Temperature dependence of the spin-density asymmetry in Ni

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Polarized neutron diffraction has been used to determine the temperature dependence of the asymmetry of the unpaired spin density in Ni. We find that 19% of the spin density has e_g symmetry at 4.2 K; this increases continuously with increasing temperature and reaches about 26% e_g at 634 K. Thus, the e_g component of the ferromagnetic moment decreases less rapidly with increasing temperature than the t_{2g} component. This suggests different temperature dependences for the spin splitting of the t_{2g} and e_g subbands.

Magnetic form-factor measurements[1] on ferromagnetic Ni show an unpaired spin density that is highly asymmetrical and which arises mostly from unpaired d electrons with t_{2g} symmetry (81% t_{2g} at 295 K). This symmetry character depends quite strongly on the details of the electronic band structure and thus provides an important check on the validity of such calculations. Alternatively, the observed symmetry may be used as input data for adjusting the interaction matrix elements in these calculations. This latter approach is used, for example, by Cooke and coworkers[2–4] in their highly successful calculations of the dynamical susceptibilities of Fe and Ni. Clearly, this symmetry character and its dependence on temperature is important to an understanding of the spin dynamics of these materials at elevated temperatures. Previous measurements showed no temperature dependence of the symmetry properties for Fe,[5] Co,[6] and a series of Co-Fe and Co-Ni alloys.[7] In this paper, we report the first observation of a thermal effect on this symmetry character for a transition metal.

The magnetic form factor of Ni can be written as[1]

$$f(K)=\frac{2}{g}(1+\alpha)f_{3d}(K) - \frac{2}{g}\alpha f_{\mathrm{NL}}(K)+\frac{g-2}{g}f_{\mathrm{orb}}(K) \ , \qquad (1)$$

where $2/g$ is the fractional spin moment, α is the fraction of the spin moment with nonlocal character, and f_{3d}, f_{NL}, and f_{orb} are appropriate form factors for the local spin, nonlocal spin, and orbital components of the moment. The form factor for d electrons in a cubic field is given by[8]

$$f_{3d}(K)=\langle j_0\rangle+(\tfrac{5}{2}\gamma-1)A_{hkl}\langle j_4\rangle \qquad (2)$$

where $\langle j_0\rangle$ and $\langle j_4\rangle$ describe the spherical and aspherical parts of the spin density, A_{hkl} depends on direction in the crystal, and γ is the fraction of the spin density with e_g symmetry. Mook[1] found that this form factor reproduces his room-temperature Ni data with $g=2.20$ taken from magnetomechanical data and with $f_{\mathrm{NL}}(K)$ contributing only at $K=0$. The best fit was obtained with Hartree-Fock Ni^{2+} functions for $\langle j_0\rangle$, $\langle j_4\rangle$, and $f_{\mathrm{orb}}(K)$ and with $\alpha=\gamma=0.19$.

We assume this formalism to determine the temperature dependence of the asymmetry parameter γ. In so doing, we use the (333)(511) pair of reflections which occur at the same scattering angle and which therefore have the same $\langle j_0\rangle$, $\langle j_4\rangle$, $f_{\mathrm{NL}}(K)$, and $f_{\mathrm{orb}}(K)$. The difference between the form factors for these reflections thus contains only an aspherical term,

$$\Delta f \equiv f_{333}-f_{511} = \frac{2}{g}(1+\alpha)(\tfrac{5}{2}\gamma-1)\langle j_4\rangle(A_{333}-A_{511}) \ , \qquad (3)$$

from which γ can be determined if α and $\langle j_4\rangle$ are known. The simplest approach is to assume the same α and $\langle j_4\rangle$ values used by Mook for his room-temperature data. Since form-factor measurements for a variety of ferromagnetic alloys show that the nonlocal moment is proportional to the average moment,[9] it is reasonable to assume that α is indeed a constant and independent of temperature. We must, however, recognize the possibility that $\langle j_4\rangle$ is temperature dependent. The wave functions, and therefore the form factors, are expected to be slightly different for spin-up and spin-down electrons.[10] As a result, the spin density contains a contribution from the paired electrons in addition to the usual unpaired-electron term. In an itinerant system, where the number of unpaired electrons may vary with temperature, this could result in temperature-dependent $\langle j_0\rangle$ and $\langle j_4\rangle$ functions. However, the magnitude to be expected for such an effect is not known. Fortunately, there is an experimental cross check on the constancy of these parameters. Since the A_{hkl} for this pair of reflections are nearly equal in magnitude and opposite in sign ($A_{333}=-0.667$, $A_{511}=0.650$), the aspherical term contributes less than 1% to the sum of their form factors and can be neglected. We can

