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Incommensurate Structures

J. D. Axe

Brookhaven National Laboratory

Upton, New York 11973 U. S. A.

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J. D. Axe

Brookhaven National Laboratory, Upton, New York 11973 U. S. A.

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A review is given of recent neutron scattering studies of displacive incommensurate structures, and the instabilities that occur within periodic crystalline structures that lead to their formation. The concept of a soft phonon, in some cases associated with an electronic screening anomaly, is useful but not always capable of a completely satisfactory description. An unusual one-dimensional liquid-like phase has been studied in the non-stoichiometric mercury compound, $Hg_{3-\delta}AsF_6$.

Incommensurate Structures

Incommensurate structures are peculiar quasicrystalline substances that lack periodic translational symmetry not in a haphazard amorphous way but because two (or perhaps more) elements of translational symmetry are present which are mutually incompatible. Suppose $A(\vec{r})$ and $B(\vec{r})$ represent the spatial distribution of two characteristic properties of a material and that

$$A(\vec{r}) = \sum_{\{\vec{G}\}} A_G \, e^{i\vec{G}\cdot\vec{r}} \qquad\qquad B(\vec{r}) = \sum_{\{\vec{G}'\}} B_{G'} \, e^{i\vec{G}'\cdot\vec{r}} \quad . \tag{1}$$

The structure is incommensurate if the sets of reciprocal lattice vectors $\{\vec{G}\}$ and $\{\vec{G}'\}$ have only the trivial elements $\vec{G} = \vec{G}' = 0$ in common. Various cases are possible depending on what A and B represent as shown in Table 1.

Table 1 here; see p. /18/

Magnetic and compositional modulation are well known and will not be considered further, although in both cases neutron studies have contributed greatly to our present understanding of these phenomena. We will instead concentrate on the latter two cases, the first of which consists of interpenetrating (or overlaid) lattices of different spacing. In contrast to the first three cases, displacive modulation involves a periodic displacement, say

$$\vec{u}(\vec{r}) = \vec{A} \cos (\vec{q}_o\cdot\vec{r} - \phi) \tag{2}$$

of the scattering centers away from an average position on a regular lattice site. It is not uncommon for the modulation amplitude, $\vec{A}$, to disappear above a certain temperature, the material thereby transforming from the incommensurate structure to a commensurate one with the average structure. This review is largely concerned with neutron scattering studies of such displacive incommensurate phase transformations, and of what they reveal of the nature of incommensurate instabilities. A final section is concerned with the unusual behavior of the quasi one-dimensional intergrowth compound, $Hg_{3-\delta}AsF_6$.

Soft Mode Instabilities and CDW's

The form of Eq. (2) suggests that we view an incommensurate phase transformation as a condensation or "freezing-in" of a phonon with wave vector $\vec{q}_o$, which might occur because the phonon frequency, $\omega^2(q_o)$, vanishes. Although introduced to explain ferroelectric ($\vec{q}_o = 0$) transformations (Cochran 1960) and subsequently generalized to include other high symmetry wave vectors on the Brillouin zone boundary (Cochran et al. 1968), there are no fundamental restrictions on the wave vector of a soft phonon instability.

On a more microscopic level, such an incommensurate transformation may result from a charge density wave (CDW) instability (Overhauser 1968) in the conduction electrons near the Fermi surface of a metal. The occurrence of such an electronic instability requires a large electronic susceptibility $\chi_o(\vec{q}_o)$ which is favored when large portions of the Fermi surface are separated by the special wave vector $\vec{q}_o$. This favorable nesting of the Fermi surface is much more probable for quasi one- or two-dimensional metals where the Fermi surface becomes independent of some components of electron momenta. The CDW instability is coupled to the phonons because of the screening effect of the conduction electrons on the "bare" phonon frequencies, $\Omega(\vec{q})$. In the random phase approximation, the observed physical phonon frequencies $\omega(\vec{q})$ are roughly of the form

$$\omega^2(\vec{q}) = \Omega^2(\vec{q}) \left[\frac{1 - \lambda^2_{\vec{q}}\chi_o(\vec{q})}{1 - v_{\vec{q}}\chi_o(\vec{q})} \right]$$

where $\lambda_{\vec{q}}$ is an electron-phonon coupling constant and $v_{\vec{q}}$ is a Fourier component of the electron-electron interaction. Theory thus predicts the CDW instability to be accompanied by a soft phonon $\omega(\vec{q}_o) \rightarrow 0$, where $\vec{q}_o$ is determined by the Fermi surface nesting. The phonon softening can be viewed as a giant Kohn anomaly (Kohn 1959). Neutrons scatter not directly from the CDW but rather from the nuclear distortions resulting from the condensed phonon mode. (From a theoretical viewpoint, a mixed spin and charge density wave appears possible, but no spin components have yet been detected in CDW's.)

CDW's in Metals

In quasi one-dimensional metals, the Fermi surface approaches a set of parallel planes oriented perpendicular to the one-dimensional axis and separated by $2k_F$. This is the most geometrically favorable situation for CDW's with nesting occurring over the whole Fermi surface.

It is often called a Peierls transformation, since Peierls (1955) first studied it in the mean field approximation long before physical manifestations were known.

The most striking confirmation of the existence of giant Kohn anomalies occurs in the quasi one-dimensional conductor KCP ($K_2Pt(CN)_4Br_x$). This is well represented by Fig. 1 which shows

Figure 1 here (for legend see p. /19 /)

neutron scattering data for longitudinal acoustic phonons propagating along $\vec{c}^*$, the one-dimensional Pt-chain direction in this material (Carneiro et al. 1976). The anomaly is so sharply confined along $\vec{c}^*$ that a conventional representation in terms of a sharp phonon dispersion surface is not possible with experimental resolution. It is interesting to note that in spite of the unstable fluctuations shown in Fig. 1, it is now generally conceded that true incommensurate long range order is not achieved in KCP, possibly because of the random potential from the nonstoichiometric ($x \approx 0.3$) Br-ions. This is somewhat unfortunate, for this material is in other respects an example, par excellence, of Peierls' original idea.

CDW instabilities also occur in a number of quasi two-dimensional transition metal chalcogenide compounds (Wilson et al. 1975). These materials have several different structural polytypes depending upon the stacking arrangement of the fundamental layers. We will discuss only the 2H-polytypes of $NbSe_2$ and $TaSe_2$, for which the most extensive neutron studies are available. Unlike KCP, these substances undergo true phase transformationa and their behavior is at once more subtle and in some aspects better understood than is that of KCP.

Figure 2 here (for legend see p. /19/)

Electron diffraction studies of both 2H-$NbSe_2$ and $TaSe_2$ showed satellite reflections appearing at low temperature (Wilson 1975). These peaks were originally thought to be commensurate with a spacing of 1/3 of the basal plane reciprocal lattice spacing $\vec{a}^*_H$, but a subsequent neutron diffraction study (Moncton et al. 1975 and 1977) showed that the ordering, which occurs at a well-defined temperature, leads initially to incommensurate structures with wave vectors $\vec{q}_\delta = (1-\delta)\vec{a}^*_H/3$ with $\delta \sim 0.02$ at the transformation temperatures (T_o = 33.4 K and 122.3 K for $NbSe_2$ and $TaSe_2$, respectively). The temperature dependence of the satellite intensities which is proportional to the square of the CDW amplitude is shown in Fig. 2. The transformations appear to be continuous (i.e. second order) although it is impossible to rule out the possibility of a small first-order discontinuity.

The most striking dynamical effect is a pronounced softening of the LA phonons propagating along $\vec{a}^*_H$. As seen in Fig. 3, the wave vector

Figure 3 here (for legend see p. /19/)

minimum is very close to $\vec{a}^*_H/3$ as would be expected. This minimum is very insensitive to the c-axis component of momentum transfer, implying strong two-dimensional character. The square of the measured phonon frequencies at the minimum is plotted vs temperature in Fig. 4. It is

Figure 4 here (for legend see p. /19/)

apparent that there is appreciable softening above T_o, and that this is reversed below T_o. It is also clear that the mode softening is far from complete at T_o, although the relatively poor experimental resolution may act to reduce the apparent sharpness of the anomaly. In addition to the inelastic scattering discussed above, there is also diffuse quasielastic critical scattering peaking near $\vec{q}_\delta$ and at $T \gtrsim T_o$.

