Investigation of critically coupled spin-phonon modes in chromium-doped MgO

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(Received 10 May 1978)

The first direct observation by inelastic neutron scattering of spin-phonon coupling for a dilute paramagnetic system Cr^{2+} in MgO, is reported. The enhancement of phonon linewidths and the absence of significant dispersion near the resonant frequency is shown to be evidence for "critically coupled" modes.

The interaction of phonons with impurity ions in crystals has been extensively studied both experimentally and theoretically. For impurities with internal degrees of freedom, the resonant hybridization of the phonon modes with the impurity-states[1] is described by a coupled-mode spectrum, similar to the magnon-phonon modes in ordered magnetic materials. Evidence of coupled spin-phonon modes in a paramagnet has recently been obtained by neutron scattering from the concentrated salt $TmVO_4$ above the Jahn-Teller ordering temperature.[2] Here[3] we present the first study of the coupled-mode spectrum for a dilute paramagnetic system $MgO:Cr^{2+}$.

In MgO the ground state of the d^4- ion Cr^{2+} is an orbital doublet ^5E. Owing to a strong orbit-lattice interaction, local lattice distortions occur and the theory of this dynamic Jahn-Teller effect has been worked out in some detail.[4] The positions of the resulting vibronic levels are determined by the tunneling frequency δ between equivalent lattice distortions, and by the spin-orbit coupling parameter D. A thermal-conductivity investigation of the resonant scattering of phonons by the vibronic levels was made by Challis *et al.*[5] Their work indicates that there are two transitions of frequencies ~0.15 and 0.8 THz from the ground state A_1 to two excited levels E^1 and E^2. In the present work we have studied the effect of the higher-frequency resonance on the dispersion and linewidth of slow transverse phonons propagating along the [1$\bar{1}$0] direction.

The sample consisted of two aligned crystals of total volume 0.3 cm^3, containing 6700 at. ppm of Cr and also 3250 at. ppm of Fe, added to the melt to increase the Cr^{2+} concentration. This was estimated to be 1100 at. ppm from measurements of the low-temperature thermal conductivity. Constant Q scans were carried out on the IN8 triple-axis spectrometer at the Institut Laue Langevin[6] [monochromator Cu(111), analyzer pyrolytic graphite (004), collimators 50′-20′-20′-80′, λ_F = 2.351 Å; a graphite filter was used to suppress harmonics]. The momentum transfers $\vec{Q}$ were close to the [220] reciprocal-lattice vector so $\vec{Q} = \vec{\tau}_{220} + \vec{q}$, with the phonon wave vector $\vec{q} \,||\, [1\bar{1}0]$. Measurements were made at 1.65 K, with the ions largely in the ground state, and also at 300 K as a control. The mean frequencies ν_m and linewidths $\Delta\nu$ of the phonon groups were determined by drawing smooth curves through the experimental points.

Figures 1(a) and 1(b) show the frequencies ν_m and widths $\Delta\nu$ plotted against the reduced wave vector q/τ_{110}. Figure 1(a) also shows the extent of the half intensity contour of the instrument resolution function, and Fig. 1(b) shows the linewidth this leads to for a nondispersive phonon spectrum. At 300 K the sound velocity deduced from the neutron

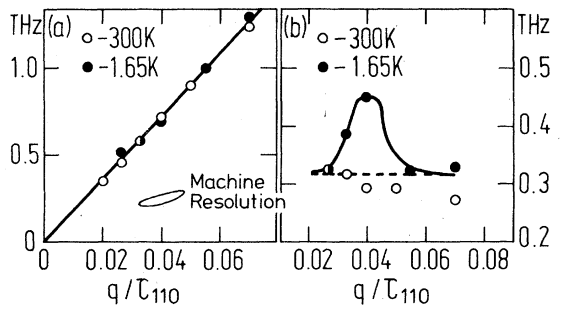

FIG. 1. (a) ν_m vs q/τ_{110}; (b) $\Delta\nu$ vs q/τ_{110}. The dashed and solid lines are computed linewidths at 300 and 1.65 K using parameters given in the text.

data is in good agreement with the ultrasonic value,[7] and the phonon linewidths are consistent with instrumental broadening. However, at 1.65 K, although there is no significant evidence for dispersion, the phonon widths are larger than the 300-K values and reach a maximum at $q/\tau_{110}=0.04$. This increase in width at 1.65 K is clearly seen in the phonon groups shown in Fig. 2. Measurements made on a less-concentrated sample (100-at. ppm Cr^{2+}) gave no difference between the linewidths at 300 and 1.65 K over the investigated range. Thus we may attribute the observed results to a coupling of the phonons to a transition of the Cr^{2+} ion.[8]

Furthermore, the apparent absence of dispersion may be qualitatively explained by an inhomogeneous strain broadening of the vibronic levels. As shown in Fig. 3(a), the dispersion curve for the coupled spin-phonon modes is only well defined in the vicinity of the anticrossing if the width of the excitations is less than the gap Δ. A broadening Γ of the vibronic transition tends to smooth out the dispersive features as indicated in Fig. 3 (b).

