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[10]Specific-heat data are available only for one of the three alloys, viz. Ti-58% V [cf. C. H. Cheng et al., Phys. Rev. 126, 2030 (1962)]. Using these data, Eqs. (4) and (5), and the uncertainties in our determination of ρ_n and T_c, one obtains $H_{c2}^*(0) = 161 \pm 5$ kG and $\alpha = 1.66 \pm 0.05$. The quoted uncertainties do not include possible errors arising from the determination of γ and from the slight dependence of γ on the annealing procedure. We regard the values of $H_{c2}^*(0)$ and α listed in Table I as more reliable.

[11]This choice is somewhat arbitrary inasmuch as the resistive transition has a finite width. However, because the resistive transition is rather narrow and because the width of the transition does not depend strongly on temperature, any other reasonable choice of H_{c2} (say, the onset of resistivity) would not change the main features and conclusions of the present work.

[12]The parameter λ_{so} can be determined most accurately when α is large and λ_{so} is small, as is the case for Ti-58% V. For Ti-44% Nb the data indicate that $\lambda_{so} > 2$, with a best value of $\lambda_{so} \approx 4.5$. This result differs from the value $\lambda_{so} = 1.5$ obtained by WHH,[2] who have fitted our data to their theory. This apparent discrepancy arose because in converting the measured H_{c2} to h, WHH used a value for H_0 which is higher than the average one. In addition, these authors calculated α from Eq. (5) using an estimated value for γ. The conclusion that λ_{so} for Ti-44% Nb is significantly larger than for Ti-58% V is valid, however, in any case.

[13]There are several possible reasons for this discrepancy: (a) Effects of finite mean free path tend to increase h; (b) strong coupling effects tend to increase h; (c) if one identifies H_{c2} with the field at which the onset of resistance (at low current densities) takes place, rather than with $H_r(0)$, one obtains slightly lower values of h.

LIGHT SCATTERING BY SPIN WAVES IN FeF_2

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The optical properties of spin waves (magnons) in the transition metal fluorides have recently received considerable attention. Most recently the direct absorption of infrared radiation by two magnons,[1,2] as well as magnon sidebands of optical absorptions, have been observed.[3-6] In addition it has been proposed that magnons might exhibit a Raman effect.[7,8] We report here the first observation of light scattering by magnons in both first and second order. We identify the first-order, or one-magnon, scattering by the magnitude and temperature dependence of the frequency shift of the scattered light, by the polarization selection rules observed to govern the scattering, and most strikingly, by the disappearance of the scattered light when the sample temperature is raised above the Néel temperature. The identification of the second-order, or two-magnon, scattering is similar, though not quite so definite, because of possible interactions with low-frequency optical phonons. We shall discuss the two scattering processes in turn.

In these experiments the sample, a $5 \times 5 \times 7$ mm^3 oriented single crystal of FeF_2,[9] is illuminated with ~50 mW of linearly polarized, 4880-Å light from an argon ion laser. Cooling is achieved by flowing He gas over the sample at a rate determined by a feedback system containing the carbon resistor which monitors the sample temperature. In this way the sample temperature is maintained to within 0.5°K of a desired value above 10°K. Light scattered through 90° is passed through a Czerny-Turner double monochromator onto a cooled S-11 photomultiplier. The photomultiplier output is then amplified and displayed on a chart recorder [10]

FeF_2 has the rutile structure[11] (D_{4h}) and becomes antiferromagnetic for $T < T_N = 78.5$°K. Although the magnon dispersion curve has not been measured, it is known from antiferromagnetic resonance (AFMR) experiments[12] that the frequency of a zone-center ($k = 0$) magnon at $T = 0$ is 52.7 cm^{-1}. One may then estimate[1] the zone-edge magnon frequency to be ~77 cm^{-1}.

In Fig. 1 are shown recorder traces of the scattered light obtained at various temperatures in the experimental geometry which we designate as (zy). The left and right letters inside the parentheses give the polarizations for the incident and scattered photons, respectively, thus indicating which element of the scattering tensor (in this case α_{zy}) is being examined in the experiment. The coordinate system is that of the crystal with z along the c axis. The most striking feature of Fig. 1 is the emergence of two peaks in the scattered light with frequency shifts of ~52 and ~154 cm^{-1} as the sample temperature is lowered from the Néel point. The magnitudes of these shifts already provide strong evidence that the smaller one is due to scattering from the single zone-center magnon observed in AFMR,[12] and that the larger one is a combination scattering from a pair of zone-edge magnons. It has the same frequency as the line which Halley and Silvera[1] have identified as two-magnon absorption in FeF_2.

