

Thermally stimulated acoustic splitting in ionic molecular crystals

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A stable splitting of an elastic wave has been observed in solids with reoriented complex ions. It is suggested that this effect stems from a heterostructural state of the material.

The modeling of a two-phase condensed medium can set the stage for the observation of a secondary bulk compressional wave.^{1,2} It would seem that a corresponding effect could occur under “natural” conditions, during a freezing of the order of the structural elements of certain crystal lattices. In this letter we are reporting results which support that possibility.

In our study of structural phase transitions in crystals with complex anions such as N_3^- , NO_2^- , NO_3^- , BrO_3^- , ClO_3^- , IO_3^- , ClO_4^- , and IO_4^- by ultrasonic spectroscopy, we were interested in the qualitative difference in the changes in the acoustic properties in some of these crystals near the same phase-transition point. In a more careful approach, it was learned that the thermal history of the sample is a governing condition for the reproducibility of the results. Further studies in several crystals which undergo an order-disorder phase transition due to an orientational melting of one sublattice revealed that some additional components can be detected in the acoustic spectra far from the points of known phase transitions. These additional components are capable of distorting the true picture of the change in the velocity and attenuation of sound near a phase transition.

To describe the observed effect, we use the example of potassium nitrate, KNO_3 . Figure 1 shows the low-temperature spectrum of the velocity and attenuation of longitudinal ultrasound in this material. Polycrystalline samples of KNO_3 were prepared by a procedure similar to the procedure for preparing ceramic samples. The densities of the test samples were 95–98% of the x-ray values. The acoustic properties were deter-

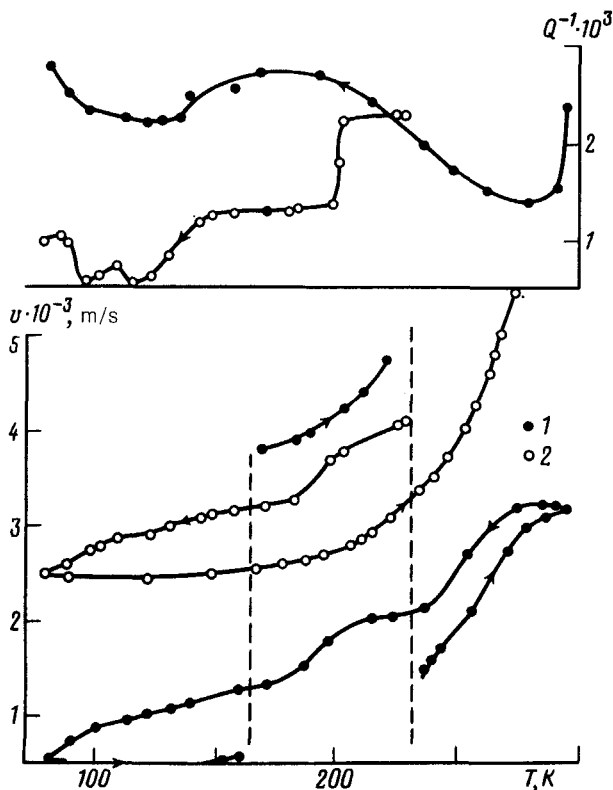


FIG. 1. Low-temperature acoustic splitting in KNO_3 II. 1—First elastic wave; 2—second elastic wave. v) sound velocity; Q^{-1}) internal friction. The arrows show the direction in which the temperature is varied.

mined by a method involving a two-composition piezoelectric transducer at a frequency ~ 100 kHz. As the temperature was lowered from room temperature at a rate ~ 1 K/min, the temperature dependence of the ultrasonic velocity changed direction near 280 K in the KNO_3 . At 230 K, a second resonance appeared. A calculation based on this resonance leads to a second elastic wave (we will somewhat arbitrarily call these the "first and second waves"). As the sample was cooled further, the two waves underwent similar variations, and the acoustic splitting was stable at liquid-nitrogen temperature. When the temperature was swept in the opposite direction (i.e., as the sample was heated), the waves behaved differently: The higher-frequency component varied monotonically, while the lower-frequency component underwent jumps at 165 K and 230 K. The curves of Q^{-1} (only the results obtained during the cooling are shown here) clearly demonstrate the change in the relationship between the attenuation levels of the observed components of the sound.

