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Pressure dependence of two-magnon Raman scattering in NiO

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We report on the pressure dependence of Raman scattering by magnon pairs in NiO for the range 0–30 GPa. The data are in excellent agreement with Bloch's empirical law describing the dependence of superexchange on volume. Using Anderson's theory, we find that the pressure dependence of the antiferromagnetic exchange constant is mainly determined by the hopping parameter of a Hubbard model involving Ni(e_g)-O($2p$) hybridization. The implications of these results to high-temperature superconductors and early Raman data are discussed.

With the discovery of high-temperature superconductivity in certain oxide compounds,[1] it is natural to scrutinize the established understanding in kindred archetype materials. There is widespread agreement that the central issue in these compounds is the interplay of charge and spin fluctuations. The paradigm theory for this interplay is that of the Anderson superexchange in a magnetic insulator[2] and the archetype material is the fcc type-II antiferromagnet NiO with spin $S=1$. For NiO, the next-nearest-neighbor (180°) antiferromagnetic exchange J is much larger than the nearest-neighbor (90°) ferromagnetic coupling so that the latter can be ignored.[3] In Anderson's theory, $J=b^2/U_{\rm eff}$ where $U_{\rm eff}$ and b are, respectively, the Coulomb interaction and the e_g hopping parameter of a Hubbard model for the Ni $3d$ electrons.[2] The underlying origin of b is Ni-O hybridization and in a model treating hybridization explicitly one finds[4] $U_{\rm eff}^{-1}=(U^{-1}+\Delta^{-1})$, where Δ is the energy to transfer an electron from the $2p$ to the e_g orbital and U is the bare d-d Coulomb interaction. Anderson[2] pointed out that if the σ-bonding contribution to the crystal-field parameter $10Dq$ is dominant, then b can be related to $10Dq$ because both involve basically the same charge fluctuation t^2/Δ; t is the matrix element for hybridization between atomic Ni (e_g) and oxygen ($2p$) orbitals. For NiO, Anderson obtained $b=10Dq/3$ and therefore[2]

$$J=(10Dq/3)^2/U_{\rm eff}\ . \tag{1}$$

In this Rapid Communication, we present measurements of two-magnon Raman scattering in NiO as a function of pressure P providing a test of Eq. (1). To the best of our knowledge, this is the first report of light scattering by magnetic excitations at high pressures.[5] The Raman data allows one to determine the dependence of J on P. This and the comparison with the known[6] pressure dependence of $10Dq$ indicate that the behavior of J reflects primarily that of b. As recently pointed out,[7] this information is directly relevant to the P dependence of T_c and to the possible occurrence of an isotope effect for superconductivity arising from an electronic mechanism associated with b. Our work also bears on Bloch's $\frac{10}{3}$ empirical law applying to the volume dependence of superexchange.[8] We find that NiO obeys this law. Finally, our results call for a reinterpretation of early data on the temperature and alloying dependence of magnetic scattering for various systems by including the strong dependence of magnon energies on lattice parameters.

The experiments were performed on single crystals of stoichiometric NiO in the range 0–30 GPa at $T=297$ K (as discussed later, we estimate the temperature in the scattering volume to be ~ 50 K higher due to laser heating). Samples of dimensions $100\times100\times20$ μm^3 were loaded into a Mao-Bell diamond anvil cell[9] along with the pressure medium consisting of a methanol-ethanol (4:1) solution. For pressure calibration, we used the standard ruby fluorescence method[10] giving an accuracy of $\Delta P=\pm0.1$ GPa at low pressures. The alcohol mixture solidifies at $P\approx10.4$ GPa ($T\approx300$ K).[10] Above the critical pressure, the widths of the ruby R lines were found to increase at the rate of ≈0.4 meV/GPa. This translates into a non-hydrostatic $\Delta P\approx1$ GPa at $P=30$ GPa. Raman spectra were obtained using 100 mW of an Ar^+ laser (focused to a spot of radius ~20 μm) at 5145 Å. This line was chosen because it falls in the vicinity of a prominent minimum in the optical absorption spectrum of NiO.[11] The spectra were not systematically investigated in regard to their symmetry properties. The polarizations of the incident and scattered photons varied throughout the experiments and, in addition, symmetry determination at high pressures was prevented by pressure-gradient-induced birefringency of the diamonds. While the latter effect generally needs to be addressed given that two-magnon line shapes usually show a strong dependence on the scattering geometry,[12] diamond birefringency did not create a problem for our data analysis. The reason is that, although the point group of NiO allows two different symmetries (Γ_1^+ and Γ_3^+) for two-magnon scattering, the intensity in the Γ_1^+ configuration is vanishingly small compared to that of the Γ_3^+ geometry.[13]