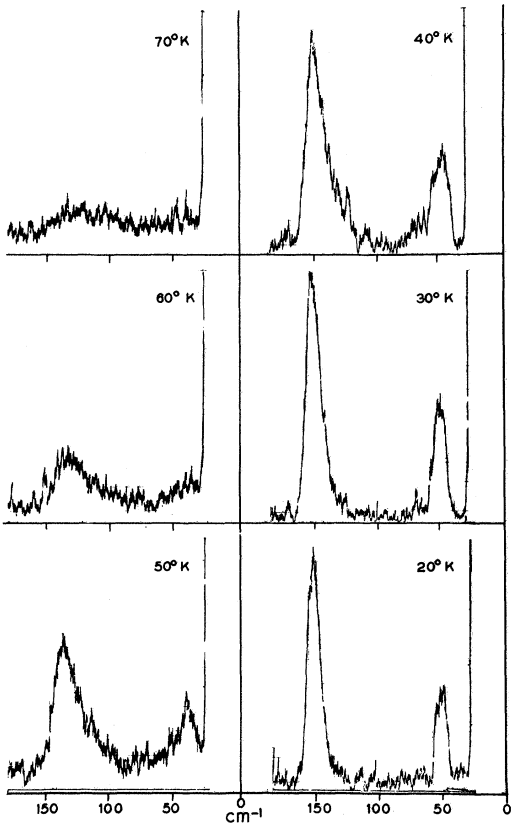

FIG. 1. Recorder traces showing frequency shifts of Stokes scattered light in the (zy) experimental geometry for various temperatures in FeF_2. The lines at ~52 and ~154 cm^{-1} are due to photons scattered by one and two magnons, respectively.

More detailed evidence for the identification of the one-magnon process is given by the temperature dependence and symmetry properties of the scattered light. In Fig. 2, the position of the ~52 cm^{-1} line is plotted versus temperature and compared with the AFMR results of Ohlmann and Tinkham.[12] Both the magnitude and temperature dependence of the shift indicate that the scattering is due to a single zone-center magnon. As for the symmetry of the scattering tensor, we observe experimentally that for the ~52-cm^{-1} line, the only nonzero elements are α_{xz}, α_{zx}, α_{yz}, and α_{zy}. This observation agrees with the selection rules obtained in Ref. 8. There it is assumed that the photons interact with the magnons indirectly through a spin-orbit coupling, as originally proposed by Elliott and Loudon.[7] Another mechanism, which couples the magnon directly to the magnetic field of the photon, has been proposed.[13] However, this gives a smaller scattering cross section than, and different selection rules from, the spin-orbit mechanism. Finally, that the observed process is indeed a scattering rather than a fluorescence was confirmed by observing the anti-Stokes line at 40°K, where $\hbar\omega/kT \simeq 2$.

All of the above points agree well with theoretical predictions. However, with regard to the predicted intensity of the scattered light, large discrepancies arise. The calculation in Ref. 8 indicates that spin-wave scattering should be 10 to 100 times weaker than Raman scattering in liquids. We observe the one-magnon line in FeF_2 to be $<10^{-4}$ the strength of

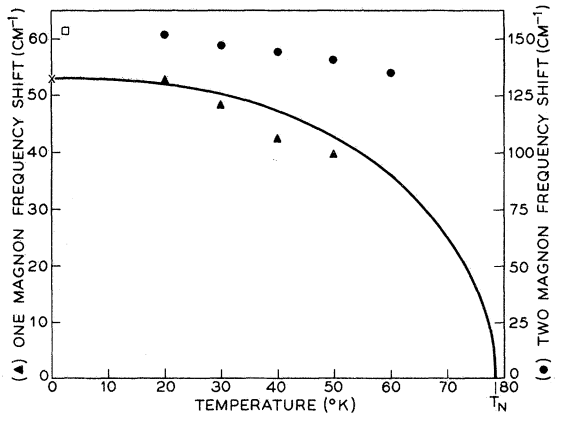

FIG. 2. Temperature dependence of Stokes frequency shifts in FeF_2. The solid line is the usual modified Brillouin function, B_2, and is taken from Fig. 5 of Ref. 12. The point × is taken from AFMR, Ref. 12. The point □ is from the two-magnon absorption reported in Ref. 1.

the 992-cm^{-1} Raman line in liquid C_6H_6. Further, the observed increase in scattering intensity with decreasing temperature is not predicted by Shen and Bloembergen,[8] although it is reminiscent of the behavior for the magnetic form factor in neutron scattering.[14]

Also, from Fig. 1 it is seen that the two-magnon line is stronger than the one-magnon line. This behavior is puzzling, if one assumes that the second-order process involves the spin-orbit coupling to the next higher order than the one-magnon process. However, if, for the two-magnon process, one invokes instead an excited-state exchange interaction in the manner of Tanabe, Moriya, and Sugano,[15] it is possible to argue that the one- and two-magnon scattering processes should be comparable in strength.[16] It also seems likely that such a mechanism would account for the symmetry we have observed for the two-magnon scattering tensor. We find that α_{xx} and α_{yy} are relatively the strongest; α_{yz}, α_{zy}, α_{xz}, and α_{zx} are strong; α_{zz} is weak; and α_{xy} and α_{yx} are vanishingly small.