An example of a nearly one-dimensional metal which does undergo a true CDW transformation is afforded by TTF-TCNQ, an organic salt composed of tetrathiofulvalene (TTF^+) cations and tetracyanoquinodimethans ($TCNQ^-$) anions. Both are planar aromatic molecules which stack, plate-like, with overlapping partially-filled π-orbitals reponsible for the electronic conductivity. Incommensurate displacive modulations appear below T_o = 54 K with a wave vector component along the stacking direction determined by the 1-D Fermi surface, $2k_F = 0.295\ \vec{b}^*$.

Diffuse planes of strongly temperature dependent x-ray scattering are observed below $\sim$ 150 K, with the wave vector $2\vec{k}_F = 0.295\ b^*$. Atomic displacements with components along both b* (longitudinal) and c* are observed. The inelastic neutron scattering data on deuterated samples (Shirane et al. 1976; Shapiro et al. 1977; Mook et al. 1977) show a distinct (but rather weak compared with KCP)dip in the TA branch with (mostly) c*-axis polarization. See Fig. 5. At the minimum, the phonon

Figure 5 here (for legend see p. /19/)

energy decreases somewhat with decreasing temperature, but appears to remain > 4 meV. If there is any anomalous dip in the LA branch at $2\vec{k}_F$, it is considerably weaker than for TA(c*), and the energies increase with increasing temperature. There is likewise no evidence for anomalies in the remaining TA(a*) mode.

Insulators

In low dimensional metals the forces responsible for the instability are due to ion-electron-ion interaction and are long ranged and oscillatory. The result, as we have seen, can be a sharp anomaly about $\vec{q}_o = 2\vec{k}_F$. In insulators studied thus far, the effective interaction ranges are shorter, leading to broader phonon anomalies which are very conveniently studied by inelastic neutron scattering. In insulators, there is no essential requirement for incommensurate instabilities which favors low spatial dimensionalities and indeed the known examples lack any obvious lower pseudo-dimensionality.

The most detailed neutron scattering study to date has been performed on K_2SeO_4 (Iizumi et al. 1977) which undergoes an incommensurate transformation at T_o = 130 K. Fig. 6 shows the dispersion of the soft

Figure 6 here (for legend see p. /19/)

phonon branch as a function of temperature. It is somewhat perverse that whereas all of the CDW transformations in metals studied thus far do not follow the prediction of a simple soft mode instability, $\omega \to 0$ at $T = T_o$, such behavior is seen in K_2SeO_4 for which no comparably simple and elegant microscopic description presents itself. On a phenomenological level, however, we can use the observed shape of dispersion relations such as that shown in Fig. 6 to deduce something about the effective force constants which couple planes of atoms perpendicular to the propagation direction. We find that from this point of view, the instability in K_2SeO_4 is brought about by an anomalously large force constant between planes of atoms which are third-nearest-neighbors.

"Lock-In" Transformations

We have seen that incommensurate structures arise from a competition of forces of varying range. However, even in the incommensurate state there are interactions at work which tend to restore periodicity. The ways in which these forces manifest themselves are illustrated in Fig. 7,

Figure 7 here (for legend see p. /19/)

which shows the temperature dependence of the wave vector of the incommensurate satellites in the transition metal dichalcogenides, $NbSe_2$ and $TaSe_2$. The most striking feature is the abrupt change of the satellite vector in $TaSe_2$ from $\vec{q}_1 = (1-\delta)\ \vec{a}_1^*/3$ to the commensurate value $\vec{a}_1^*/3$ which occurs at $T \sim 0.76\ T_o$. $NbSe_2$ does not achieve the $a_1^*/3$ commensurate state even at the lowest attainable temperatures, but as in $TaSe_2$ the satellite wave vector shows a pronounced temperature dependence, whose origin is closely related to the "lock-in" phenomenon itself.

Similar lock-in transformations have also been observed in other incommensurate systems. It would be inappropriate to present an extended discussion of these interesting transformations here, although neutron scattering observations were responsible both for their discovery and initial elucidation (Moncton et al. 1977). The key point is to recognize that purely sinusoidal modulation (Eq. (2) with ϕ = constant) cannot take advantage of the periodic potential of the average lattice. The regions where the displacements are in phase with the potential are exactly canceled by equally large and numerous out-of-phase regions. However, with the proper spatial variation of $\phi(\vec{r})$ the in-phase regions grow at the expense of the out-of-phase regions, thus lowering the total energy. A careful analysis of this effect (McMillan 1976) shows that this also produces a gradual pulling of the wave vector $\vec{q}_o$ away from its initial (zero amplitude) value toward one commensurate with that of the average lattice. This phase modulation also produces additional secondary satellite reflections which are initially weak but which grow to intensities comparable to the primary satellites near lock-in. Such behavior has been observed in $TaSe_2$.

Phasons

What happens if we extend the soft mode picture of the phonons just above T_o to discuss the lattice dynamics of the incommensurate state? A simple analysis assuming purely sinusoidal static displacements (McMillan 1975; Axe 1976) produce results shown schematically in Fig. 8.

Figure 8 here (for legend see p. /19/)

Above T_o, there is a soft branch with a minimum frequency $\omega(\vec{q}_o) \to 0$ as $T \to T_o$. Below T_o the added presence of the static displacements require new harmonic modes to be constructed from linear combinations of phonon wave vectors $(\vec{q} + \vec{q}_o)$ and $(\vec{q} - \vec{q}_o)$ respectively. This results in a splitting of the modes into an upper "branch" for which

$$u_+(\vec{r},t) \sim \cos(\vec{q}_o \cdot \vec{r} - \phi)\, e^{i(\vec{q}\cdot\vec{r}-\omega_+ t)} \tag{3}$$

and a lower branch for which

$$u_-(\vec{r},t) \sim \sin(\vec{q}_o \cdot \vec{r} - \phi)\, e^{i(\vec{q}\cdot\vec{r}-\omega_- t)} \tag{4}$$

Comparison of Eqs. (2)-(4) shows that for small q the upper branch is equivalent to a time dependent modulation of the amplitude of the static displacements whereas the lower branch represents a modulation of their phase. Inevitably, the term "phason" has become accepted nomenclature for these latter modes, which are gapless and exhibit linear acoustic-like dispersion, $\omega_-(q) = vq$. However, the velocity, v, has no relation to the velocity of sound and the phasons are not to be confused with acoustic phonons, as Fig. 8 makes clear.

Of course, we have already pointed out that the static displacements are in general more complex than Eq. (2) suggests. Furthermore, we have seen that incomplete phonon softening renders the whole soft mode picture of little more than qualitative value in many cases. Nevertheless, we know on more general grounds that the absolute phase of the static distortion is not fixed by energetic considerations in an incommensurate structure and this fact alone guarantees a gapless phason branch. (Technically, phasons are Goldstone modes associated with a broken continuous symmetry. Only a pinning of the overall phase of the static distortion by lock-in terms or impurities will cause a gap to appear in the phason spectrum.) Fröhlich (1954) first recognized the unusual character of these excitations and used them to construct a novel and as yet unobserved mechanism for superconductivity.

In view of the unusual nature of phason excitations, the possibility that they make interesting contributions to various thermal and transport properties and the fact that inelastic neutron scattering seems ideally suited to their study, it is curious (and somewhat disconcerting) to note how little has in fact been learned, through no lack of effort. In fact, the author is presently unaware of any convincing direct evidence for the existence of low frequency propagating phason modes in any of the displacive incommensurate phases thus far studied, although there is commonly observed unresolved additional scattering which may represent very low frequency propagating and/or overdamped excitations. Fresh experiments and ideas are needed.

$Hg_{3-\delta}AsF_6$: A One-Dimensional Liquid

This remarkable material, whose structure is shown in Fig. 9 consists

Figure 9 here (for legend see p. /19/)

of a tetragonal AsF_6-lattice in which there are open non-intersecting channels running parallel to both basal plane edges. These channels are filled with tightly packed chains of Hg ions. The observed interchain Hg-Hg distance is such that $3-\delta$ ($\delta \sim 0.18$) Hg ions can be accommodated within a unit cell dimension of the AsF_6 lattice (Shultz et al. 1977). The low temperature diffraction pattern consists of two distinct series of Bragg reflections from separate, well ordered and incommensurate sublattices. The material is thus an example of an incommensurate structure of the intergrowth type (Table 1). (In these materials, the

Goldstone phason modes are independent acoustic phonons propagating on their respective sublattices and they have been directly observed by neutron scattering (Hastings et al. 1977; Heilmann et al. (1978)).