Figure 1 shows Raman data of NiO at ambient pressure, measured outside the cell, and at $P=16.5$ GPa. In the spectra, Ω denotes the Γ_3^+ scattering by pairs of magnons and 2LO (L) labels the two-phonon overtone band associated with the longitudinal-optical (LO) branch; its maximum is at approximately twice the energy of the phonon at the L point of the Brillouin zone.[13] The other features at ~125, 190 meV (dashed lines) and at ~165 meV are due to the pressure medium and the diamonds, respectively. As expected, the Raman lines are blue shifted at higher pressures. More important, the relative shifts

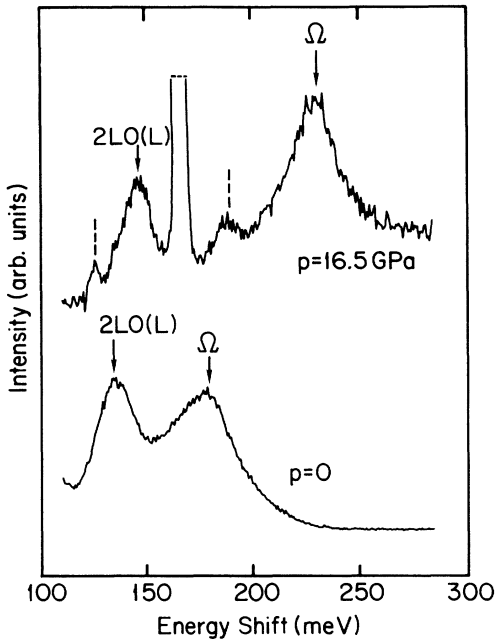

FIG. 1. Raman spectra of NiO at ambient pressure (bottom trace) and at $P=16.5$ GPa (top trace). The temperature in the scattering volume is $T\approx 350$ K. Bands labeled Ω and 2LO (L) are due, respectively, to two-magnon and two-phonon scattering. The latter involves predominantly pairs of LO modes at the L point of the Brillouin zone. Dashed lines denote features associated with the pressure transmitting medium (methanol-ethanol). The truncated peak at -170 meV is the optical phonon of diamond. The resolution is -0.5 meV.

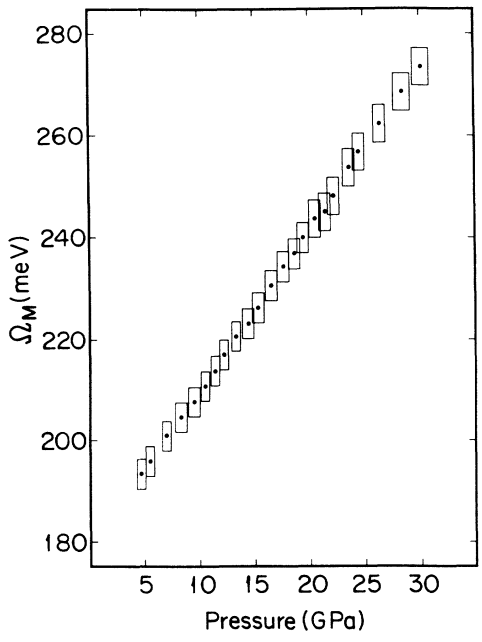

FIG. 2. Pressure dependence of the maximum of the two-magnon band (Ω_M) at $T\approx 350$ K. Boxes represent experimental uncertainty.

