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A BRILLOUIN SCATTERING INVESTIGATION OF NiO

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ABSTRACT

Brillouin scattering from single crystals of NiO show that, apart from the expected phonon peaks, there is a broad central peak. The phonon peaks have Fano-like line-shapes indicating a strong coupling between them and the broad feature, and lead to elastic constants that differ considerably from ultrasonic values. The broad feature is probably 'magnetic' in origin since it disappears at the Néel temperature. We speculate that it may be the lower of the two AFMR modes predicted for easy-plane antiferromagnets but which has previously been observed only in EuTe and MnO. The interaction between the phonons and the 'magnetic' excitation provides a phenomenological explanation for the differences in the elastic constants determined by different techniques.

INTRODUCTION

Nickel oxide with its simple NaCl structure is considered to be one of the classical antiferromagnets. More specifically, together with MnO, it is one of the classical 'easy plane' cubic antiferromagnets contrasting with materials like MnF₂, FeF₂, CoF₂ and NiF₂ which have 'easy axes'. In spite of being a 'classic' there are a number of properties, both magnetic and elastic, which are still not fully understood. From a magnetic standpoint its easy plane anisotropy demands that the acoustic branch of the magnon dispersion curve be non-degenerate and should give rise to two AFMR frequencies. The higher of these two modes (at $\sim 36\text{cm}^{-1}$) has been detected using IR techniques,¹⁻³ but only very recently using Raman scattering.⁴ The lower AFMR mode has remained elusive; inelastic neutron scattering results⁵ show evidence of a mode at $\sim 8\text{cm}^{-1}$, while IR experiments³ claim that it must lie below 2cm^{-1} . Another puzzle are the elastic properties of this material; there are two reports which show very pronounced changes around the Neél temperature,^{6,7} but which disagree on the magnitude of the changes.

Here we report a Brillouin scattering study of NiO. In the spectra, apart from the usual peaks expected for phonons, we observe a broad feature centered at the laser line and extending out beyond the phonon peaks. We argue that this could be the as yet unobserved lower of the two AFMR modes. The elastic constants obtained from Brillouin scattering are very different from existing literature values measured by ultrasonic techniques. However the strong interaction between the phonons and the lower AFMR mode exhibited in the Brillouin spectra, offer an explanation for the disagreement as well as some insight into the anomalous elastic properties previously reported for NiO.⁶⁻⁹

EXPERIMENT

The samples were prepared using a chemical vapor deposition technique¹⁰⁻¹² involving the thermal decomposition of NiBr₂ in the presence of water vapor and were deposited on (100) faces of MgO crystals. The substrates were later removed by dissolving them in dilute sulfuric acid. The resulting 25 μm thick unsupported NiO samples were used for the Brillouin and Raman

experiments. They were characterized with x-rays which showed that the in- and out-of plane lattice constants were the same and were in good agreement with published values.

Brillouin scattering, for which many excellent reviews can be found in the literature,^{13,14} is the inelastic scattering of light by low frequency excitations (usually acoustic phonons). It probes excitations with wavevector q , whose magnitude and direction are determined by the directions of the incident and scattered light relative to the crystallographic axes of the sample. Figure 1 shows three Brillouin spectra recorded in the scattering geometries described in the figure caption. The central peak (i.e. the two almost vertical lines in the center of the spectra) is due to the unshifted laser radiation scattered by surfaces, impurities, microcracks etc. Because this peak is so intense it must be attenuated by a filter to avoid overloading the detector. The two sharp rises on either side of the central peak are an experimental artifact caused by the insertion and removal of the attenuating filter: the physically significant features in the spectra in Fig 1 are on the outside of these sharp rises. Each spectrum in Fig. 1 shows the presence of 'sharp' peaks (labeled T and L for longitudinal and transverse) which are expected and can be assigned to phonons propagating along the specified q direction. The spectra also contain a broad feature which extends from the central peak to beyond the longitudinal phonon peak, and whose origin is unknown.