Above 120 K, the Bragg peaks of the Hg-lattice disappear to be replaced by a series of narrow sheets of scattering perpendicular to and spaced at a regular interval along the Hg-chain axes. Such a one-dimensional diffraction pattern shows that the position along the chain of an arbitrarily chosen origin Hg-ion is not longer fixed either with respect to the AsF_6 lattice or with respect to neighboring Hg-chains. Although the sheets of scattering were initially thought of as elastic "Bragg sheets" this notion violates very general theorems which show the impossibility of true long range periodic order in one dimension. Emery and Axe (1978) analyzed the behavior of a one-dimension chain of atoms bound by harmonic nearest neighbor forces. In this model sheets of scattering have a typically liquid-like diffraction pattern shown in Fig. 10, although in this figure the parameter σ/d which

Figure 10 here (for legend see p. /19/)

characterizes the mean square thermal fluctuations relative to the mean near neighbor spacing, d, is for illustrative purposes chosen to be considerably larger than is appropriate for $Hg_{3-\delta}AsF_6$ ($\sigma/d \approx 2.5\times10^{-2}$ at 300 K).

For small (σ/d) the peak profiles are predicted to be Lorentzian, the width of successive peaks, n = 1,2,..., being proportional to n^2, the proportionality constant expressible in terms of the velocity of sound along the chain, v_1. Experiments measuring the width of successive sheets up to n = 7 were subsequently performed (Heilmann et al. 1979). The results, shown in Fig. 11, not only confirm the predicted

Figure 11 here (for legend see p. /19/)

n^2 dependence, but the value of v_1 derived from the measured widths is within 20% of the directly measured values (Heilmann et al. 1978). Thus the Hg-chains do, at high temperature, behave like independent columns of one-dimensional harmonic liquid.

Acknowledgments

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References

Axe, J. D. 1976 Proceedings of Gatlinburg Neutron Scattering Conference, R. M. Moon, Ed. ERDA CONF-760601-P1, 353-378.

Carneiro, K., Shirane, G., Werner, S. A., and Kaiser, S. 1976 Phys. Rev. B 13, 4258-4263.

Cochran, W. 1960 Adv. Phys. 9, 387-412.

Cochran, W., and Zia, A. 1968 Phys. Stat. Sol. 25, 273-274.

Emery, V. J., and Axe, J. D. 1978. Phys. Rev. Lett. 40, 1507-1511.

Fröhlich, H. 1954 Proc. Roy. Soc. A 223, 296-307.

Hastings, J. M., Pouget, J. P., Shirane, G., Heeger, A. J., Miro, N. D., and MacDiarmid, A. G. 1977 Phys. Rev. Lett. 39, 1484-1488.

Heilmann, I. U., Hastings, J. M., Shirane, G., Heeger, A. J., and MacDiarmid, A. G., Solid State Commun. 29, 469-473

Heilmann, I. U., Axe, J. D., Hastings, J. M., Shirane, G., Heeger, A. J., and MacDiarmid, A. G. 1979 Phys. Rev. B, to be published.

Iizumi, M., Axe, J. D., Shirane, G., and Shimaoka, K. 1977 Phys. Rev. B 15, 4392-4400.

Kohn, W. 1959 Phys. Rev. Lett. 2, 393-396.

McMillan, W. L. 1975 Phys. Rev. B 12, 1187-1194.

McMillan, W. L. 1976 Phys. Rev. B 14, 1496-1508.

Moncton, D. E., Axe, J. D., and DiSalvo, F. J. 1977 Phys. Rev. B 16, 801-810; ibid 1975 Phys. Rev. Lett. 34, 734-736.

Mook, H. A., Shirane, G., and Shapiro, S. M. 1977 Phys. Rev. B 16, 5233-5237.

Overhauser, A. W. 1968 Phys. Rev. 167, 691-698.

Peierls, R. F. 1955 Quantum Theory of Solids, Clarendon Press, Oxford.

Shapiro, S. M., Shirane, G., Garito, A. F., and Heeger, A. J. 1977 Phys. Rev. **B 15**, 2413-2418.

Shirane, G., Shapiro, S. M., Comes, R., Garito, A. F., and Heeger, A. J. 1976 Phys. Rev. **B 14**, 2325-2331.

Shultz, A. J., Williams, J. M., Miro, N. D., MacDiarmid, A. G., and Heeger, A. J. 1978 Inorg. Chem. **17**, 646-652.

Wilson, J. A., DiSalvo, F. J., and Mahajan, S. 1975 Adv. Phys. **24**, 117-159.

TABLE 1

Incommensurate Structure Type	$A(\vec{R})$	$B(\vec{R})$	Examples
1. Magnetic	Magnetic density M	Nuclear density ρ	Cr, R.E. metals
2. Compositional	Av. density $\langle \rho_1 + \rho_2 \rangle$	Diff. density $\langle \rho_1 - \rho_2 \rangle$	CuAu II, feldspars,
3. Intergrowth Overgrowth	Lattice ρ_1	Lattice ρ_2	Ar on graphite $Hg_{3-\delta}AsF_6$
4. Displacive	Displacement field $u(\vec{R})$	Average density $\langle \rho \rangle$	Quasi 1-D and 2-D metals, others.

Legends

Figure 1. Intensity contours of inelastic scattering in KCP showing extremely sharp Kohn anomaly near $\vec{q} = 0.3\ \vec{c}^*$ (after Carneiro et al. (1976)).

Figure 2. Temperature dependence of incommensurate satellite intensities in $TaSe_2$ and $NbSe_2$ (after Moncton et al. (1977)).

Figure 3. Phonon dispersion relations for Σ_1 phonon branches in $TaSe_2$ and $NbSe_2$ (after Moncton et al. (1977)).

Figure 4. Temperature dependence of soft phonon energy in $TaSe_2$. T_o marks the onset of CDW formation (after Moncton et al. (1977)).

Figure 5. Dispersion of acoustic phonons propagating along b* in TTF-TCNQ (after Shapiro et al. (1977)).

Figure 6. Dispersion of Σ_2, Σ_3 soft mode branch of K_2SeO_4 in an extended zone scheme (after Iizumi et al. (1977)).

Figure 7. Temperature dependence of the satellite wave vector $\vec{q}_\delta = (1-\delta)a^*/3$ in $TaSe_2$ and $NbSe_2$ (after Moncton et al. (1977).

Figure 8. Schematic illustration of the dispersion relation for a material undergoing an incommensurate displacive phase transformation.

(a) Above T_o there is a soft branch with a minimum at q_o.

(b) Below T_o there is a "splitting" of the modes into a gapless "phase" branch and an upper "amplitude" branch.

Figure 9. The structure of $Hg_{3-\delta}AsF_6$ (after Shultz et al. (1978)).

Figure 10. The diffraction pattern of a one-dimensional harmonic liquid. For small (σ/d) the width of successive peaks is proportional to n^2.

Figure 11. A comparison of experimental and theoretical values of the successive peak widths in $Hg_{3-\delta}AsF_6$ (after Heilmann et al. (1979)).