We would like to suggest that this behavior of the acoustic properties of KNO_3 stems from a dynamic reorientation of NO_3 groups in planes in which they have two nonequivalent positions. As the temperature is varied, the numbers of differently oriented NO_3 groups undergo a redistribution. Structurally, this effect reflects the coexistence of solid phases KNO_3 II and KNO_3 III. We can offer the following arguments to support this suggestion.

The pseudohexagonal orthorhombic lattice of KNO_3 II, which is stable under ordinary conditions, converts into trigonal KNO_3 I near $T = 401$ K as it is heated; the long-range order in the sublattices of the NO_3^- nitrate groups disappears.³ The ferroelectric KNO_3 III phase is stable at high pressures, but it can be produced in a metastable state at atmospheric pressure through rapid cooling from 450 K. The KNO_3 III phase can apparently be likened to a state with a glass-crystal phase in an anionic sublattice.⁴ The KNO_3 I phase is a plastic crystal,^{5,6} while the KNO_3 III phase retains disordered NO_3 molecules in a relative number of about 20% (Refs. 7 and 8). The KNO_3 II \rightarrow KNO_3 I \rightarrow KNO_3 III transitions are thus partial-ordering phase transitions. The degree of dynamic orientational disorder of the NO_3 molecules in the successive potassium nitrate sublattices may also be reflected in the acoustic data.

If the KNO_3 III phase is indeed responsible for the effect observed in KNO_3 II at 230 K, a corresponding splitting should occur upon the appearance of the metastable KNO_3 III phase from the KNO_3 I phase at elevated temperatures. Figure 2 shows results on the change in the lower-frequency component of the sound velocity (curve 1 in Fig. 1) in the case of high-temperature thermal cycling. It can be seen from these data that as the sample is cooled from 540 K, a jump in v occurs at 375 K (the phase transition KNO_3 I \rightarrow KNO_3 III). Near $T = 300$ K, the sign of dv/dT changes, and we detect the second, higher-frequency component, with a propagation velocity of 4500 m/s ($T = 300$ K) or 3720 m/s ($T = 250$ K). Beyond this point, the curve is like curve 2 in Fig. 1. The component represented by curve 1 in Fig. 1 is not present in this case.

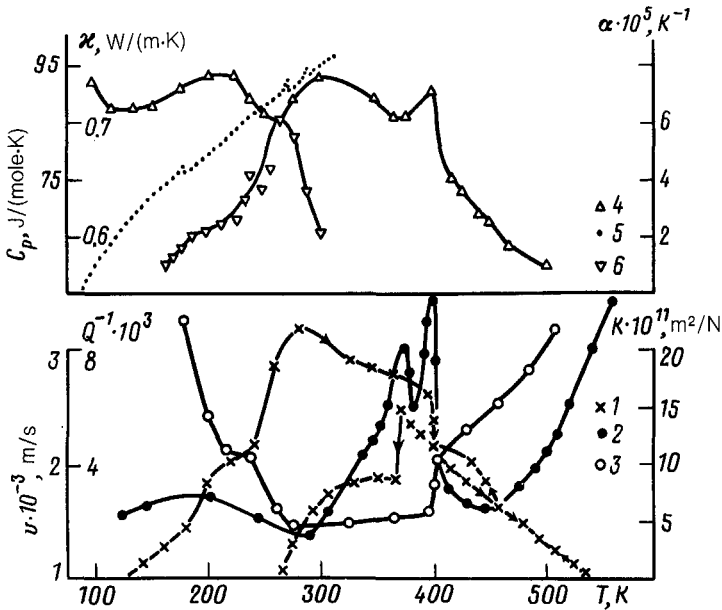


FIG. 2. Temperature dependence of (1) the sound velocity v , (2) the internal friction Q^{-1} , (3) the compressibility k , (5) the heat capacity C_p , (4) the thermal conductivity κ , and (6) the thermal expansion coefficient α of KNO_3 .

