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ACOUSTIC METHODS FOR PHASE TRANSITIONS INVESTIGATIONS [1]

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We demonstrate the advantage of acoustic methods for the study of phase transitions of different type. Because the order parameter is always coupled to the elastic wave strain, phase transitions are usually accompanied by strong anomalies in sound velocity and attenuation. The most favorable case appears when the order parameter is bilinearly coupled to the strain, because then the susceptibility is directly measured by acoustic methods. But even for the case of an instability out of the Brillouin zone center (antiferrodistortive transition, incommensurate transition) quite useful information can be gained on the dynamics of the ordering quantity, the order parameter-strain coupling coefficient and the order of the phase transition. These points will be illustrated on several examples of order-disorder phase transitions, incommensurate phases and glasses.

I. INTRODUCTION

It is the aim of present paper to show the importance of acoustic measurements for the investigation of phase transitions of different type. The experimental methods used in this field are either local or macroscopic measurements. Local measurements are NMR, EPR,... whereas X-rays, dielectric, specific heat, acoustic methods, etc. probe the macroscopic response of the system under investigation. E.g. a typical ultrasonic wavelength $\lambda \approx 50\mu m$ is large as compared to the correlation lenght ξ of structural fluctuations and can therefore be considered as spatial homogeneous. Acoustic measurements have been successfully applied for the study of phase transitions in quite different systems:

a) Ferroelectrics (KDP, NH_4LiSO_4, TGS,...)
b) Ferroelastics (KCN, $CsLiSO_4$,...)
c) Jahn-Teller transitions ($NiCr_2O_4$, $TbVO_4$,...)

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d) Martensitic phase transformations (metal alloys)
e) Order-Disorder transitions (Orientational degree of freedom is order parameter, NH_4Cl, KSCN,...)
f) Charge-density wave transitions (KCP, $TaSe_2$,...)
g) Superionic conductors ($RbAg_4I_5$, $Rb_3H(SeO_4)_2$,...)
h) Liquid helium-4 (λ-transition)
i) Incommensurate phases (K_2SeO_4, Rb_2ZnCl_4, $(NH_4)_2BeF_4$,...)
j) Pseudospin Glasses ($NH_{4x}Rb_{1-x}H_2PO_4$,...), Orientational Glasses (KCN_xBr_{1-x}, ...)
k) High T_c Superconductors
l) Fullerenes (C_{60},..)

Of course the list above is far from being complete. Including other types of phase transitions like magnetic ordering, gas-liquid transitions and phase transitions in liquid crystals would multiply the number of materials. Since there exists a number of excellent rewiew articles [1,2,3,4,5] on the present subject we can concentrate on some selected examples only.

These examples will concern:

-Order-disorder phase transitions (particularly KSCN)
-Incommensurate phases in general
-Orientational and Pseudospin Glasses (KCN_xBr_{1-x})

Sound waves may be used as a tool for dynamic as well as for static measurements. As long as the product of the frequency of the sound wave ω and the longest characteristic time τ of the system is small i.e. $\omega\tau << 1$, a measurement of sound velocity is a static method. If $\omega\tau >> 1$ even sound velocity is a dynamic measurement. In contrast to the velocity, sound attenuation is always a dynamic quantity and can be used to determine the characteristic lifetime of microscopic processes occuring in the system. ¿From these considerations the need to vary the frequency ω appears evident. Several methods have been established for this and other purposes:

- X-ray scattering	10^{16}Hz
- Neutron scattering	10^{12}Hz
- Brillouin scattering [6]	10^{10}Hz
- Bragg scattering of light [7]	10^{9} Hz
- Ultrasonics [8]	10^{6}Hz-10^{8}Hz
- Vibrating reed technique [9]	10^{3}-10^{5}Hz
- Static methods	0-50Hz

II. THEORETICAL BACKGROUND

Theories of different degree of sophistication have been used for the description of sound waves near structural phase transitions.

- Mean Field Theory
- Mean Field + small fluctuation corrections
- Scalling Hypothesis, Universality, Renormalization Group Approach

In any case the acoustic anomalies around T_C appear due to the coupling of the order parameter Q and the strains e_i in the Landau type free energy [1] or the Landau-Ginzburg-Wilson Hamiltonian [10].

