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Normal Modes of Vibrations in CuCl

C. Carabatos,* B. Hennion, K. Kunc,† F. Moussa, and C. Schwab*

Centre d'Etudes Nucléaires de Saclay, Saclay, France

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The frequency-wave-vector dispersion relation $\nu(\vec{q})$ for the normal vibrations of a CuCl single crystal at room temperature has been measured for the [100]-, [110]-, and [111]-symmetric directions using inelastic neutron scattering.

In view of the interest in studying the lattice dynamics of crystals with zinc-blende structure, we present in this paper the results of coherent inelastic neutron scattering on cuprous chloride (CuCl). Our particular attention was drawn by this material because of its peculiar behavior relative to other crystals with the same symmetry, as pointed out by Martin.¹

The present experiments were performed by means of the triple-axis crystal spectrometer at

the EL3 reactor, Saclay. A collimated beam of monochromatic neutrons, produced by Bragg reflection from a germanium single crystal, was incident upon the CuCl specimen. The energies of the scattered neutrons were determined by Bragg reflection from a second germanium single crystal. The experiments were carried out by using either constant- Q or constant- ν techniques, for waves propagating along the high-symmetry directions [100], [110], and [111].

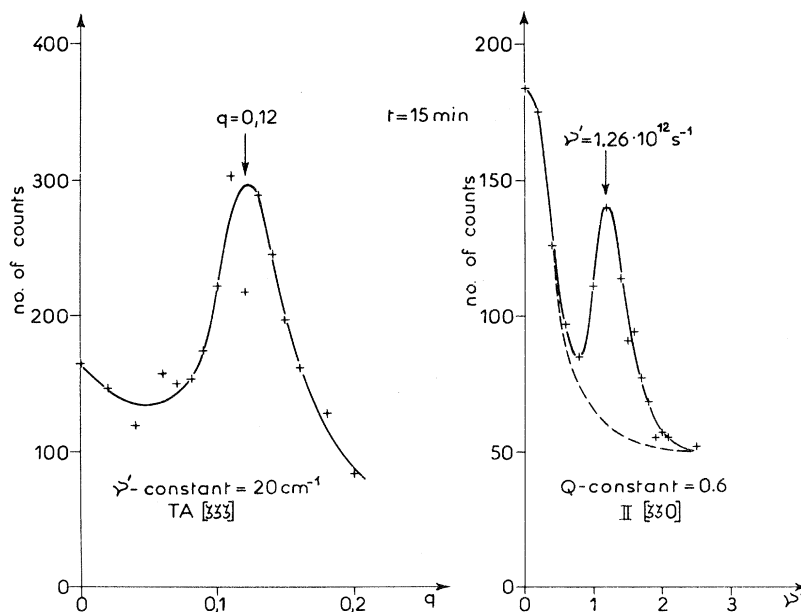


FIG. 1. Typical neutron groups obtained on a CuCl single crystal.

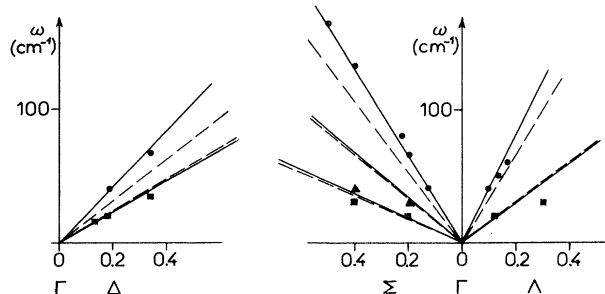


FIG. 2. Long-wave acoustic phonons and calculated sound velocities from the elastic constants of Hallberg (Ref. 2), solid line, and of Inogouchi (Ref. 3), broken line.

The specimen of CuCl used for most measurements was a single crystal in the form of half a cylinder 1.6 cm in diameter and 2.8 cm long, prepared by one of us (C.S.). The cylinder axis was approximately parallel to a [110] crystallographic axis. The crystal purity was determined by a spectrochemical analysis with the following results: Ca + Mg < 3 × 10⁻⁵, Sn < 10⁻⁵, Zn < 2 × 10⁻⁵, Si < 10⁻⁵ by weight; its mosaicity was estimated to be less than 0.2 deg.

All the determinations were made at room temperature, most of them with the (110) planes horizontal and parallel to the momentum of the neutrons; some were made with the (100) planes, but with a second smaller sample, for the purely transverse branches in the [110] direction.

Two typical neutron groups corresponding to the experimental methods are shown in Fig. 1. The main difficulties arose from the high neutron-absorption cross section of chlorine; we verified that the larger specimen absorbed between 50 and 70% of the incident-neutron flux, explaining the low counting rates.

The first measurements in the vicinity of Γ al-

lowed removal of the ambiguity in the recent determination of the elastic constants,^{2,3} namely, in favor of those of Hallberg (see Fig. 2). The optical frequencies at the point Γ, found previously by infrared absorption and reflectivity measurements,⁴ agree with our neutron results to within 5%. The LA and TA phonons observed by Hadni *et al.*⁵ were confirmed to correspond to the point X in the reciprocal space.