It can thus be assumed that the acoustic splitting does indeed reflect a simultaneous coexistence of different solid phases.

From the changes in v and Q^{-1} near $T = 400$ K in Fig. 2, we see that the phase transition KNO_3 III \rightarrow KNO_3 I has been detected correctly from the acoustic data. The adiabatic compressibility of sodium nitrate found from ultrasonic measurements of the velocities of longitudinal and transverse elastic waves by a pulsed technique, at a frequency of 1.67 MHz, agrees with the data from resonance measurements. The splitting is not detected, however, because of the strong sound absorption. The thermal properties found for KNO_3 during heating (the heat capacity C_p was determined by adiabatic calorimetry on a high-precision UUNT apparatus; the thermal conductivity κ was measured on an IT- λ -400 apparatus; and the thermal expansion coefficient α was measured with a capacitive dilatometer). These properties exhibit structural features on their temperature dependence, but these properties are less sensitive to a partial dynamic reorientational disordering of the NO_3^- anions.

Among the nitrates of monovalent metals, the effect described above has been detected in NaNO_3 (140 K) and AgNO_3 (185 K), while it has not been detected in RbNO_3 , CsNO_3 , or TlNO_3 . These differences are apparently associated with the parameter r_c/r_a (the ratio of ionic radii), which is close to its limiting value for an aragonite-calcite structural transition in the nitrates of the first group. Here are a few other compounds and the points at which the splitting begins as the temperature is lowered: KBrO_3 (150 K), NaNO_3 (230 K), NaClO_4 (190 K), $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ (125 K), and NH_4ClO_4 (135 and 95 K). In the case of ammonium perchlorate, the two splittings, at different temperatures, may be due to a disorder in both the anionic and cationic sublattices.

We conclude with the following comments. The effect which we have described here is also seen in compounds of more complex composition, in particular, in bismuth and thallium two-phase high- T_c superconductors with superconducting transition temperatures ~ 110 K (80 K) and ~ 125 K (90 K), respectively, in the region of their "metallization" (500–700 K). The effect in these high- T_c superconductors is evidently of the same nature, since the glass transition temperature in a Bi-Ca-Sr-Cu-O sample quenched from the melt lies in this interval ($T \sim 650$ K).⁹ In several compounds (e.g., NaNO_2) a subtler effect is detected: The individual acoustic components (1 and 2 in KNO_3) undergo a further splitting, into closely spaced sublevels, forming bands. Acoustic spectra of this sort may reflect changes in the ordering of the rotational motions of molecular groups around several axes of the crystal (with various moments of inertia) and may, in a sense, constitute an analog of the optical spectra of materials.

¹V. S. Arakelyan *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **27**, 656 (1978) [JETP Lett. **27**, 619 (1978)].

²T. J. Plona, Appl. Phys. Lett. **36**, 259 (1980).

³I. Náray-Szabó, *Inorganic Crystal Chemistry*, Adler.

⁴S. S. Bukalov and L. A. Leites, Izv. Akad. Nauk SSSR. Ser. Fiz. **53**, 1715 (1989).

⁵D. M. News and L. A. K. Staveley, Chem. Rev. **66**, 267 (1966).

⁶E. Y. Wang, J. Electrochem. Soc. **123**, 435 (1976).

⁷K. O. Strømme, Acta Chem. Scand. **23**, 1625 (1969).

⁸M. H. Brooker, J. Phys. Chem. Solids **39**, 657 (1978).

⁹K. B. R. Varma *et al.*, Appl. Phys. Lett. **55**, 75 (1989).

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