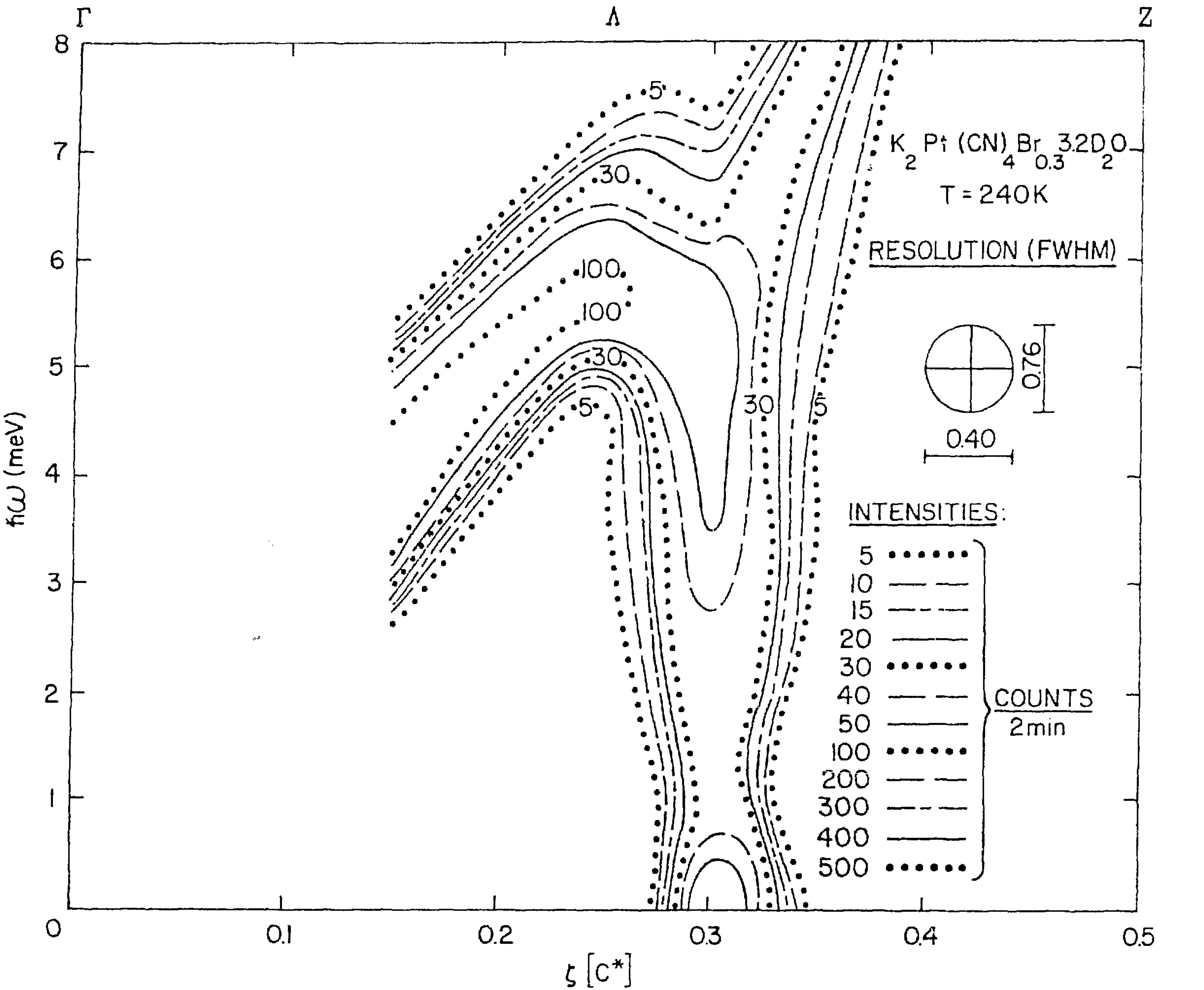


FIGURE 1

9-682-75

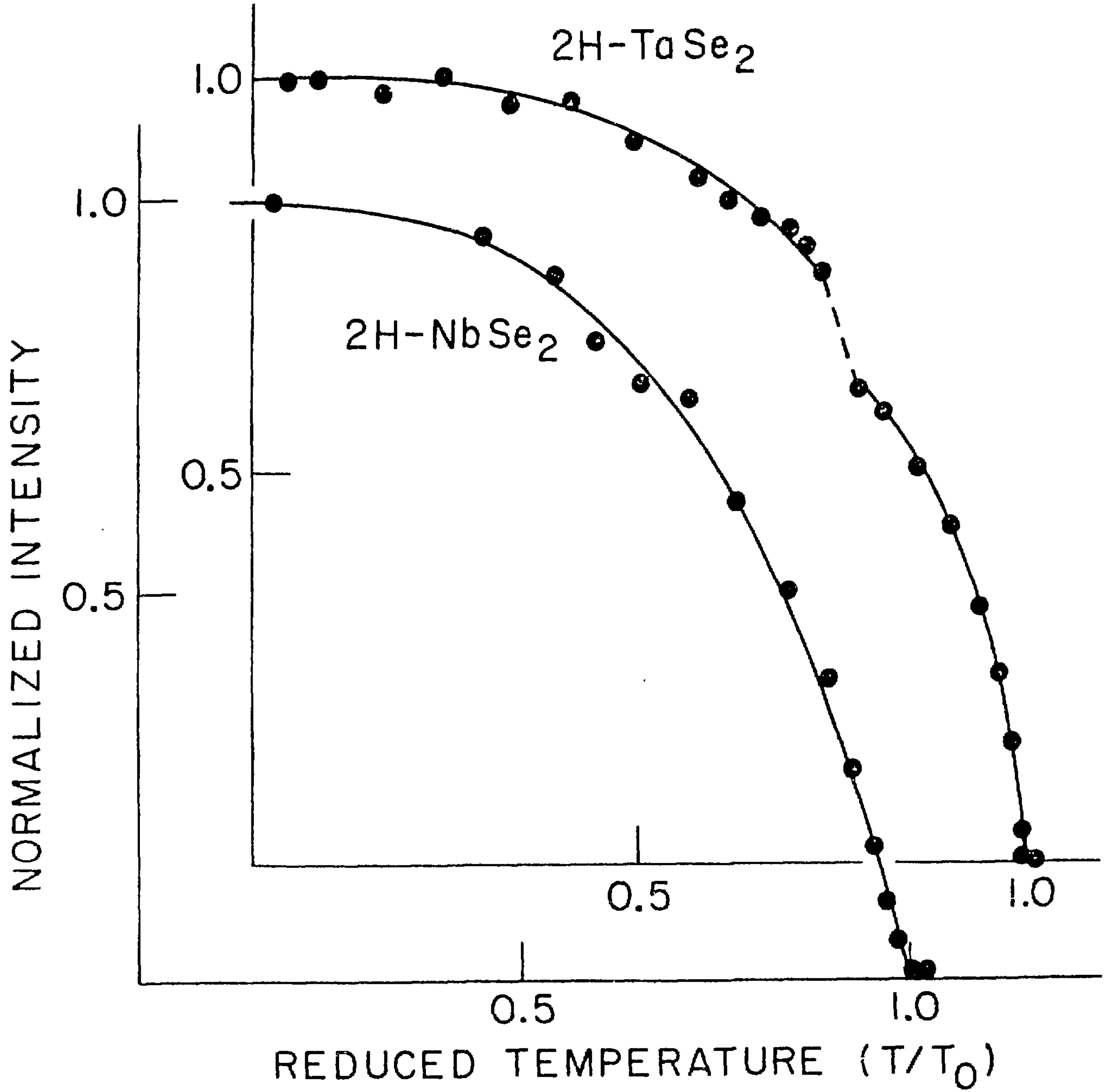


FIGURE 2