To analyze the experimental results in more detail, we use the simple two-level model first introduced by Jacobsen and Stevens.[9] In the pseudospin representation the Hamiltonian is given by

$$H=\sum_q \hbar\omega_q a_q^\dagger a_q+\sum_n \hbar\omega_{0n}S_{zn}$$
$$+N^{-1/2}\sum_{q\,n}\hbar B_q e^{i\vec{q}\cdot\vec{R}n}(a_q+a_{-q}^\dagger)\,(S_{+n}+S_{-n}),$$

where ω_q is the phonon frequency, ω_{0n} the resonance frequency of the $\vec{S}_n$ at the site $\vec{R}_n$ and B_q is the spin-phonon coupling matrix element.

The neutron scattering cross section may be obtained from the phonon Green's function if the coupling of the neutrons to the impurity levels is neglected. However, the Green's function must first be ensemble averaged over the random spatial distribution of spins over the N sites and over the distribution $f(\omega_0)$ of resonance frequencies. Using the diagramatic method of Toombs and Sheard[10] we can show that

$$[D_q(\omega)]^{-1}=[D_q^0(\omega)]^{-1}-P_q(\omega),$$

where $D_q^0=2\omega_q/(\omega^2-\omega_q^2)$ is the unperturbed Green's function and the phonon self-energy is given by

$$P_q(\omega)=c\int_0^\infty |B_q|^2\tanh\tfrac{1}{2}\beta\omega_0\frac{\omega_0}{(\omega+i\Gamma_s)^2-\omega_0^2}$$
$$\times f(\omega_0)\,d\omega_0,$$

to lowest order in the spin-phonon coupling. Here Γ_s describes the homogeneous lifetime broadening of the spin levels and c is the fractional concentration. To describe the strain broadening of the levels we take a Lorentzian distribution $f(\omega_0)$ of frequencies ω_0 with mean frequency $\bar{\omega}_0$ and width Γ_{st}. We neglect possible variations in B_q from site to site, and approximate $\omega_0=\bar{\omega}_0$ in the population factor $\tanh\frac{1}{2}\beta\omega_0$ (where $\beta=\hbar/kT$), which is ~1 at low temperatures. Extending the lower limit of the integral to $-\infty$ by assuming $\Gamma_{st}\ll\omega_0$ gives

$$P_q(\omega)=\tfrac{1}{2}c\epsilon^2\bar{\omega}_0\omega_q\tanh\tfrac{1}{2}\beta\bar{\omega}_0\frac{\bar{\omega}_0}{(\omega+i\Gamma)^2-\bar{\omega}_0^2},$$

where $\Gamma=\Gamma_s+\Gamma_{st}$ and ϵ is a dimensionless coupling parameter[10] defined by $B_q=\frac{1}{2}\epsilon(\bar{\omega}_0\omega_q)^{1/2}$.

From this we derive an expression for the one-phonon coherent neutron scattering cross section $S(q,\omega)$ which is proportional to the imaginary part of the Green's function[11]

$$S(q,\omega)\propto\frac{4\omega_q^3\Delta^2\omega\Gamma}{[(\omega^2-\omega_q^2)(\omega^2-\omega_r^2)-\omega_q^2\Delta^2]^2+(\omega^2-\omega_q^2)^2(2\omega\Gamma)^2},$$

where $\omega_r^2=\bar{\omega}_0^2+\Gamma^2$. For $\Gamma\to 0$ this reduces to two δ-function spikes at frequencies given by the coupled-mode dispersion relation

$$(\omega^2-\omega_q^2)(\omega^2-\omega_r^2)-\omega_q^2\Delta^2=0$$

shown in Fig. 3(a), where $\Delta=(c\epsilon^2\bar{\omega}_0^2\tanh\frac{1}{2}\beta\omega_0)^{1/2}$ is the gap at the crossover at $\omega_q=\omega_r$ or $q=q_0$. The form of the neutron line shape for a scan with

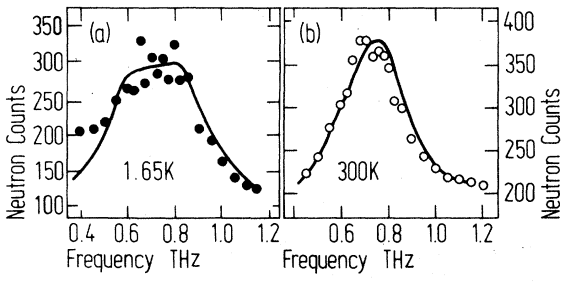

FIG. 2. Phonon groups at (a) 1.65 K and (b) 300 K for $q/\tau_{110}=0.04$. The solid lines are computer-generated line shapes as described in the text.