then define an average form factor at this K which is given by

$$\langle f\rangle \equiv \tfrac{1}{2}(f_{333}+f_{511}) = \frac{2}{g}(1+\alpha)\langle j_0\rangle + \frac{g-2}{g}f_{\mathrm{orb}}(K) \ , \qquad (4)$$

where $f_{\mathrm{NL}}(K)$ has been dropped because it contributes only at small K. We note that the $\langle j_0\rangle$ term is the major part of $\langle f\rangle$, so that any temperature dependence in either α or $\langle j_0\rangle$ should be observed in $\langle f\rangle$. In fact, we find that $\langle f\rangle$ is constant, within 5% limits, and conclude that α and $\langle j_0\rangle$ are temperature independent. In that case $\langle j_4\rangle$ should also be temperature independent and Eq. (3) can be used to obtain $\gamma(T)$ from $\Delta f(T)$.

Polarized-neutron flipping-ratio measurements were made on an isotopic single crystal of ^{60}Ni in the temperature range from 4 to 634 K. For $T \leq 295$ K, the data were taken with the sample in a superconducting magnet in an applied field of 4.25 T and with neutron wavelengths of 0.875 and 1.045 Å. The elevated-temperature data were obtained in an iron-core magnet at 0.68 Å and with an applied field of 1.35 T. The observed flipping ratios were corrected for incomplete incident polarization, flipper efficiency, and secondary extinction with the extinction correction factor extracted from the wavelength dependence of the (111) flipping ratio. These are all small corrections which, in total, amounted to only a few percent under the worst experimental conditions. Room-temperature results for the first 10 Bragg reflections are compared with Mook's[1] data in Table I. Here, p/b is the magnetic-to-nuclear-amplitude ratio and the values tabulated are obtained directly from the corrected flipping-ratio data. Since $p = 0.27\mu f$, where μ is the magnetic moment per atom, both μ and b must be known to extract the form factors. The nuclear amplitude of our ^{60}Ni sample was determined to be 0.291×10^{-12} cm by comparison of these p/b values with those of Mook for natural Ni by assuming $b_{\mathrm{Ni}} = 1.03 \times 10^{-12}$ cm. Both sets of form-factor values were calculated using the presently accepted room-temperature magnetization of Ni as $0.579\mu_B$/atom.[11] The agreement is quite satisfactory.

TABLE I. Room-temperature form-factor data for ^{60}Ni.

hkl	$\sin\theta/\lambda$	p/b	f[a]	f_{Mook}[b]
111	0.246	0.4171	0.776	0.786
200	0.284	0.3690	0.687	0.697
220	0.402	0.2329	0.434	0.443
311	0.472	0.1708	0.318	0.318
222	0.493	0.1658	0.309	0.308
400	0.569	0.0842	0.157	0.155
331	0.620	0.0895	0.167	0.167
422	0.697	0.0573	0.107	0.107
333	0.739	0.0565	0.105	0.109
511	0.739	0.0210	0.039	0.036
		±0.0004	±0.001	±0.004

[a] $p = 0.27\mu f$, $\mu = 0.579\mu_B$/atom, $b = 0.291 \times 10^{-12}$ cm.
[b] $\mu = 0.579\mu_B$/atom, $b = 1.03 \times 10^{-12}$ cm.

The temperature dependence of p/b for the (333)(511) pair of reflections is given in Table II. Also shown are magnetization values taken from the compilation by Crangle and Goodman.[11] Here, spontaneous moments are used for $T < 600$ K while the magnetizations at 1.35 T are used for $T \geq 600$ K.

