Neutron Inelastic Scattering by Coupled Defect-Phonon Modes in KCl-CN

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(Received 28 May 1974)

A clear splitting, present only at low temperatures, is observed where the unperturbed phonon curve crosses the CN^- T_{1u} and T_{2u} levels in a KCl crystal doped with 6×10^{19} CN^- cm^{-3}. Calculated dispersion curves require coupling constants which agree within experimental uncertainty with those determined ultrasonically. The absence of the splitting at high temperatures can be explained because the phonon gain and loss processes in the interaction with the CN^- level cancel almost completely.

It is well known that the resonant scattering of excitations otherwise describable as plane waves leads to coupled modes which can be described as a mixture of the wave functions of the excitation and the scattering system. For light, the phonon-photon coupled modes are referred to as the "polariton," and similar effects occur with magnons, etc. Coupled modes can also arise from a random distribution of defects, even at low concentrations. For sound, or phonons, the coupling to the spin of magnetic defects leads to coupled modes as was first shown by Jacobsen and Stevens.[1] This is still an active subject for theoretical research, but a general result common to all approaches is that close to resonance the normal modes of the crystal cease to be simply excitations in the displacement field but contain a magnetic contribution as well. Furthermore a phonon contribution also appears in what could otherwise be described as the normal modes of the paramagnetic defect.[2]

It is clear that similar behavior can be expected for phonons interacting with any resonant scatterer. Thus it has been shown that similar dispersion relations can be obtained for scattering of phonons by nonmagnetic defects. We wish to present here the first direct experimental evidence for the fact that a low concentration of defects does indeed lead to coupled modes. We will show that it is possible to scatter neutrons from the phonon component of the coupled mode.

The system chosen was KCl-CN because of the large interaction which exists between the phonons and the librational modes of the CN^- ion. The lowest energy levels for CN^- in KCl consist of a ground state, split by tunneling into three states separated by 1.1 and 2.0 cm^{-1} from the ground state.[3] Above these tunneling states there are three librational levels[4] at 13.5, 16.4, and 18.6 cm^{-1}.

Results obtained by Byer and Sack[5] reveal a large change in velocity of sound (~2% in the low-temperature limit for 1.65×10^{19} cm^{-3} CN^-) for phonons of E_g symmetry in KCl doped with various concentrations of KCN. The data reveal that the change increases as the temperature is lowered until a temperature of roughly 15°K is reached. As the temperature is lowered still further an additional increase occurs, but it is smaller. This behavior may be understood if it is assumed that the major interaction occurs between the E_g phonon and the librational levels —the change in self-energy of the phonon will tend to saturate when the temperature becomes sufficiently low for $\hbar\omega_i/kT>1$, where $\hbar\omega_i$ is the energy of the librational level.

Viewed in a similar fashion, Byer and Sack's results indicate that an even stronger interaction exists between phonons of T_{2g} symmetry and the lower tunneling states at 1.1 and 2.0 cm^{-1}; however, these are too low in energy to be accessible with neutron inelastic scattering and will have no effect on these experiments. The experimental task then is not only to obtain the dispersion curves in the crossover region, but also to compare the neutron data with the ultrasonic results. It should be noted that these effects will only appear at low temperatures, that is, at temperatures such that $\hbar\omega_i/kT\gtrsim1$, where $\hbar\omega_i$ is the energy of the librational levels.

The specimen used in these experiments was grown by G. Schmidt of Cornell University. It

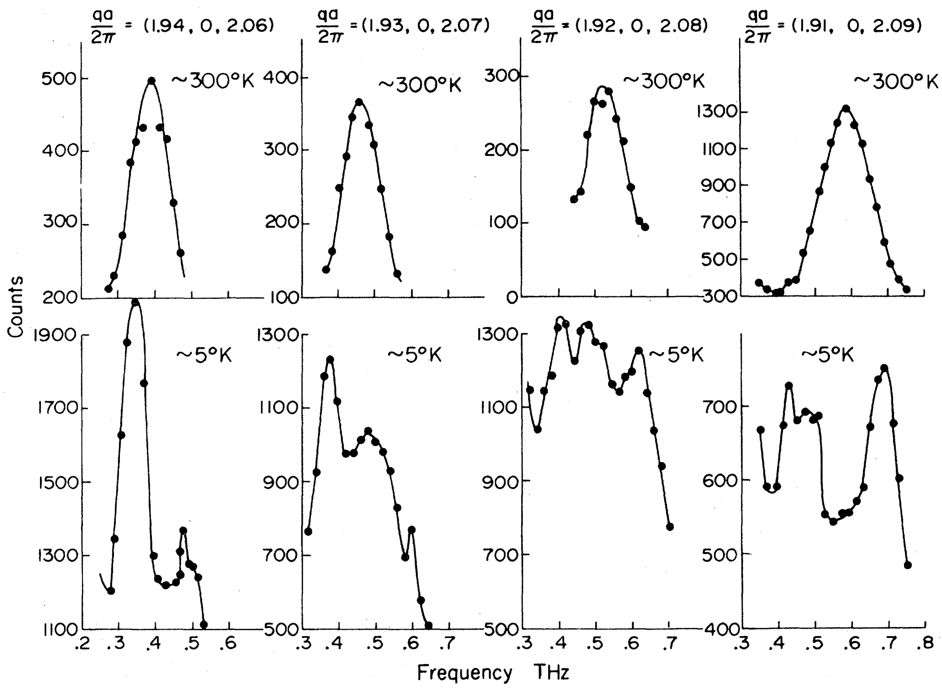

FIG. 1. Phonon peaks at room and liquid-helium temperatures for KCl + 6×10^{19} CN cm^{-3}. The data were taken at various monitor counts. The solid lines were not calculated and are included only to guide the eye.

was a single crystal of KCl doped with CN^-. From infrared absorption[6] a concentration of 6.0 $\times10^{19}$ ions/cm^3 (0.4%) was obtained. The approximate dimensions of the sample used were 2 cm $\times 2\times 5$ cm. The experiments were performed on the Oak Ridge high-flux isotope reactor on a triple-axis spectrometer of conventional design. We have studied phonons of E_g symmetry with wave vector in the ⟨110⟩ direction polarized in the ⟨1$\bar{1}$0⟩ direction. The polarization and wave vector are identical to those studied by Byer and Sack.[5]

Results for four phonons in the crossover region are shown in Fig. 1. The dispersion relations at 4°K in the vicinity of the cross over region are shown in Fig. 2.