are significantly larger for the magnetic scattering. In addition, the intensity of the two-magnon band (compared to that of the phonons) increases and its width decreases with increasing P. The smaller width reflects most likely the pressure-induced enhancement of the Néel temperature leading to a reduction in the ratio T/T_N. At, e.g., $P\sim 15$ GPa, the width is $\sim 10\%$ of the band energy which compares well with values at ambient pressure and $T\ll T_N$.[13] At still higher pressures, and like the ruby R lines, Ω exhibits an apparent broadening resulting from pressure inhomogeneities in the scattering volume following the solidification of the pressure-transmitting medium. The position of the maximum of the two-magnon band Ω_M as a function of pressure is shown in Fig. 2. Within experimental error, the data are well accounted for by a linear relationship. Our results together with x-ray measurements[14] of the P dependence of the lattice parameter a (fitted to Murnaghan's equation of state)[15] give the two-magnon Grüneisen constant $\gamma=-\partial\ln\Omega_M/\partial\ln V=3.5\pm 0.1$; V is the volume. The corresponding value for the 2LO (L) feature is a factor of ≈ 3.0 smaller. Because the magnetic scattering nearly overlaps with the phonon from diamond and a feature due to the alcohol mixture at ambient pressure, Ω's position could not be determined below $P\sim 5$ GPa. However, linear extrapolation of the data gives $\Omega_M=(179\pm 2)$ meV at $P=0$. The latter value, slightly lower than that reported in the literature,[13] allows us to determine the temperature increase in the scattering volume due to laser heating. From the Ω_M-T data of Ref. 12, we find $T=(350\pm 10)$ K at the sample. Laser heating effects are also apparent in the ambient-pressure spectrum of Fig. 1 obtained with the sample in contact with air. Here, the laser power was adjusted until the position of the two-magnon peak matched the value extrapolated from the pressure measurements.

In general, there is not a simple relationship between Ω_M and the magnetic exchange constants. The theory describing Raman scattering by pairs of magnons in antiferromagnets is well established.[12] For $T\ll T_N$, the spectra are expected to reflect a two-particle density of states at $\mathbf{K}=\mathbf{K}_1+\mathbf{K}_2=0$ ($\mathbf{K}_1$ and $\mathbf{K}_2$ are the wave vectors of the magnons) modified by wave-vector-dependent weighting factors (different factors for the different irreducible components of the Raman tensor) and magnon-magnon interactions.[12] The relative importance of the latter anharmonic terms distinguishes two magnon from conventional two-phonon scattering. In the magnon case, the particles created in the scattering process are necessarily close in real space and, therefore, effects due to anharmonicity significantly alter the spectral line shapes, even at $T=0$.[12] Thus, information on exchange constants—contained in the density of states giving magnon frequencies at critical points of the Brillouin zone—can only be gained after a comparison with calculations dealing with magnon-magnon coupling.[16] Moreover, finite-temperature corrections are still more difficult to implement.[12] In the case of NiO, however, the situation simplifies considerably because the structure is cubic and magnetic interactions are dominated by the antiferromagnetic exchange.[3] If one neglects the other exchange and anisotropy parameters (which are at least 1 order of magnitude smaller),[3] scaling indicates that the maximum of the two-magnon band at *zero* temperature Ω_M^0, as well as the Néel temperature T_N, are simply proportional to J. In addition, corrections

for $T \neq 0$ can be accounted for by the scaled expression

$$\Omega_M(T,P) = \Omega_M^0(P) F[T/T_N(P)] , \quad (2)$$

applying at arbitrary temperatures and pressures. Experimentally, this is sufficient to determine J from the value of Ω_M at $T = 350$ K. In detail, we used data on the T dependence of Ω_M at ambient pressure[13] (giving F) and solved Eq. (2) graphically for $\Omega_M^0 = 10.2J$ and $T_N = 2.37J$.[17] The results are shown in Fig. 3. The log-log plot as a function of lattice parameter includes the value of J at ambient pressure obtained from inelastic neutron scattering experiments.[3] Assuming $J \propto a^{-\epsilon}$, we find $\epsilon = 9.9 \pm 0.5$. We notice that an $\sim 10\%$ larger value would have been obtained by ignoring the difference between the measured Ω_M and Ω_M^0.