1-449-75

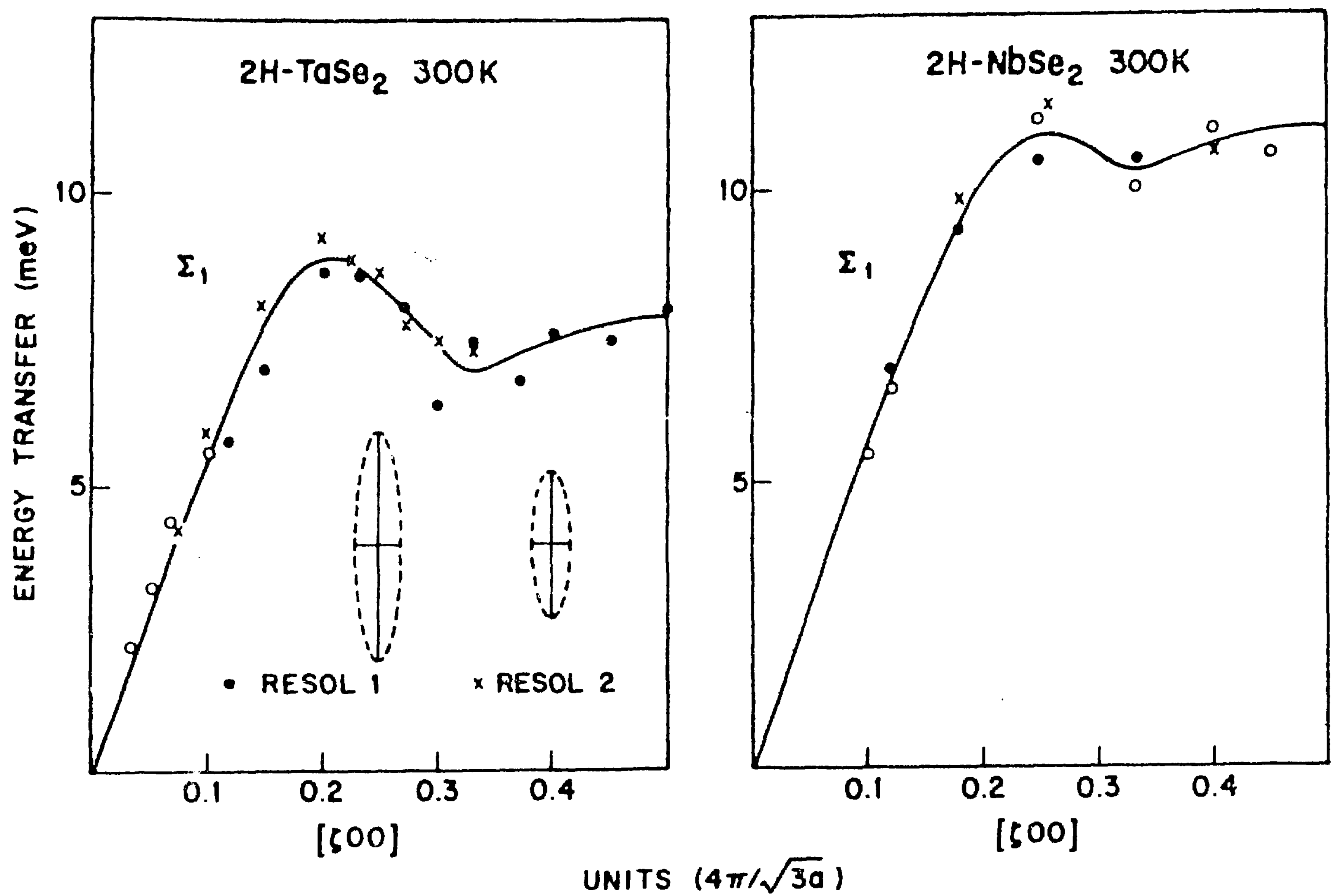


FIGURE 3

9-504-77

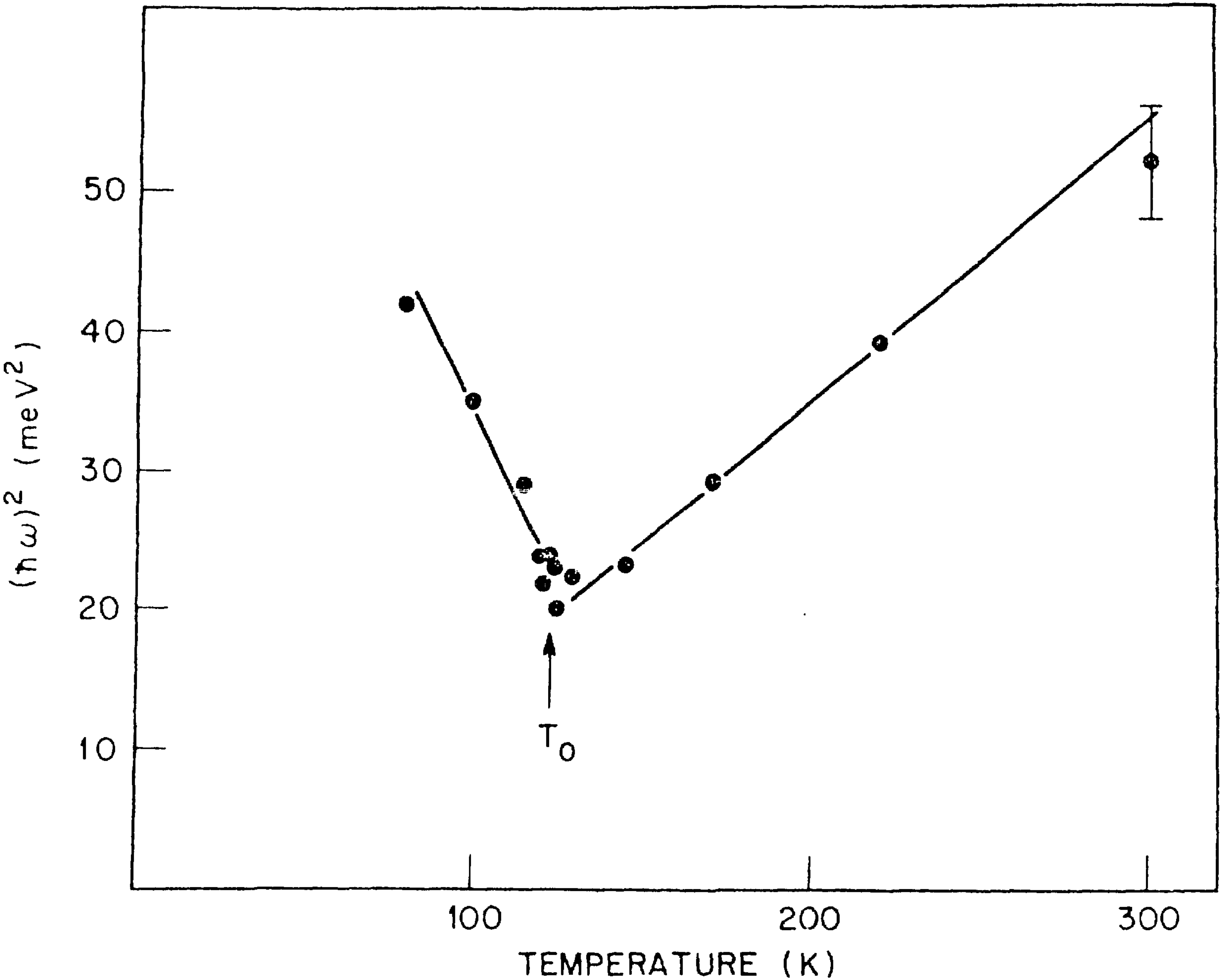