It is clear from Fig. 1 that the neutron peaks show structure at 5°K which is nonexistent at room temperature. The structure is consistent with the presence of one strong peak and two weaker peaks. Although the resolution is only barely adequate (at best) to resolve the two weaker peaks, their presence is expected when the dispersion relations for the coupled modes are calculated.

It can be shown[7] that the shift in phonon frequency due to the interaction with a resonant scatter-

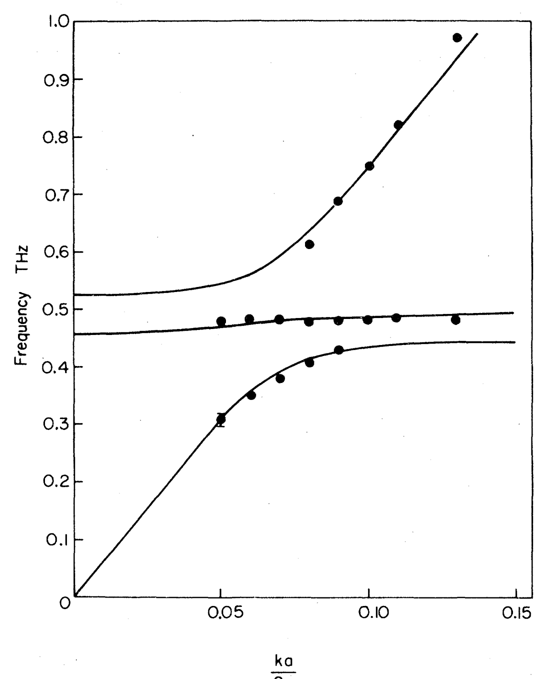

FIG. 2. Experimental (points) and calculated (solid line) dispersion relations for phonons in KCl + 6×10^{19} CN cm^{-3} at ~ 5°K.

er is given by

$$\frac{\Delta\omega}{\omega_k}=\rho_d\sum_i\frac{A_i}{\omega_i}\left(\frac{\omega^2}{\omega_i^2}-1\right)^{-1}\times\frac{1-\exp(-\beta\omega_i)}{1+\sum_i g_i\exp(-\beta\omega_i)},\qquad(1)$$

where ω_i is the frequency of level i, of degeneracy g_i; $\beta=\hbar/k_BT$, A_i is the coupling constant to level i, ω_k is the unshifted frequency, ω is the shifted frequency, and ρ_d is the number of defects per unit volume. At high temperatures, the factor $1-\exp(-\beta\omega_i)$ weakens the dispersion introduced by the interaction. The resonant frequencies are ~20°K and therefore the effect would be expected to become unobservable at room temperature, and a single phonon peak would be observed.

When all the energy levels of the CN^- ion in KCl are considered, a large number of potential transitions are revealed. Although symmetry considerations can be expected to reduce their number, it should be recalled that Byer and Sack[5] have noted that in some respects this system is anomalous. Nevertheless, if group theory is applied in a straightforward manner, we note that an E_g phonon can only induce transitions between the T_{1u} levels in the tunnel-split multiplet and the T_{1u} and T_{2u} librational levels. Therefore if the complexities peculiar to the CN^- are neglected, we obtain two possible transitions:

$$\hbar\omega_1/c=16.4-1.1=15.3\ \text{cm}^{-1},$$

$$\hbar\omega_2/c=18.6-1.1=17.5\ \text{cm}^{-1}$$

In the low-temperature limit, close to resonance, Eq. (1) becomes approximately

$$\Delta\omega/\omega_k=B_1(\omega^2-\omega_1^2)^{-1}+B_2(\omega^2-\omega_2^2)^{-1}.\qquad(2)$$

By using this expression, and leaving B_1 and B_2 as adjustable parameters, the solid lines in Fig. 2 were obtained. The value of B_1/ω_1^2 is 0.008 and of B_2/ω_2^2 is 0.07, if ω_1 and ω_2 are in terahertz.

From Byer and Sack's ultrasonic results we obtain a value for the sum $B_1/\omega_1^2+B_2/\omega_2^2=0.06$. Considering the difficulty in making an absolute determination of CN^- concentration, we consider the agreement to be satisfactory.

We conclude that the extra peaks which appear at low temperatures are due to neutrons inelastically scattered from the phonon component of levels which would be the CN^- librational levels in the absence of any phonon-defect interaction. At room temperature the phonon virtual gain and loss processes cancel almost completely and the extra peaks disappear. Because of the low concentration of CN in the sample, the CN^- modes themselves are unobservable. Therefore the extra peaks that appear at low temperature must be due to the mixing of phonons into the CN^- librational levels.

The authors wish to express their gratitude to B. N. Brockhouse and R. F. Wood for the many very helpful suggestions they have made.

*Research supported by the National Research Council of Canada.

†Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

‡Operated by Union Carbide Corporation under contract with the U. S. Atomic Energy Commission.

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