interpret as a maximum connected with the ferroelectric transition, is of the same order and shape as several unexplained fluctuations in f at other temperatures. In the published data, the fluctuation in f near T_c is not clearly established as reproducible. Finally, the fluctuation near T_c is of the same order as the general scatter of the data points and could actually be interpreted as a minimum rather than a maximum if a slightly different choice is made as to which of the scattered data points are considered to be more reliable. In light of all these features of the data published by Hazony *et al.*, it is reasonable to say that the previous data are consistent with a negative result, and that the present data, with smaller scatter of the

data points and better temperature resolution, further establish that negative result.

VI. CONCLUSIONS

The temperature dependence of f for FAS is consistent with the anomalous lattice-mode theory of ferroelectric transitions and clearly indicates the displacive nature of the FAS transition. The linewidth variation for FAS indicates a temperature dependence for the structure of the ferroelectric alums, which deserves further study by appropriate experimental and theoretical techniques. The negative results for KFCT suggest an order-disorder model for the KFCT transition but do not exclude one particular displacive mechanism, as was discussed in Sec. V.

Hydrodynamic Theory of Spin Waves

B. I. HALPERIN* AND P. C. HOHENBERG

Bell Telephone Laboratories, Murray Hill, New Jersey 07974

(Received 8 August 1969)

A hydrodynamic theory of spin waves is developed for certain magnetic systems in analogy with the derivation of two-fluid hydrodynamics for liquid helium. The systems considered are "isotropic" and "planar" ferromagnets and antiferromagnets. In each system, low-frequency spin waves are predicted to exist at long wavelengths for any temperature below the transition to the paramagnetic phase. The real part of the frequency is given exactly in terms of thermodynamic quantities. The damping rate is proportional to the square of the real part of the frequency in each case, and hence is negligible in the long-wavelength limit, compared to the real part. These results for the damping rates are new, and disagree with previous microscopic calculations for the Heisenberg ferromagnet and antiferromagnet. An experiment using neutron diffraction is proposed to test the hydrodynamic theory in the almost isotropic antiferromagnet RbMnF_3 . The assumptions necessary to derive the hydrodynamic theory are discussed in detail, as are the limits of validity of the theory, and the applicability of the results to real systems.

1. INTRODUCTION

A NUMBER of models of magnetic systems are similar to superfluid helium in that ground states of their ordered phases exhibit broken symmetry with respect to a continuous symmetry of the Hamiltonian.^{1,2} It is therefore reasonable to attempt to deduce dynamic properties of magnetic systems from macroscopic hydrodynamic considerations, just as one can derive the theory of two-fluid hydrodynamics for the properties of superfluid helium.^{3,4} By hydrodynamic considera-

tions we mean a theory utilizing only the conservation laws for the Hamiltonian, the symmetry properties of the ground state, and assumptions that one can expand certain quantities in powers of the gradients and magnitudes of the deviations from equilibrium, when these derivations are sufficiently small and slowly varying.

The motivation for carrying out a hydrodynamic investigation of magnetic systems is twofold. In the first place, we hope to increase our understanding of magnetic systems; in particular, we may make predictions about the spectrum of spin fluctuations as measured by inelastic diffraction of neutrons in certain real systems. In the second place, one can gain insight into the foundations of two-fluid hydrodynamics for

* Address for academic year 1969-70: Department of Physics, Harvard University, Cambridge, Mass. 02138.

¹T. Matsubara and H. Matsuda, *Progr. Theoret. Phys. (Kyoto)* **16**, 416 (1956); **16**, 569 (1956); **17**, 19 (1957); P. R. Zilsel, *Phys. Rev. Letters* **15**, 476 (1965); D. D. Betts and M. H. Lee, *ibid.*, **20**, 1507 (1968).

²See also M. E. Fisher, *Rept. Progr. Phys.*, **30**, 615 (1967).

³L. D. Landau, *J. Phys. (USSR)* **5**, 71 (1941). (Reprinted in *Ref. 4* below.) See also L. D. Landau and E. M. Lifshitz, *Fluid*

Mechanics (Addison-Wesley Publishing Co., Inc., Reading, Mass., 1959), Chap. 16.

⁴I. M. Khalatnikov, *Introduction to the Theory of Superfluidity* (W. A. Benjamin, Inc., New York, 1965).