TABLE II. Temperature dependence of the e_g population for ^{60}Ni.

T (K)	$p/b(333)$	$p/b(511)$	μ (T)[a]	$\langle f\rangle$[b]	Δf[c]	γ[d]
4	0.0591	0.0203	0.616	0.0695	0.0679	0.190±0.002
200	0.0591	0.0193	0.601	0.0703	0.0714	0.179±0.002
295	0.0565	0.0210	0.579	0.0721	0.0661	0.195±0.003
390	0.0526	0.0197	0.546	0.0714	0.0649	0.199±0.003
440	0.0491	0.0191	0.521	0.0705	0.0621	0.208±0.004
484	0.0467	0.0184	0.483	0.0726	0.0631	0.204±0.007
527	0.0401	0.0162	0.432	0.0702	0.0596	0.215±0.004
556	0.0377	0.0157	0.392	0.0734	0.0605	0.213±0.006
600	0.0261	0.0117	0.305	0.0668	0.0509	0.242±0.006
619	0.0195	0.0084	0.226	0.0665	0.0529	0.236±0.004
634	0.0117	0.0062	0.137	0.0704	0.0433	0.266±0.008

[a] Magnetic moment in μ_B/atom from Ref. 11.
[b] $\langle f\rangle = \tfrac{1}{2}(f_{333}+f_{511})$.
[c] $\Delta f = f_{333} - f_{511}$
[d] From Eq. (3) with $g = 2.185$, $\alpha = 0.19$, $\langle j_4\rangle = 0.090$.

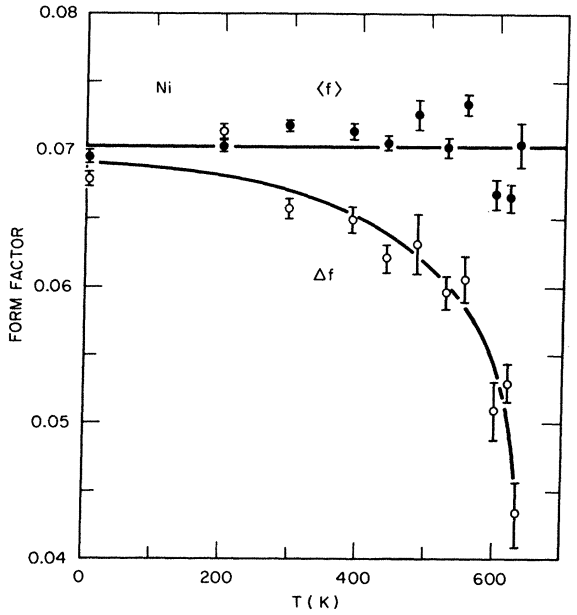

FIG. 1. Temperature dependence of the average $\langle f \rangle$ and the difference Δf form factors for the (333)(511) pair of Bragg reflections of Ni. Δf and $\langle f \rangle$ are defined by Eqs. (3) and (4), respectively. The solid curves serve only as a visual aid and have no theoretical significance.

The corresponding $\langle f \rangle$, Δf, and γ values are given in Table I and in Figs. 1 and 2. The average form factor remains essentially constant with a value of 0.070 to be compared with a calculated value of 0.068 for the Hartree-Fock Ni^{2+} ion. By contrast, the difference form factor decreases continuously with

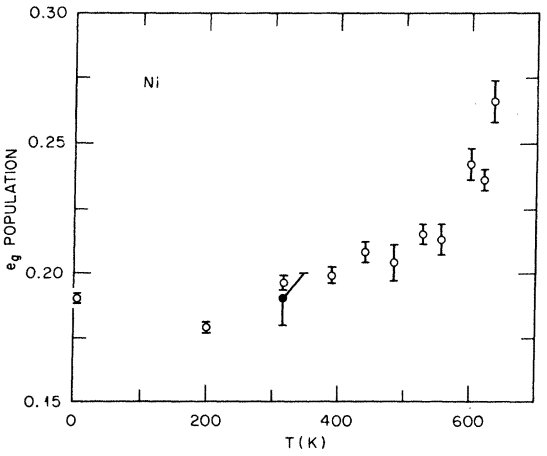

FIG. 2. Temperature dependence of γ, the e_g population, in Ni as determined from Eq. (3). The filled data point is from Mook (Ref. 1).