The general form of the interaction between the strain and the order parameter is determined by the symmetry change at the second order phase transition and can be calculated by group theoretical methods [11]. The form of the coupling remains valid for all these theories, but the effects of the coupling (i.e. the exact temperature dependence of the elastic constants and attenuation) can be different for different theories.

Examples for the application of these theories are:

a) KH_2PO_4 (KDP) [12], Ammonium Oxalate Hemihydrate [3], $CsLiSO_4$ [13], KSCN [14]
b) NH_4LiSO_4 [15], TSCC [16], terbium molybdate [17]
c) liquid helium-4 [4], $KMnF_3$ [18,19], $SrTiO_3$ [20]

The determination of critical exponents is rather difficult task and has to be done with greatest caution. Especially near structural phase transitions lattice defects (impurities, dislocations, sector boundaries, growth bands, domains,...) play an important role and can even overcome the critical behaviour [21]. To the authors knowledge, there is no particular example of a detailed study of the influence of well defined defects on the acoustic anomalies near T_c.

To calculate the elastic response of a crystal one expands the free energy in terms of the order parameter Q and the strain e and coupling terms, which in a simplified way can be written as:

$$F(Q,e) = A/2Q^2 + B/4Q^4 + h(\delta Q/\delta x)^2 + 1/2C^0e^2 + aQe + bQ^2e + d/2Q^2e^2 + f/3Q^3e + gQ(\delta Q/\delta x)e + \cdots \quad (1)$$

Where $A = \Omega(T - T_0)$ and all the other coupling coefficients are assumed to be constant. In (1) we have included all the terms which are needed for the discussion of our present examples.

The temperature and frequency dependence of the elastic response can be caltulated from (1) by well known methods [17,22] and we need not to go into these details here. We will discuss the different contributions of (1) to the elastic response near Order-Disorder phase transitions, Incommensurate phases and Pseudospin-Glasses.

III. EXAMPLES FOR ACOUSTIC STUDIES OF PHASE TRANSITIONS

A) ORDER-DISORDER PHASE TRANSITIONS (KSCN)

Order-Disorder phase transitions are usually described in terms of a pseudospin model. If the orientational degrees of freedom Q are coupled to the strains e_i one speaks of a compressible pseudospin model. Such a model has been used to describe the order-disorder phase transition in KSCN [23]. The advantage is that one obtains an analytic expression for the free energy in the mean field approximation and consequently all terms in the order parameter part of the free energy $F(Q)$

are known. From the temperature dependence of the spontaneous strain one can determine the coupling coefficient b which affects the longitudinal elastic constants in KSCN. In KSCN a, f and g of equation (1) are zero by symmetry. $b \neq 0$ for longitudinal modes and $b = 0$ for transverse modes and $d \neq 0$ for longitudinal and transverse modes. Knowing the magnitude of the coefficient b one can use (1) to calculate the temperature dependence of the longitudinal elastic contants.

$$C_{\text{long}} = C^0_{\text{long}} - b^2 f(Q)(1 + i\omega\tau)^{-1} + dQ^2 \qquad (2)$$

$f(Q)$ is a function of the order parameter which is calculated from the free energy of the pseudospin model [24]. Equation (2) was used to compute the temperature dependence of the elastic constants in KSCN. The results [24] agree well with the temperature dependence of the elastic constants measured in the static limit $\omega = 0$ [25]. At ultrasonic frequencies a quite different behaviour was observed [25] and was attributed to the biquadratic coupling dQ^2e^2 in (1). This implies that at ultrasonic frequencies (10^7 Hz) one is in fact in the limit $\omega\tau >> 1$, and the relaxation time of the order parameter $\tau >> 10^{-7}$s. This is clearly much too slow to be measured by inelastic neutron scattering and a measurement of the frequency dependence of the sound attenuation for longitudinal waves is the only possible way to determine the relaxation time of the order parameter in KSCN. This is thanks to the coupling of the type bQ^2e which for all longitudinal modes is present for all symmetries and leads to a frequency dependence of the sound velocity and attenuation (equation (2)). A schematic picture of this behaviour is shown in Figure 1*a* and 1*b*. In contrast to this the coupling of the form dQ^2e^2 does not produce any frequency dependence of the elastic constant and attenuation. Since the transverse elastic constants are affected only by this term, they are independent of the applied frequency.