Our experimental results are plotted in Fig. 3 together with preliminary model adjustments. A rigid-ion model with five valence force parameters⁶ matches the observed data only very roughly. Merely accounting for only electronic polarizabilities substantially improved the agreement of the calculated curves. However, fitting both the complete deformable-bond model^{7,8} and the shell model revealed some difficulties due to the extreme flatness of the TA branches in the three directions of the reciprocal space. At present we cannot decide if the apparent discrepancies in the Λ and Σ directions result from an imperfect parameter fit, from the lack of flexibility of the models used, or from the presence of the 3d electrons of copper; we continue the attempts to fit the models.

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*Permanent address: Laboratoire de Spectroscopie, Institut de Physique, Strasbourg, France.

†Permanent address: Laboratoire de Physique des Solides, Faculté des Sciences, Paris, France.

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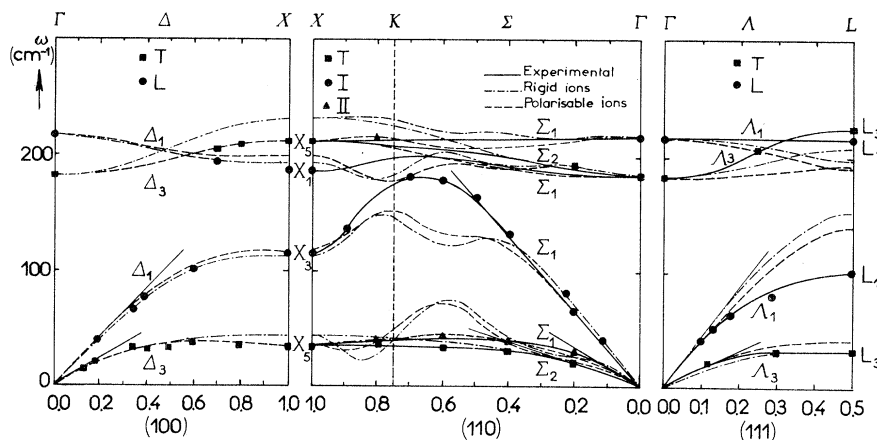


FIG. 3. Experimental and theoretical dispersion relations of CuCl.

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Temperature Dependence of the Charge Oscillation Around Nearly Magnetic Impurities

G. Grüner and C. Hargitai

Central Research Institute for Physics, Budapest, Hungary

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In the NMR measurements reported here, it is found that the amplitude of the electron-density oscillation, α , around manganese and chromium impurities in aluminum is temperature dependent. Between 180 and 400°K the temperature dependence can be represented by $\alpha(T) = \alpha(0)[1 - (T/\Theta)^2]$, with $\Theta \sim 740^\circ\text{K}$ for manganese and $\Theta \sim 960^\circ\text{K}$ for chromium impurities. We suggest that this temperature dependence is brought about by the localized spin fluctuations at the impurity sites.

In dilute alloys the impurities are surrounded by an oscillating charge perturbation which can be given, far enough from the impurity, as¹⁻³

$$\delta\rho(r) = (\alpha/r^3) \cos(2k_F r + \varphi). \quad (1)$$

In simple theories like the Hartree-Fock approximation of the Anderson model,⁴ the amplitude of this oscillation is thought to be independent of temperature whenever there are no magnetic moments on the impurities.⁵ In this case the dependence of α on the atomic number Z of impurities can be expressed using the scattering phase shifts of the impurities that are, in turn, simply related to Z through the Friedel sum rule. It is generally accepted that in aluminum the $3d$ transition-metal impurities carry no magnetic moments. One would expect, therefore, that the amplitude of the charge-density oscillation as a function of the atomic number should have a maximum between chromium and manganese. In a recent experiment,⁶ however, it was revealed that at room temperature the first-order quadrupole wipeout numbers, which are roughly proportional to α , for the dilute alloys Al:Cr, Al:Mn, and Al:Fe are 1600, 1400, and 1600, respectively. This fact clearly contradicts the Hartree-Fock theory of the Anderson model. Moreover, if the wipeout numbers are supposed to be temperature independent, these room-temperature data contradict even the Friedel sum rule. But, as was shown by Langreth,⁷ at $T=0$ the Friedel sum rule is valid in the Anderson model whenever the perturbation expansion in terms of intra-

atomic Coulomb interaction, U , can be applied. So the temperature independence of wipeout numbers would invalidate experimentally any perturbation-theoretical approach in the Anderson model even in the nearly magnetic limit. Our purpose was, therefore, to see whether the wipeout numbers for Al:Cr, Al:Mn, and Al:Fe are temperature dependent or not and, if they are, where this temperature dependence comes from.

The redistribution of the electronic charge around impurities yields a field gradient³

$$g(\vec{r}) = (8\pi/3)\mu \delta\rho(\vec{r}), \quad (2)$$

where μ is the enhancement factor (for aluminum $\mu \sim 23$). The distribution of the field gradient gives rise to a reduction of the host NMR signal intensity D , defined as the peak-to-peak amplitude of the derivative signal. At impurity concentration c ,

$$D/D_0 = (1-c)^n, \quad (3)$$

where n is the signal intensity of the pure host. In aluminum alloys of low impurity concentrations the first-order quadrupole effect dominates, so Eq. (3) refers to the satellite transitions only, and the change of the central component can be neglected. It has been shown⁸ that the phase φ in (1) is not essential in the analysis, and the first-order wipeout number n defined in (3) is proportional to the oscillation amplitude α . Therefore, by measuring the signal amplitude of the host nuclei as a function of the impurity concentration, the amplitude of the charge oscillation can be de-