(i) Magnons

An indication of the broad peak's origin can be inferred from the spectrum in Fig. 2 which was recorded at 300°C and in which the broad peak has essentially disappeared. Experimentally we find that it vanishes quite abruptly over a range of ~50°C around T_N (250°C); sample heating by the laser beam precludes a more accurate determination. Based on the preceding argument it is reasonable to assume that the broad feature observed in Brillouin spectra from NiO is magnetic in origin and is possibly due to the lower of the two expected AFMR modes. Our attempts to obtain more information about the behaviour of this feature have been unsuccessful: up to the highest magnetic fields which we can apply (~7 KG) there is no appreciable change in the shape of the broad peak. Cooling the sample to liquid nitrogen temperatures does not noticeably change the spectrum either.

Although a combination of Brillouin scattering and microwave excitation has been used quite extensively to study canted-antiferromagnets,¹⁵ we are aware of only one antiferromagnetic material which has been studied using this technique: EuTe.¹⁶⁻²⁰ In EuTe (at 2K) both branches are observed as sharp features in the Brillouin spectra; in NiO the upper band at 36 cm^{-1} lies outside of the range of the Fabry-Perot interferometer. The reason for the lower mode in NiO appearing as a broad central peak rather than a sharp resonance is not at present clear; it could be an indication of the complex angular dependence of the frequency of this mode,^{16,20} or it could be due to some form of damping. The strong interaction of the phonons with this 'magnetic' peak (which will be discussed in the next section) is an indication that this second alternative is probably important. In light of neutron scattering²¹⁻²³ experiments on NiO which were unable to unambiguously determine the axis of in-plane alignment and from which it may be concluded that the in-plane anisotropy is small, since the lower AFMR mode depends on this in-plane anisotropy, it is not surprising that in NiO it is found at a very low frequency. This would also be consistent with investigations of MnO by conventional resonance techniques^{24,25} in which a mode is observed at high fields ($>10\text{ kG}$) which extrapolates roughly to zero frequency at zero field.

Although the AFMR resonance has been detected in many easy axis antiferromagnets (FeF_2 ,^{26,27} CoF_2 ,²⁸ and MnF_2 ²⁹) using Raman spectroscopy, and second order Raman magnon scattering has been observed in NiO,³⁰ only very recently has a Raman observation of the AFMR mode in NiO⁴ been reported. Our results essentially confirm these recent findings: Raman spectra from our sample are shown in Fig. 3; the lower portion at room temperature the upper at liquid nitrogen temperature. Because of the large optical absorption at certain wavelengths in the visible spectrum, the portion of the sample which is probed by the laser beam in a Raman experiment can be considerably heated. Figure 4 shows the position of the 'room temperature' magnon line for different laser powers at two different excitation lines. We interpret the shift as a function of laser power as due to an increase in the local temperature, the shift being larger for the blue light for which the absorption is greater. The position, extrapolated to zero power, is 33.5 cm^{-1} in excellent agreement with 34.0 cm^{-1} found in Ref. 1 and 33.8 cm^{-1} in Ref. 4. Note

however that the position measured with 200 mW of blue light ($\sim 27 \text{ cm}^{-1}$) corresponds to a temperature of $\sim 150^\circ\text{C}$. Since the effect of laser heating was not reported in Ref 4 we assume that they used a cylindrical lens to focus the laser beam. Our results also show that the frequency of the mode increases as the temperature is lowered which is also in agreement with previous results.^{1,4} A feature which was puzzling to us, viz. the splitting of the magnon line observed as the sample is cooled and as can be seen in Fig. 3, has been explained as a surface magnon in Ref 4. However since our sample was not opaque and our experiments were performed with the laser beam entering from the back of the sample, further experiments may be required to confirm this assignment.