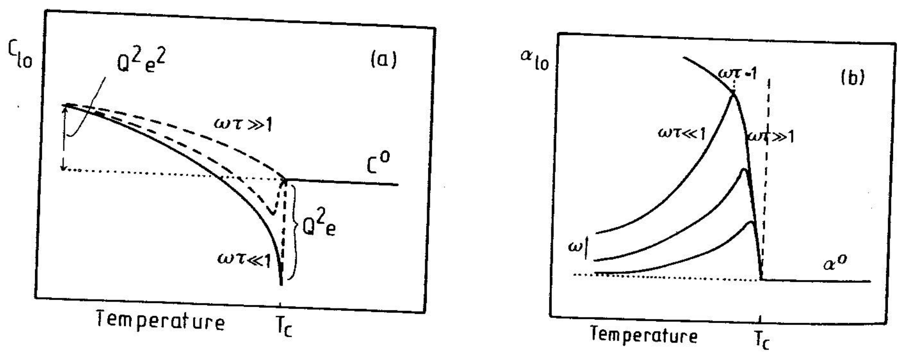

Fig. 1. Temperature and frequency dependence of the longitudinal elastic constant (*a*) and sound attenuation (*b*) due to the coupling bQ^2e and dQ^2e^2. Due to the temperature dependence of the relaxation time $\tau = \tau_0/(T_c - T)$ a crossover from $\omega\tau << 1$ to $\omega\tau >> 1$ is possible close to T_c.

B) INCOMMENSURATE PHASES

The essential difference of incommensurate phases to ordinary phase transitions is the presence of two branches in their vibrational spectrum: Amplitudon (similar to the soft mode at a normal phase transition) and Phason (quasi-acoustical vibration). Both vibrations can contribute to the temperature dependence of the elastic response [26,27]. Because the soft mode wavevector $k_i = k_c(1 - \delta)(k_c = a^*/n)$ appears at a general point of the Brillouin zone, the bilinear coupling in (1) is forbidden (due to translational invariance) - i.e. $a = 0$ in (1) - and the lowest order term is proportional Q^2e. This is the case for all incommensurate phase transitions and therefore the anomalies of the longitudinal elastic constants display essentially the same behaviour as shown in Figure 1*a* (see equation 2). In many cases they are measured to study the dynamics of the amplitude fluctuations in the incommensurate phases [28,29] (the relaxation time of the order parameter in equation 2 is substituted by the relaxation time of the amplitude mode). It is important to nóte, that the acoustic anomalies around the incommensurate phase depend strongly on the nature of the lock-in transition:

If $n = 2$ (the unit cell of the lock-in phase becomes doubled, e.g. $RbH_3(SeO_3)_2$, $(NH_4)_2BeF_4$ there is an additional contribution from an "upper mode" which leads to a negative jump and a strong attenuation similar as in Figure 1*a,b* even for transverse modes. A very interesting situation appears for $n = 3$ (e.g. K_2SeO_4, Rb_2ZnCl_4). This is the exceptional case where the phason contributes to the elastic response. The analysis shows, that the phason contribution enters through the invariant of type fQ^3e in (1) and influences the transverse elastic constants [26,27]. In the explicit formula for the elastic constants the misfit parameter $\delta(T)$ enters unambigously and can therefore be determined very precisely by elastic measurements

$$\Delta C_{\text{trans}} \alpha - f^2 Q^4/\{h\delta(T)^2\}. \qquad (3)$$

The temperature dependence of the incommensurate wave vector $k_j = k_c(1 - \delta)$ determined in this way agrees well with the results of neutron measurements [26]. An estimation shows, that the contributions of the gradient terms (g-term) in (1) to the acoustic anomalies are neglicable ($10^{-8} - 10^{-10}$).

A very interesting feature is the observation of an assymmetric behaviour of shear waves with the same strain but different propagation direction ($C_{ij} \neq C_{ji}$) in $BaMnF_4$ [30], $RbH_3(SeO_3)_2$ [31] and SiO_2 [32]. It has been tentatively attributed to a "certain texture" with wave vector along the modulation axis with characteristic dimensions of about ultrasonic wavelenght ($\approx 50\mu$m), but still the problem remains unsolved.