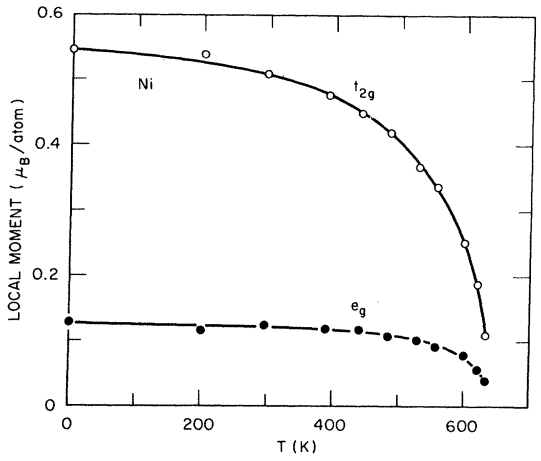

FIG. 3. Temperature dependence of the t_{2g} and e_g subband magnetizations in Ni.

increasing temperature. The corresponding e_g population shown in Fig. 2 increases from 19% at 4.2 K up to about 26% at 634 K.

The temperature dependence of γ is represented in a different way in Fig. 3 which shows the magnetization versus temperature for the t_{2g} and e_g subbands of Ni. Here, we assume that the symmetries are associated only with the local spin moment which has a magnitude of $(2/g)(1+\alpha)\mu$ or $0.671\mu_B$/atom at 4.2 K. Figure 3 shows clearly that the t_{2g} magnetization falls off more rapidly with temperature than the e_g magnetization. For example, at 600 K the e_g retains about $\frac{2}{3}$ of its saturation value while the t_{2g} has fallen below $\frac{1}{2}$ of saturation. The origin of this difference in thermal behavior for the two subbands is not presently understood. The only intrinsic temperature dependence in the electronic band structure is in the Fermi distribution function. However, calculations by Cooke[12] indicate that this thermal effect, although significant, is insufficient to account for the observations. We suggest that the increasing e_g population is caused by a different temperature dependence of the spin splitting for the two subbands. Specifically, we expect the t_{2g} splitting to decrease more rapidly with temperature than does the e_g. Recent angle-resolved photoemission results[13] for Ni give splittings of 0.3 eV for the t_{2g} band and 0.17 eV for the e_g band. It would be very interesting if such measurements could be extended to elevated temperatures.

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[1]H. A. Mook, Phys. Rev. 148, 495 (1966).
[2]J. F. Cooke and H. L. Davis, in *Magnetism and Magnetic Material-1972 (Denver),* edited by C. D. Graham and J. J. Rhyne, AIP Conf. Proc. No. 10 (AIP, New York, 1973), p. 1218.
[3]J. F. Cooke, J. Appl. Phys. 50, 7439 (1979).
[4]J. F. Cooke, J. W. Lynn, and H. L. Davis, Phys. Rev. B 21, 4118 (1980).
[5]R. C. Maglic, in *Magnetism and Magnetic Materials-1971 (Chicago),* edited by C. D. Graham and J. J. Rhyne, AIP Conf. Proc. No. 5 (AIP, New York, 1972), p. 1420.
[6]F. Menzinger and A. Paoletti, Nuovo Cimento 10B, 565 (1972).
[7]G. Kadar and F. Menzinger, Solid State Commun. 12, 909 (1973).
[8]R. J. Weiss and A. J. Freeman, J. Phys. Chem. Solids 10, 147 (1959).
[9]L. Dobrzynski, Int. J. Magn. 6, 291 (1974).
[10]R. E. Watson and A. J. Freeman, Phys. Rev. 120, 1125 (1960).
[11]J. Crangle and G. M. Goodman, Proc. R. Soc. London Sect. A 321, 477 (1971).
[12]J. F. Cooke (private communication).
[13]F. J. Himpsel, D. E. Eastman, P. Heimann, and J. A. Knapp, in Proceedings of the 26th Conference on Magnetism and Magnetic Materials [J. Appl. Phys. (in press)].