(ii) Phonons

Brillouin scattering is now a well established technique for determining elastic properties. Although it does not normally achieve the accuracy of ultrasonic experiments, it can be used on small samples and on samples at high temperatures and pressures where ultrasonic experiments are difficult. To date however we are not aware of a single bona fide example in which Brillouin and ultrasonic data are not in agreement. It is interesting to note that agreement between Brillouin and ultrasonics has been obtained in a very wide variety of situations: e.g. a cubic material measured to high accuracy,³¹ a trigonal crystal measured up to 1800 K,³² ferroelectric materials,³³ etc. NiO appears to be the first exception to the rule; not only do the elastic constants obtained from Brillouin scattering differ dramatically from those obtained by ultrasonics, but the results obtained in different scattering geometries are not selfconsistent. Although we will argue in our concluding section that this peculiar behaviour may be due to an interaction of the phonons with the spin system, our results will be presented in detail so that the reader will be aware of all the steps which are made, and thereby allow a better evaluation of our conclusions and speculations.

First we recall that our sample was characterized with x-rays to verify that it grows with the [100] axis normal to the film and that the in- and out-of-plane lattice spacings are equal. The material has cubic symmetry and its elastic properties should therefore be described by three independent elastic constants C_{11} , C_{12} and C_{44} .

The scattering geometries which can be applied to our thin film sample are backscattering and platelet. (see Fig 1 of Ref. 32). In backscattering the magnitude of the wavevector (q) of the phonons probed is $2nk$ where n is the refractive index and k is the wavevector of the incident light, the direction of q is confined to a small cone around the $[100]$ film normal and hence yields information on C_{11} and C_{44} . In the platelet geometry the magnitude of q is $\sqrt{2}k$ and its direction can lie anywhere in the (100) plane. The frequency of the phonons are taken directly from the peak positions in spectra like those in Figs 1 and 2. We note here that this may be partly responsible for the inconsistencies to be described later since some of the Brillouin phonon lines, notably the shear mode in Fig. 1b, show a line shape reminiscent of a Fano-like^{34,35} interaction. The characteristic feature of such an effect, the dip which appears just before or after the peak, is caused by the phase coherent interaction of a discrete mode with a 'continuum' background. The quality of the present data does not allow us to use any type of line fitting with any reliability. With the above caveat, the sound velocities (v) are obtained from the measured frequency shift divided by q . The elastic constants are then equal to ρv^2 where ρ is the density (6.67 g/cm^3).

Figure 5 shows the longitudinal and transverse elastic constants (ρv^2) measured in the platelet geometry in the plane of the NiO film. The full lines are obtained by fitting C_{11} , C_{12} and C_{44} . At $\theta = 0^\circ$ the expected values of (ρv^2) are C_{11} and C_{44} while at 45° they are $(C_{11} + C_{12} + 2C_{44})/2$ and $(C_{11} - C_{12})/2$. The values of C_{11} , C_{12} and C_{44} obtained from the fit are: 358, 134 and 93 GPa respectively. They are clearly in disagreement with literature values^{6,8} which lie in the ranges 225-270, 95-125 and 105-110 respectively. Not only do the values of the C_{ij} differ, but the sign of the elastic anisotropy is also reversed: in our results the longitudinal (transverse) velocity decreases (increases) away from the $[100]$ direction, the literature values require the opposite behaviour. Our experiments performed in the backscattering geometry confirm the sign of the elastic anisotropy measured in the platelet geometry and thereby eliminate any possible error due to misorientation in the plane. The values obtained for C_{11} and C_{44} in the backscattering geometry are not consistent with those in Fig 5. Since the evaluation of velocities from backscattering data requires the refractive index, and since literature values³⁶ can range from 2 to 2.7 and are also

wavelength dependent, we determined n at 514 nm from reflectance measurements; we obtain $n = 2.31 \pm .02$. With this value we obtain $C_{11} = 426$ GPa and $C_{44} = 88$ GPa; although C_{44} could be reconciled with the platelet result 93 GPa, C_{11} lies well outside the error bars. It should also be noted that an error in n which would yield agreement for C_{11} would produce a discrepancy in C_{44} . We shall return to a discussion of this point later.