C) ORIENTATIONAL- AND PSEUDOSPIN- GLASSES

One of the most impressive examples of elastic measurements on orientational glasses have been performed on the KCN_xBr_{1-x} [33] and $K_xRb_{1-x}CN$ [34] mixed crystals [39]. The phase transition in the pure system is proper ferroelastic and thus accompanied by a softening of the shear elastic constant C_{44}. It is described by the free energy (1) with $a \neq 0$, $f = 0$ and $g = 0$.

$$C_{44} = C_{44}^0 - a^2\chi(T) = C_{44}^0(T - T_C)/(T - T_0) \quad (4)$$

$\chi(T)$ is the quadrupolar susceptibility, T_c is the actual phase transition temperature and T_0 is the temperature, where the cyanide ions would order in the absence of the bilinear order parameter -strain coupling.

This is the most favorable case for acoustic measurements, because the acoustic strain field directly probes the ordering quantity (orientational order parameter of quadrupolar symmetry in KCN) at the frequency and wavenumber of the sound wave. Therefore the quadrupolar susceptibility χ is directly measured through the measurement of the elastic shear constant C_{44}. Several theories have been proposed for the description of the elastic response in mixed cyanide crystals [34,35,36] and verified by acoustic measurements [33,34,37].

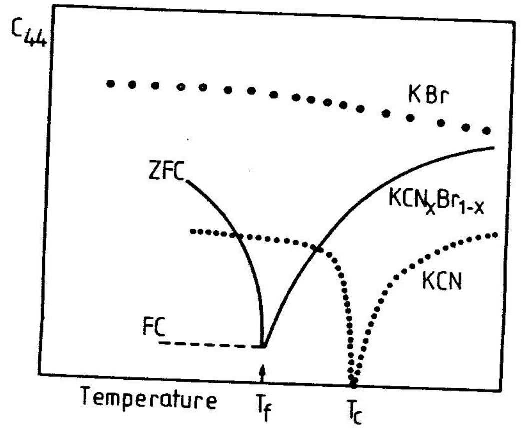

Fig. 2. Temperature dependence of the transverse elastic constant C_{44} for pure KCN (·), pure KBr (o) and zero field cooled (-) and field cooled (--) elastic constants for mixed cyanide crystals KCN_xBr_{1-x}. ¿From Fossum et al [37] and Hessinger et al [33].

In mixed cyanide crystals the elastic susceptibility (4) is modified by the effect of random static strains which induce random fields [36]:

$$C_{44} = C_{44}^0 \cdot \frac{T - T_c(x)(1-q)}{T - T_0(x)(1-q)} \quad (5)$$

$q(x,T) = [< s_i >_T^2]av$ is a quenched random-strain-field induced Edwards-Anderson order parameter. Random pseudospin interactions leads to a nonzero q below the glass transition, whereas a random field yields $q \neq 0$ at all temperatures [40]. The temperature dependence of C_{44} for different mixed cyanide crystals has been measured to study the effect of random interactions and random fields [37]. Figure 2 shows a schematic picture of these measurements, which have been used together with equation (5) to determine the temperature dependence of the Edwards-Anderson order parameter q [37]. From these investigations the influence of random fields in the mixed cyanides was verified. Similar as in the spin glasses the zero field cooled and the field cooled susceptibilities become different at the freezing temperature T_f, which was impressively demonstrated by quasi static shear torque measurements [33]. The results are schematically shown in Figure 2.

Much less is known about the elastic properties of the mixed crystals $(NH_4)_xRb_{1-x}H_2PO_4$ around the pseudospin glass transition. Although there are some attempts to study the acoustic properties of longitudinal modes of these mixed crystals [38] no detailed analysis of a compressible pseudospin glass has been performed so far.

IV. SUMMARY

We have briefly described the anomalies of the sound velocity (elastic constant) and attenuation occurring near structural phase transitions. In conclusion we may say that acoustic measurements give important information on different types of phase transitions (here order-disorder phase transitions, incommensurate transitions and glasses were studied). Of course acoustic measurements should not stand alone, but should be combined with complementary measurements.

REFERENCES

[1] W. Rehwald : Advances in Physics *22* (1973)

[2] B. Lüthi , W. Rehwald : *Ultrasonic studies near structural phase transitions. Topics in Current Physics, Structural Phase Transirions I*, (Eds. K.A.Müller and H.Thomas), Springer, 1981

[3] J.B. Berger : Phase Transitions *14* (1989), 31

[4] C. Elbaum : J. Physique C5 *42* (1981), 855

[5] J.O. Fossum : J. Phys. C: Solid State Phys. *18* (1985), 5531

[6] P.A. Fleury , K. Lyons : *Structural Phase Transitions I*, (Eds. K.A. Müller and H.Thomas), Springer, 1981