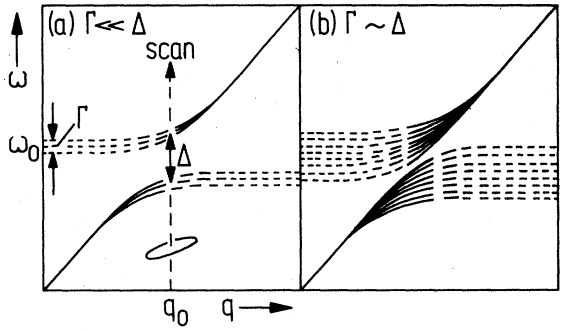

FIG. 3. Coupled-mode dispersion curves showing the effect of inhomogeneous broadening.

$q = q_0$ is then qualitatively as follows. For weak damping $\Gamma \ll \Delta$ [Fig. 3(a)] the spikes are broadened, each having a width $\sim\frac{1}{2}\Gamma$. With increasing Γ the two peaks broaden and shift and, for the critical case $\Gamma = \Delta/\sqrt{2}$, merge into a single peak [Fig. 3(b)]. For large damping $\Gamma \gg \Delta$, the single peak narrows and becomes approximately Lorentzian with width $\Delta^2/2\Gamma$.

The observed linewidths are substantially influenced by the finite machine resolution. We have therefore computed line shapes by numerical convolution of the machine resolution function with the theoretical expression for the scattering probability, taking $\omega_r/2\pi = 0.7$ THz. The program computed the resolution function from parameters adjusted until the computed function agreed with measurements taken by scanning the spectrometer through the 220 Bragg point. The resolution function used in the convolution integral was truncated at an intensity of e^{-9} of the peak level; it was shown analytically[6] that variations in Δ and in the phonon slope away from the $[1\bar{1}0]$ could reasonably be neglected in the convolution integral. So the form of the scattering function $S(q, \omega)$ was taken to be isotropic in q space. For $q/\tau_{110} = 0.04$ the calculations show that the observed width is consistent with a range of values of Γ and Δ. But calculations of widths for other values of q enable the coupled-mode parameters to be quite closely defined, and give $\Gamma/2\pi = 0.2 \pm 0.05$ THz, $\Delta/2\pi = 0.2 \pm 0.05$ THz, and $\bar{\omega}_0/2\pi = 0.67 \pm 0.1$ THz. Phonon groups calculated with these parameters are shown in Fig. 2 (for the 300-K group we take $\Delta \to 0$). Complete agreement between theoretical and experimental line shapes cannot be expected, since the actual distribution of ω_0 values is not known. The theoretical q-variation of linewidth is compared with experimental data in Fig. 1(b). The value of $\bar{\omega}_0/2\pi$ agrees reasonably well with previous data—0.8 THz (Ref. 5), 0.7 THz (Ref. 12), and 1.1 THz (Ref. 13).

The above value for the splitting Δ gives the spin-phonon coupling parameter $\epsilon = 15 \pm 4$.[14] This is consistent with the value of $\epsilon \simeq 16$ deduced from the relaxation time for elastic phonon scattering observed in thermal conduction,[5,13] though the close agreement is perhaps fortuitous. The lifetime broadening of the ionic levels due to spin-lattice relaxation is thus quite small:

$$\Gamma_s/2\pi = (3\epsilon^2\bar{\omega}_0^4/8\omega_D^3)\coth(\tfrac{1}{2}\beta\bar{\omega}_0) = 0.04 \text{ THz}$$

(ω_D is the Debye frequency). Regarding Γ as being due entirely to strain broadening, the random microstrains are then $\sim 3 \times 10^{-4}$, which is broadly consistent with acoustic-paramagnetic-resonance studies.[6]

Thus by means of neutron scattering we have obtained a direct measurement of the A_1-E^2 transition frequency, and a computer analysis of the linewidths has yielded both the spin-phonon coupling and the magnitude of internal strains. In contrast with the case of KCl:CN^-, where the dispersive coupled-mode structure was resolved by neutron scattering,[15] our system MgO:Cr^{2+} corresponds to the critical case $\Gamma \sim \Delta$, where the dispersion is very weak but coupled-mode effects are nevertheless contained in the phonon linewidths. This case may also apply to interstitials in irradiated copper, but the experimental results[16] for this system were inconclusive.

ACKNOWLEDGMENTS

We are very grateful to B. Dorner, C. Escribe, and K. Ziebeck of the Institut Laue Langevin, and to J. Milne of the Atomic Energy Research Establishment, Harwell, for their help with the neutron experiments, and to J. Lange, Hong Kim, and M. Locatelli for help and advice.

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