FIGURE 4

9-503-77

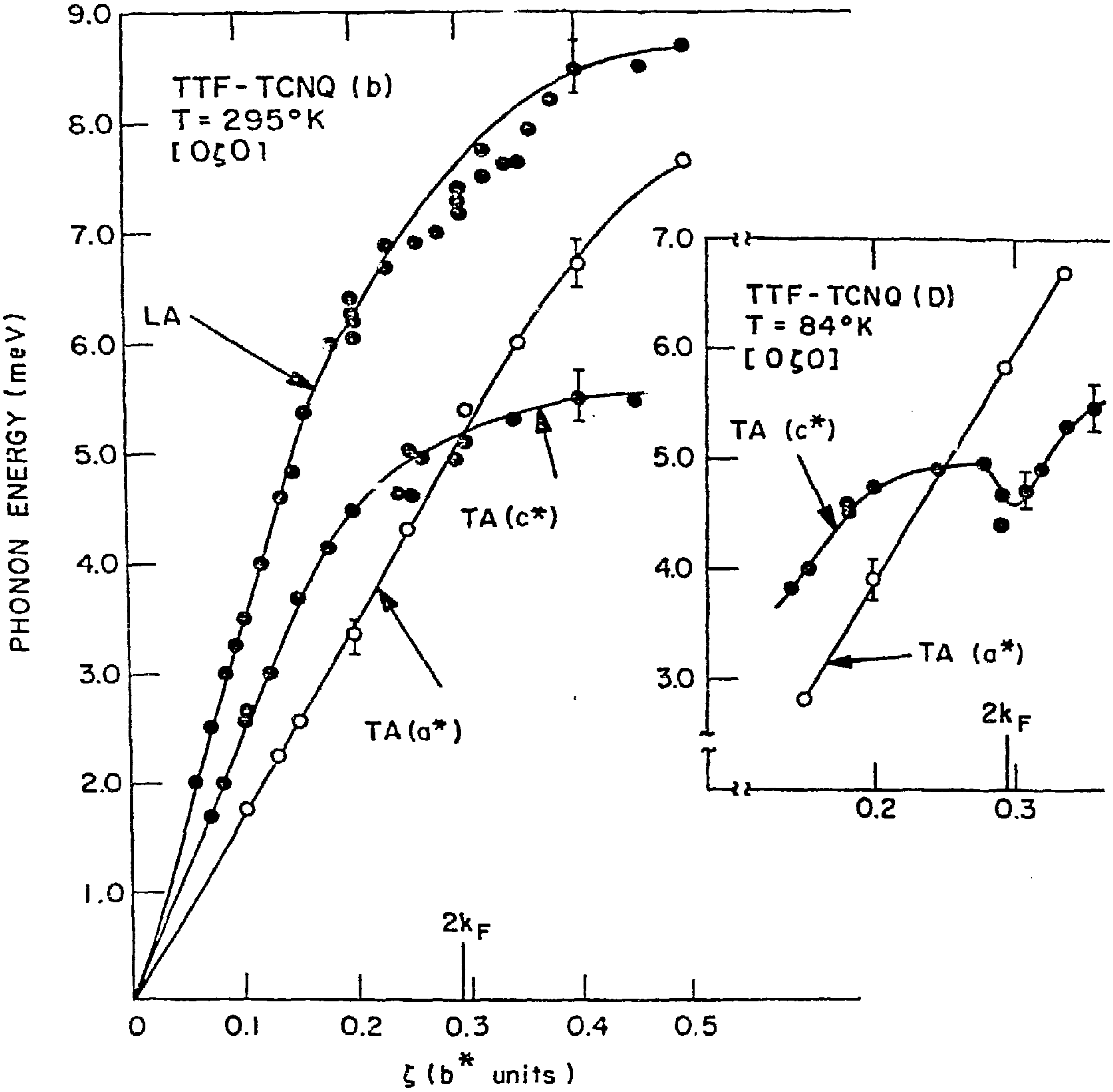
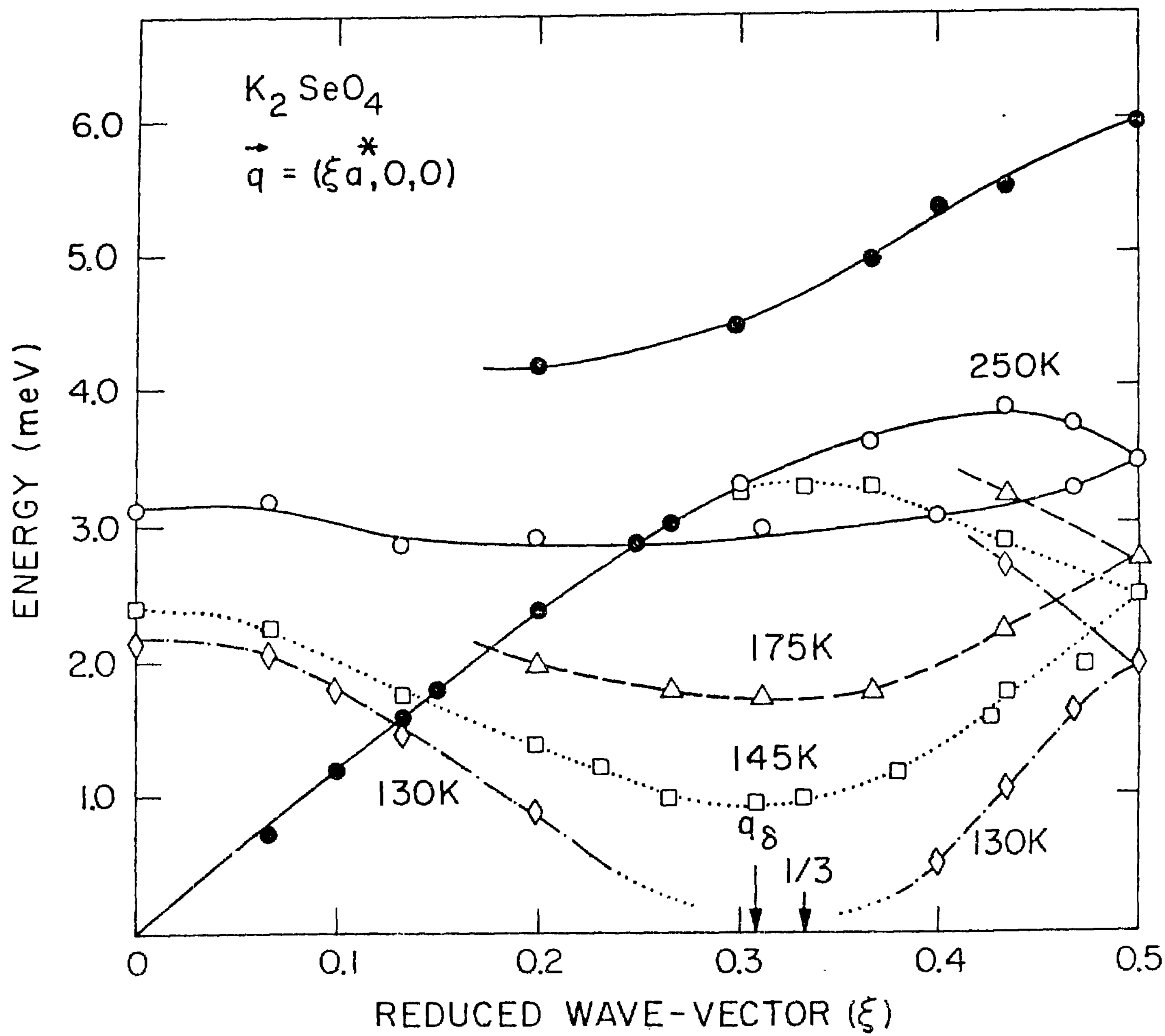