[7] A. Yariv : *Quantum Electronics* (2^{nd} Edition) J.Wiley and Sons (1975)

[8] E.P. Papadakis : *Physical Acoustic XII*, (Eds. W.Mason and R.Thurston), Academic press, New York (1976)

[9] T.A. Read , C.A. Wert , M. Metzger : *Methods of Experimental Physics 6A* (Eds. Lark-Horovitz, V.A.Johnson), Academic New York (1974), 291

[10] F. Schwabl : Ferroelectrics *24* (1980), 171

[11] A.D. Bruce , R.A. Cowley : Advances in Physics *29* (1980)

[12] M.E. Lines , A.M. Glass : *Principles and Applications of Ferroelectrics and Related Materials.* (Eds. W.Marshall, D.H.Wilkinson), Clarendon Press. Oxford (1977)

[13] A.T.Anistratov , A.V.Zamkov , L.A.Kot , I.N.Stolovitskaya , A. Shabanova : Ferroelectrics *48* (1983), 103

[14] A. Fuith , J. Kroupa : Birefringence study of the 415K phase transition in KSCN. J.Phys.: Condens. Matter *2* (1990), 2355

[15] P. Kubinec, W. Schranz, H. Kabelka: J. Phys.: Condens. Matter *4* (1992), 7009

[16] A.G. Smolensky, I.G. Siny, A.K. Tagantsev, S.D. Prokhorova: Ferroelectrics *64* (1985), 221

[17] W. Yao, H.Z. Cummins, R.H. Bruce: Phys. Rev. B*24* (1981), 424

[18] R.M. Holt, K. Fossheim, J.O. Fossum: J. Physique C5 *42* (1981), 1097

[19] K. Fossheim, J.O. Fossum: *Critical Dynamics of Sound. Proc. (NATO ASI) on Multicritical Phenomena.* (Eds. R. Pynn, A. Skjeltorp) New York: Plenum Press 113 (1984)

[20] E. Sandvold, I. Legreid, K. Fossheim, J.O. Fossum: Phase Transitions *11* (1988), 145

[21] A.P. Levanyuk, V.V. Osipov, A.S. Sigov, A.A. Sobyanin: Sov. Phys. JETP *49* (1979), 176

[22] J.C. Slonczewski, H. Thomas: Phys. Rev. B*40* (1989), 3599

[23] W. Schranz, H. Warhanek, R. Blinc, B. Zeks: Phys. Rev. B*40* (1989), 7141

[24] W. Schranz, T. Streuselberger, A. Fuith, H. Warhanek: Acoustic anomalies in KSCN. to be published

[25] W. Schranz, A. Fuith, H. Warhanek: *Proceedings of the 20th Spring Conference on Ferroelectricity*, Güntersberge 1992, 73

[26] V.V. Lemanov, S.K. Esayan: Ferroelectrics *73* (1987), 125

[27] V.V. Lemanov: Ferroelectrics *78* (1988), 163

[28] J. Berger, J.P. Benoit, C.W. Garland, P.W. Wallace: J. Physique *47* (1986) 483

[29] I. Hatta, M. Hanami, K. Hamamo: J. Phys. Soc. Jpn. *48* (1980), 160

[30] I.J. Fritz: Phys. Lett. *51A* (1975), 219

[31] S.K. Esayan, V.V. Lemanov, N. Mamatlukov, L.A. Shuvalov: Sov. Phys. Crystallogr. *26* (1981) 619

[32] B. Berge, G. Dolino, M. Vallade: J. Physique *45* (1984), 715

[33] J. Hessinger, K. Knorr: Phys. Rev. Lett. *65* (1990), 2674

[34] C.W. Garland, J.O. Fossum, A. Wells: Phys.Rev. B*38* (1988), 5640

[35] K.H. Michel: Phys. Rev. Lett. *57* (1986), 2188

[36] K.H. Michel: Phys. Rev. B*35* (1987), 1405

[37] O. Fossum, C.W. Garland: Phys. Rev. Lett. *60* (1988), 592

[38] E. Sandvold: *Phase Transitions in Ferroelectric Systems.* Thesis, University of Trondheim (1987)

[39] U.T. Höchli, K. Knorr, A. Loidl: Advances in Physics *39* (1990) 405

[40] K. Binder, A.P. Young: Rev. Mod. Phys. *58* (1986) 801