Our interpretation of the ~154-cm^{-1} line in FeF_2 as due to two magnons is based quantitatively upon the frequency of the line and qualitatively upon its temperature dependence. In Fig. 2, the frequency of the line for various temperatures is compared with that reported for two-magnon absorption[1] at 5°K. The agreement is very good. Further, the temperature variation we measure is in accord with Halley and Silvera's observation that the two-magnon frequency falls off with increasing temperature more slowly than does the one-magnon (AFMR) frequency.[1] In the ordinary Raman effect, we have observed[17] an optical phonon (B_{1g}) at ~75 cm^{-1} in FeF_2 which could conceivably modify the above discussion of the 154-cm^{-1} line. Indeed there exists the remote possibility that the line is caused by a combination of one magnon with one phonon. Additional experiments are in progress to investigate this possibility.

We have also observed a second-order scattering in MnF_2 ($T_N = 67.7$°K). The frequency shifts of 101 and 112 cm^{-1} which we measure in different experimental geometries are in excellent agreement with the reported two-magnon absorption frequencies in MnF_2.[2] The symmetry of the scattering tensor is the same as that of the ~154-cm^{-1} line in FeF_2. Again, however, there is a low-frequency optical phonon[16] (B_{1g}, at ~63 cm^{-1}), which may be involved. Our failure to observe the one-magnon scattering in MnF_2 is quite likely a result of the extremely low frequency (8.5 cm^{-1}) of the zone-center magnon in this material.[18]

The experiments reported here demonstrate that light scattering can be a valuable tool in the study of magnetic materials. The information regarding the frequency shift and its temperature dependence obtained from the one-magnon scattering is the same as that in AFMR experiments. Two-magnon scattering gives information on the weighted magnon density of states and should allow, for example, determination of the second- and third-neighbor exchange parameters, J_2 and J_3, in materials like FeF_2 and MnF_2. Detailed studies of the linewidths, line shapes, and magnetic-field effects are in progress for both these materials.

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SUPERHEATING AND SUPERCOOLING IN THE SUPERCONDUCTING TRANSITION OF SMALL INDIUM SPHERES

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Supercooling in the normal-to-superconducting phase transition has been observed experimentally,[1,2] and also has been discussed theoretically[3-6] for type-I superconductors. For a bulk sample the supercooling field is

$$H_{sc} = 1.69 H_{c2} = 1.69\sqrt{2}\,\kappa H_c, \qquad (1)$$

where κ is the Ginzburg-Landau parameter, $\kappa = \lambda/\xi$, and H_c is the thermodynamical critical field for the bulk superconductor. The supercooling characteristic of a number of metals has been observed by Faber,[1] but only near the critical temperature T_c. These results have been used[5] to give reliable values of κ near T_c.

Superheating in the superconducting-to-normal transition has been predicted theoretically.[3,4,7] The superheating field for a sphere with radius $r \gg \lambda$, where λ is the London penetration depth, is[7]

$$H_{sh} = \tfrac{2}{3} 2^{-1/4} \kappa^{-1/2} H_c. \qquad (2)$$

The factor $\frac{2}{3}$ accounts for the demagnetizing field of the sphere, and the rest of the expression is the result valid for a semi-infinite sample in parallel field, with $\kappa \ll 1$.

The large superheating predicted by (2) has been difficult to observe in the sample geometries used in previous experiments. Garfunkel and Serin[2] found $H_{sh} = 1.17 H_c$ in tin, and Burger and Valette[8] found $H_{sh} = 1.65 H_c$, also in tin. The superheating field predicted by (2) is $H_{sh} = 2.7 H_c$, using $\kappa = 0.1$ for tin[5] and omitting the factor $\frac{2}{3}$ in order to get the result for their geometry. The difficulty in obtaining superheating is in general attributed to flaws in the surface and end effects. Once the transition to the normal state has started at a "weak" point, the new phase propagates over the entire specimen and only the superheating typical for the defect is observed.

The idea of the present experiment is to observe the transition of a sample containing many small spheres. A new phase cannot propagate in such a sample, so that a nucleation process is necessary in each sphere. The minimum supercooling field and the maximum superheating field[9] measured are then characteristic of the material and not of the defects.

The sample[10] used consisted of two-thirds volume of dry indium spheres mixed with one-third volume of quartz powder. The spheres were made by sonoration of 99.999% pure indium in an organic liquid. They have diameters ranging from about 1 to 5 μ. We find a critical temperature $T_c = 3.396 \pm 0.002$°K, which is close to the values listed by Roberts.[11] The pure nuclear quadrupole resonance is observable in this sample at 4.2°K, indicating that strains and surface effects are not important enough to wipe out the resonance.

The sample was placed in the rf coil of the tank circuit of a marginal oscillator of the Pound, Knight, and Watkins[12] type, and the oscillator frequency as function of applied field was measured at various temperatures. The external magnetic field was produced by a superconducting solenoid, calibrated with a proton resonance. The axis of the solenoid was parallel to the axis of the rf coil. We obtained the curves of frequency versus field directly on an X-Y recorder by feeding the X axis with a voltage proportional to the magnet current, while the oscillator frequency was fed to a digital-to-analog converter and then to the Y axis of the recorder.

A typical hysteresis loop is given in Fig. 1. The decrease in oscillator frequency is proportional to the fraction of the sample that has