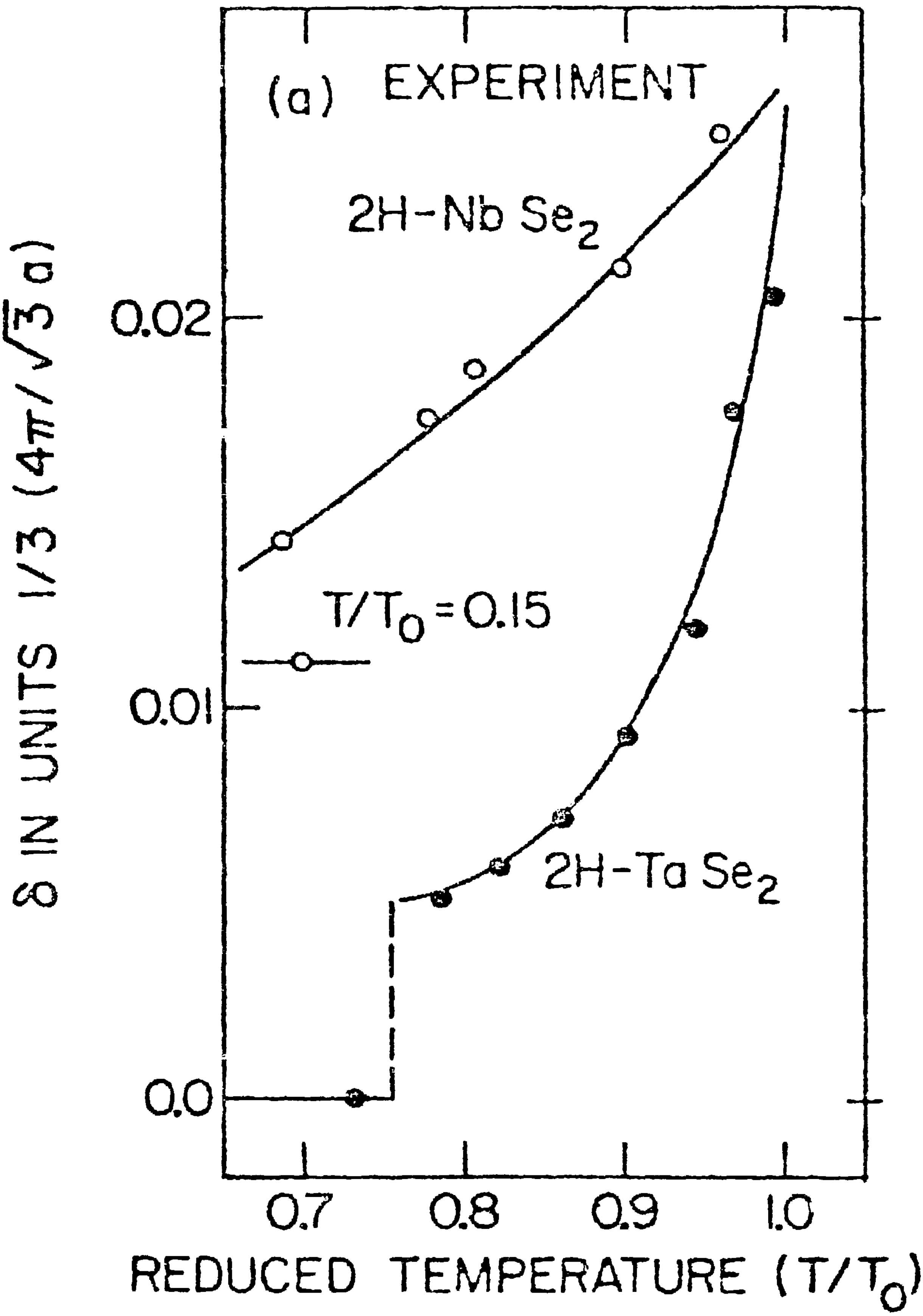
FIGURE 5

10-652-79



3-1565-76

FIGURE 6



5-817-76

FIGURE 7

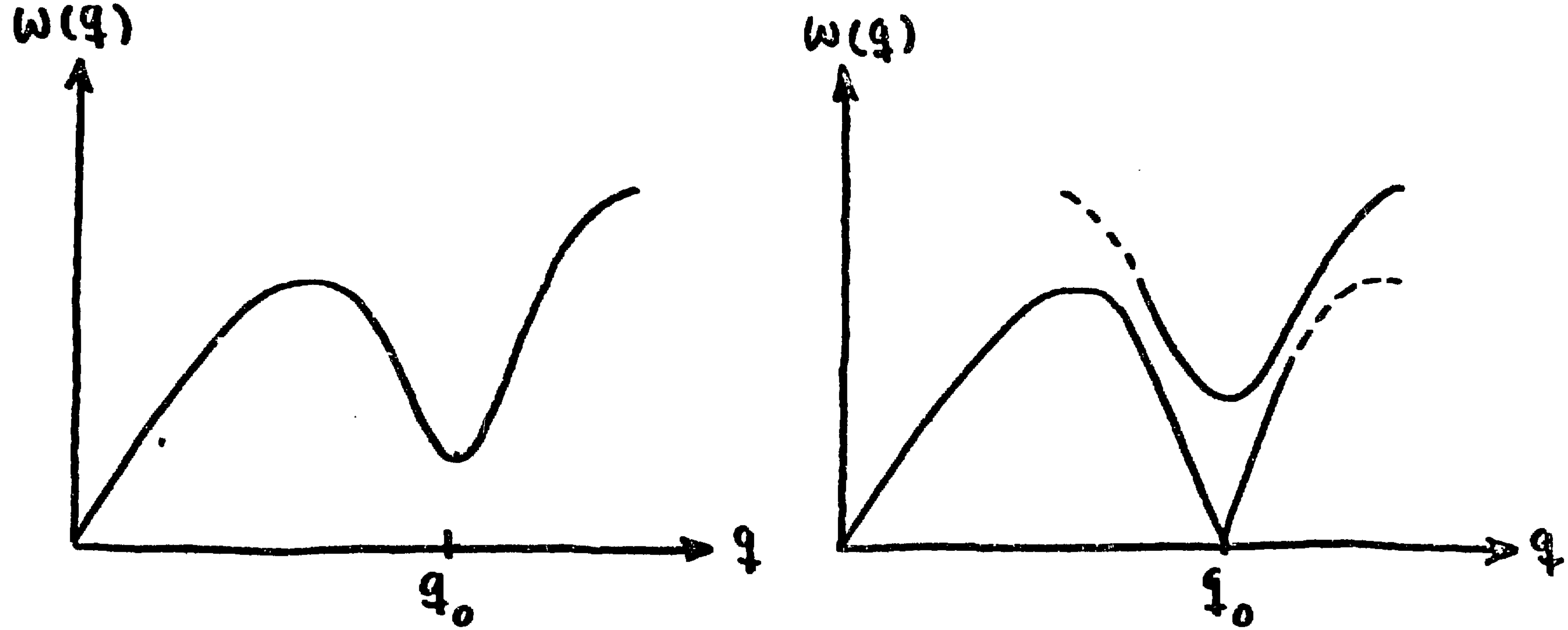


FIGURE 8

6-182-76