Figure 6 shows the values of ρv^2 as a function of temperature, full symbols are from backscattering open symbols are platelet measurements. The squares correspond to C_{44} the circles are for C_{11} and the triangles for $(C_{11}-C_{12})/2$. When the sample was in the furnace we were unable to observe the weak peaks corresponding to the combination $(C_{11} + C_{12} + 2C_{44})/2$. Our results are again very different from those in Ref 6 which show a strong temperature dependence of C_{11} and $(C_{11}-C_{12})/2$. An interesting point however is that above the Néel temperature the elastic anisotropy determined by ultrasonics has changed sign and now agrees with our determination, and also the discrepancy between the ultrasonic and Brillouin results is much smaller. These facts are strongly suggestive that the origin of the differences is related to the magnetic ordering.

DISCUSSION

To summarize our results: (i) there is a broad feature in the Brillouin spectra whose origin is unknown but which disappears above the Néel temperature. (ii) The phonon peaks riding on the background of the broad feature sometimes show a Fano-like line-shape indicative of coupling between a discrete peak and a continuum. (iii) The elastic constants obtained from Brillouin scattering are very different from those measured by ultrasonics. (iv) The Brillouin scattering results from different scattering geometries are not selfconsistent. (v) The discrepancies above the Néel temperature are smaller but they do not disappear.

The preceding facts can be understood at least phenomenologically if we assume, guided by the Fano line-shape of the phonons, that the interaction of the phonons with some other excitation in the crystal makes the elastic constants frequency dependent. This assumption would explain: (i) the difference in the magnitude of the temperature changes measured in Refs 6 and 7 since in the

latter, being a resonance technique, the frequency is probably quite small. (ii) In Ref 6 the frequency of the measurements is not given but they make the following statement "Slightly different values are obtained when various quartz transducers are used...". (iii) Since the Brillouin experiments are in the 10-70 GHz range it explains the lack of agreement with ultrasonics and also the inconsistency of our backscattering results (~ 70 GHz) with the platelet results (~ 20 GHz).

If we speculate that the excitation with which the phonons interact is the lower AFMR mode, all discrepancies between techniques might be expected to vanish above T_N clearly contradicting experimental results. However it may be that the phonons interact with the spin system as a whole and not with one specific mode in the magnon spectrum. Since magnetic susceptibility studies⁶ show that at T_N the cusp is less than 0.5% of the total susceptibility, and that the susceptibility remains large at temperatures well above T_N , this explanation is plausible but raises the question as to why this phenomenon has not been observed before in other materials.

In order to understand the present results on NiO more work is clearly needed. Ultrasonic or Brillouin experiments on single domain crystals may prove valuable as well as a detailed ultrasonic study of the frequency dependence of the sound velocities. A combination of Brillouin scattering and microwave excitation may also provide interesting information. On the other hand, a material in which a possible magnon-phonon interaction leads to such strange behaviour, might also exhibit properties of considerable technological interest and therefore deserve greater attention.

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FIGURE CAPTIONS

- Fig. 1. Room temperature Brillouin spectra of NiO. The central (off scale) peaks and the dips on either side are of instrumental origin. Longitudinal and transverse phonons are labeled L and T respectively. (a) was recorded in the backscattering geometry with q along $[100]$. (b) and (c) were taken in the platelet geometry with q along $[100]$ and $[110]$ respectively
- Fig. 2. Same as Fig. 1a but at 300°C .
- Fig. 3. Raman spectra recorded using 100 mW of 476 nm radiation from a Kr laser. The upper and lower spectra correspond to nominal temperatures of 80 and 300 K respectively.
- Fig. 4. Frequency shift of the magnon line as a function of laser power for 528 nm (circles) and 476 nm (triangles).
- Fig. 5. Angular dependence of elastic constants in the (100) plane of NiO. The symbols are experimental points, the full line is a fit to the data.
- Fig. 6. Temperature dependence of elastic constants of NiO. Full and open symbols are from backscattering and platelet experiments respectively. Circles, squares and triangles are for C_{11} , C_{44} and $(C_{11}-C_{12})/2$

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