The comparison between our data and results[6] on the P dependence of $10Dq$ indicate that J is approximately proportional to $(10Dq)^2$. This and Eq. (1) suggest that U_{eff} (≈ 7.5 eV) has a much weaker dependence on pressure or, alternatively, that hybridization effects (contained in the parameter b) determine the behavior of J. These considerations can be put in a much broader context. The above value of ϵ in NiO agrees extremely well with the empirical prediction $J \propto V^{-10/3}$ derived by Bloch[8] on the basis of data on FeO, CoO, and several garnets and ferrites (Bloch assumed that all exchange parameters vary similarly with volume). In addition, the $\approx a^{-5}$ dependence of $10Dq$ shown by Ni^{2+} in NiO is also followed by other $3d$ ions octahedrally coordinated with F^{1-}, Cl^{1-}, or O^{2-} in a series of hosts.[6] Hence, the available data suggest that $10Dq \propto J^{1/2} \propto a^{-5}$ may generally apply to $3d$ magnetic insulators. As far as we know, the reason why this relationship works has not been definitively settled. The ubiquitous a^{-5} behavior is found in, e.g., theoretical predictions[18] for the width of the d band of transition metals (without hybridization) and as the leading term in the electrostatic model of crystal-field splittings.[19] However, these manifestations cannot possibly account for the behavior of superexchange given that the insulators are strongly covalent and that d-d overlaps are irrelevant for their magnetism. We should further note that molecular-orbital calculations[20] predict $10Dq \propto a^{-\gamma}$ with γ ranging from 3.7 to 5.5 for different $3d$ ions. Although this agrees roughly with the experiments giving $\gamma \approx 5$, it is apparent that there is much room for improvement. Moreover, such calculations are not necessarily the proper road to identify the origin of the a^{-5} dependence.

Because NiO shares many of its physical properties with the parent insulating compounds of high-T_c superconductors,[1] our results are pertinent to the understanding of these materials. This refers, in particular, to attempts of correlating the behavior of the exchange interaction with the isotope effect[7] and the pressure dependence of T_c.[7,21] Our measurements are consistent with the estimate for $\partial \ln J/\partial P$ in La_2CuO_4 given by Fisher *et al.*[7] and, as indicated earlier, with Bloch's $\frac{10}{3}$ law which is the main assumption in the work of Kaneko *et al.*[21] However, given the incomplete identification of the mechanism underlying the empirical findings, it is not at all obvious why the highly anisotropic and $S = \frac{1}{2}$ copper oxides

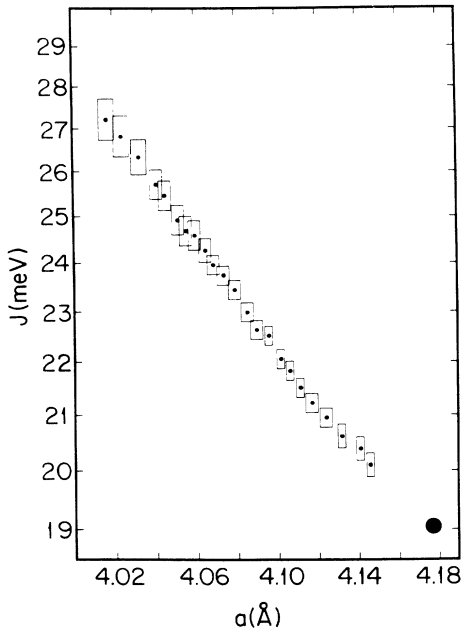

FIG. 3. The antiferromagnetic next-nearest-neighbor exchange constant (J) as a function of lattice parameter a. Values of J were derived from measurements of Ω_M using Eq. (2). Lattice parameters were obtained from a-P data reported in Ref. 14. The ambient-pressure value of J (●) is from a fit to inelastic neutron scattering measurements of the magnon dispersion (Ref. 3).

should follow the same trend shown by NiO. Raman scattering measurements under pressure in the cuprates can certainly clarify this issue. In this regard, we notice that the information that can be gained from Raman scattering relates directly to the behavior of the in-plane exchange constant which is the one that presumably matters for superconductivity.[22] This is unlike measurements of T_N depending strongly on the coupling in the third direction.

We conclude with a brief discussion of the implications of our work for early Raman results. Here, we wish to emphasize the importance of considering the dependence of exchange constants on volume in the interpretation of data. For instance, NiO exhibits an $\approx 0.3\%$ increase in a from $T \approx 0$ K to $T_N/2$.[23] According to $J \propto a^{-10}$, this amounts to an $\approx 3\%$ drop in Ω_M which accounts for roughly half the actual drop.[13] However, this effect has not been considered in the comparison with theoretical calculations for NiO or other materials. This also applies to work on solid solutions. In, e.g., $Ni_{1-x}Ca_xO$ the measured shifts of the two-magnon peak with Ca concentration[24] are considerably smaller than what one could expect from the increase in the lattice parameter.

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[17]The proportionality constants were obtained from experimental data. Specifically, the values are $\Omega_M^0 = 194.5$ meV (Ref. 13), $J = 19.0$ meV (ambient pressure, Ref. 3), and $T_N = 45.1$ meV [M. Foex, Compt. Rend. **227**, 183 (1948)].

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