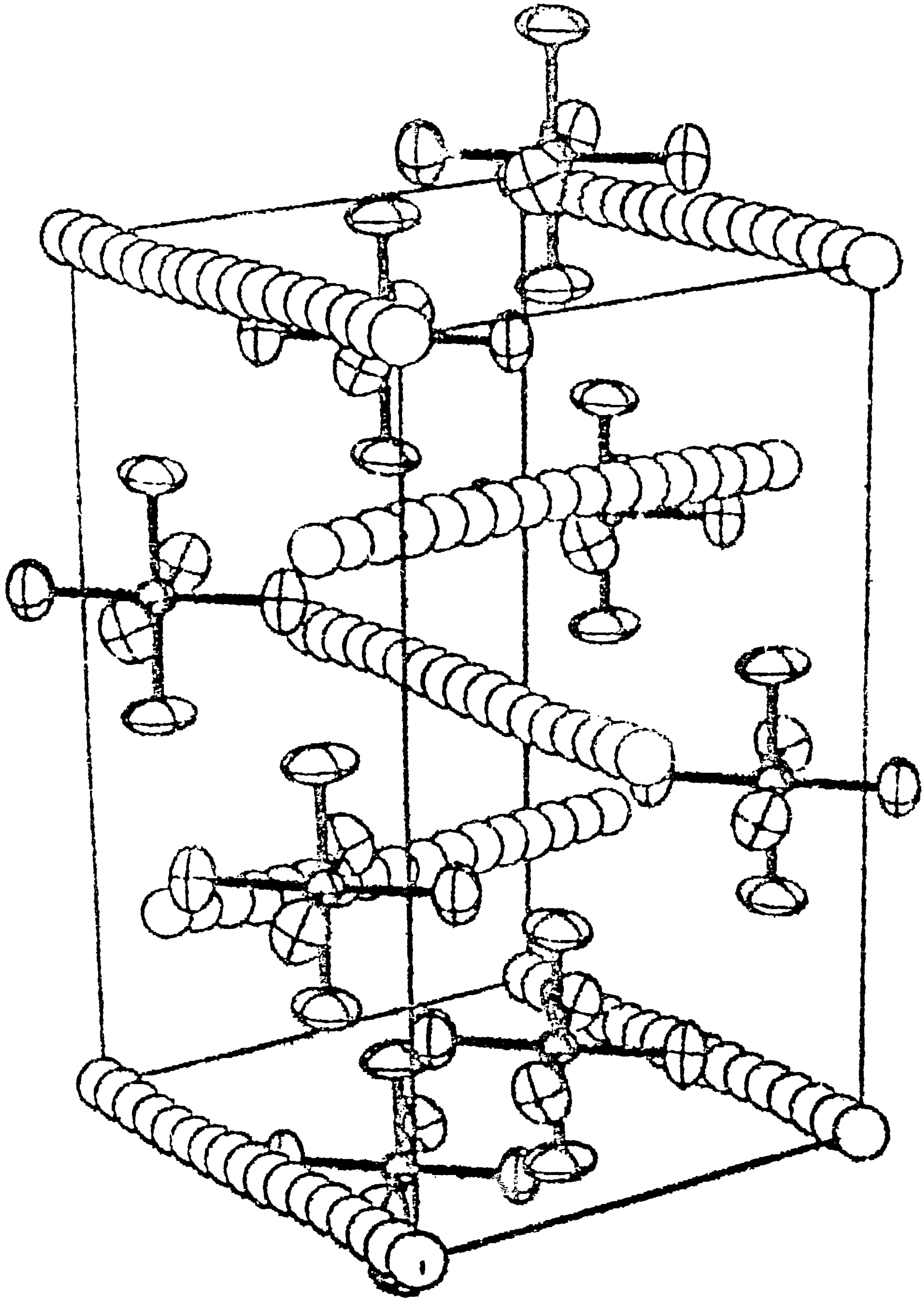


FIGURE 9

6-1088-78

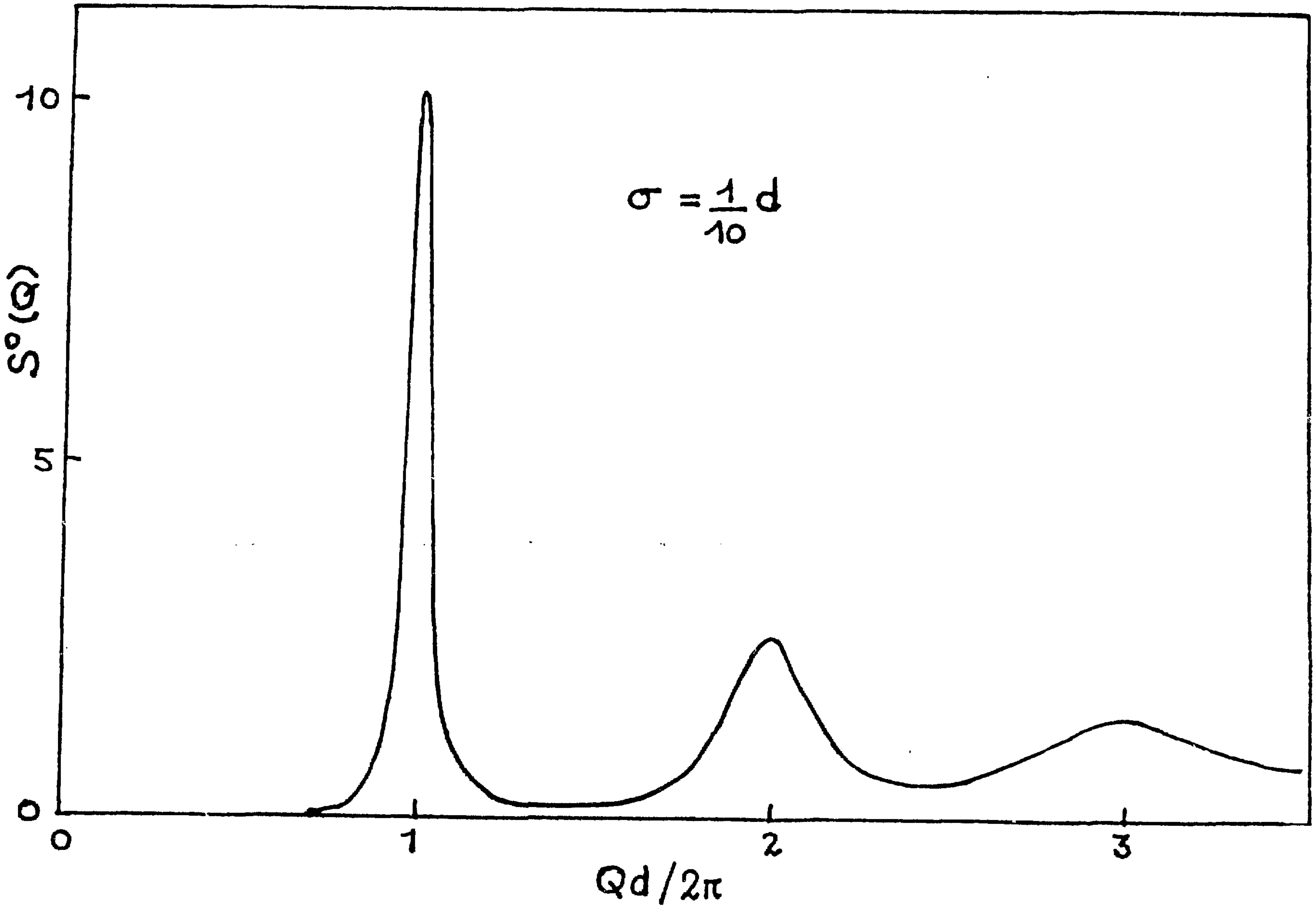


FIGURE 10

6-1085-78

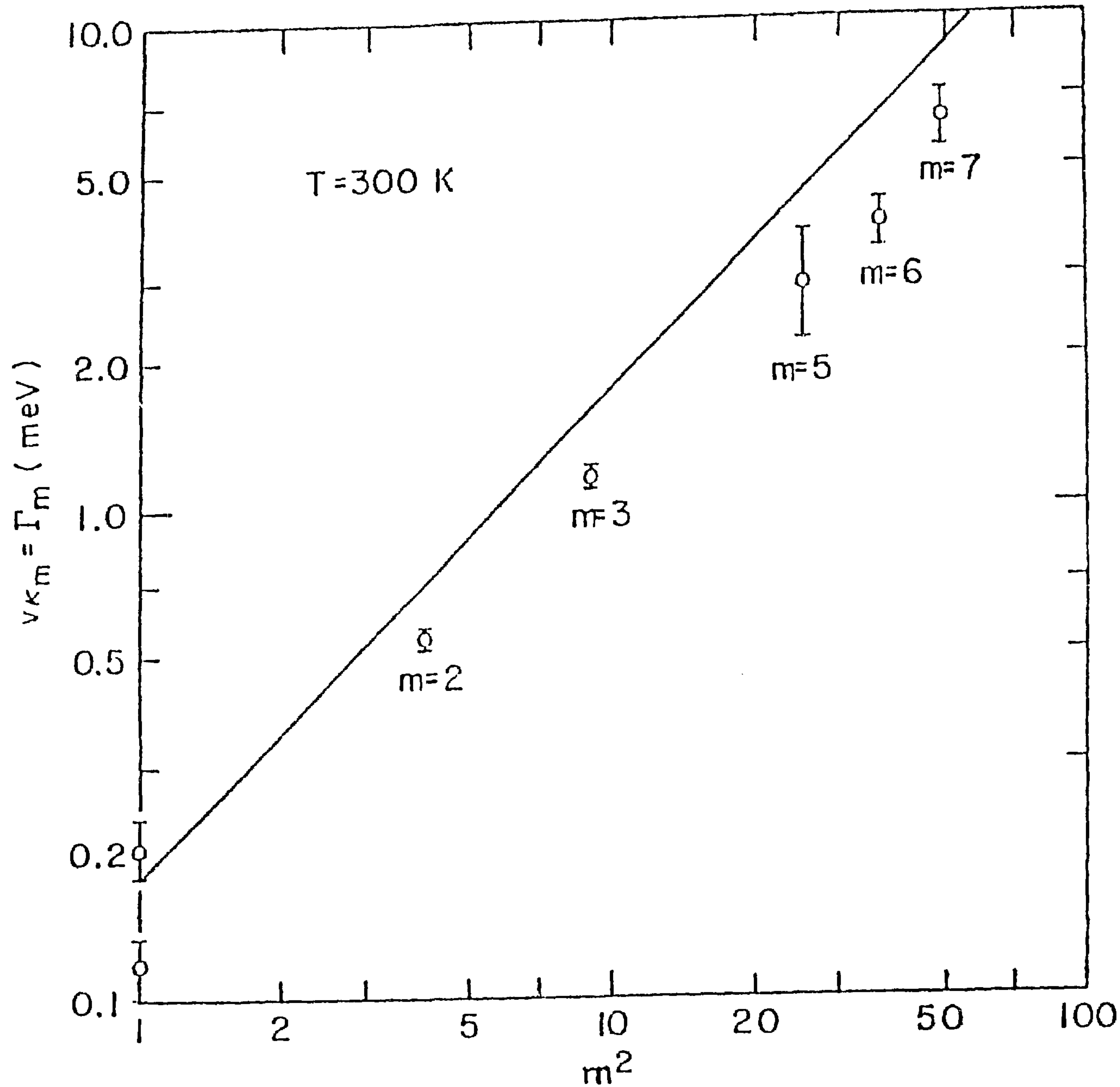


FIGURE 11

5-358-79