Magnetic Structure of $NaNiF_3$

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The structure of $NaNiF_3$ has orthorhombic symmetry ($Pbnm$-D_{2h}^{16}). It is found, using neutron diffraction, that it undergoes a magnetic transition at $T_n \simeq 149°K$ to an antiferromagnetic mode of the type G_x. This mode belongs to the magnetic space group $Pb'n'm$ which allows ferromagnetism in the z direction. Weak ferromagnetism in this direction was indeed found in previous experiments. This result is in contrast to a recent suggestion made by Judin and Sherman. It is nevertheless in accord with what one expects and finds in structures of this type (orthoferrities, for example). On the basis of the present data it is suggested that it is probably the antisymmetric exchange interaction which is responsible for the weak ferromagnetism in this compound.

I. INTRODUCTION

THE structure of the compound $NaNiF_3$ belongs to orthorhombic space group $Pbnm$ (D_{2h}^{16}). It was previously investigated in the temperature range 77–300°K by means of x rays,[1] polycrystalline magnetization,[1] and single-crystal magnetization.[2,3] It was reported[1–3] to be antiferromagnetic with a Néel temperature of about 150°K. The latter study[3] suggested an admixture of weak ferromagnetism F_z with three modes of antiferromagnetism G_x, C_x, and A_z, which belong to two different irreducible representations[4] of the crystallographic space group in the product space of atoms and spins. In terms of magnetic space groups, F_z and G_x belong to $Pb'n'm$, whereas C_x and A_z belong to $Pb'nm$. This suggestion is in disaccord with Landau's theory of second-order phase transitions.[5] We report here the results of neutron powder diffraction measurements in the range of liquid helium to room temperature undertaken in order to determine the correct magnetic structure of $NaNiF_3$.

II. EXPERIMENTAL

The material, sodium trifluoronickelate, was precipitated from a mixture of boiling solutions of hydrated nickelous chloride and of sodium fluoride. Prior to mixing the sodium fluoride solution was acidified with hydrofluoric acid. The precipitate was dried in vacuum at 200°C for 3 h. The final product was a yellow (tending somewhat to green) powder. Gravimetric analysis of the dried powder yielded: Ni, 41.6; F, 40.0 (calculated Ni, 42.32; F, 41.09). X-ray powder photographs showed no lines other than those of the pure substance.

Neutron diffraction patterns obtained at room, liquid-nitrogen, and liquid-helium temperatures are shown in Fig. 1. A fourth pattern (not shown) of the cryostat with no sample in it exhibited a single aluminum (111) reflection at $2\theta = 25.5°$. The intensity of this reflection amounted to about 70% of the observed

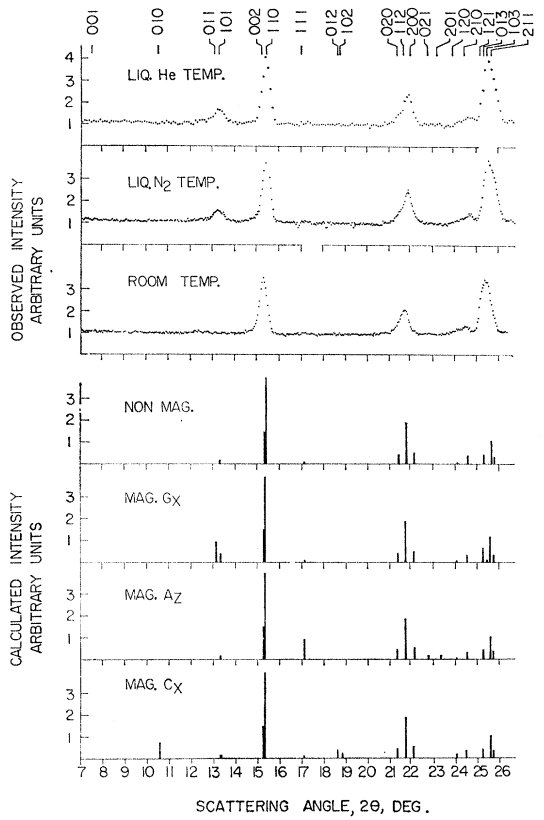

FIG. 1. Observed and calculated neutron ($\lambda \sim 1.03$Å) diffraction patterns of $NaNiF_3$. The nuclear reflections (nonmagnetic) are included in the intensities of the magnetic modes. 70% of the observed reflection appearing at 25.5° is due to a contribution from the (111) reflection of the aluminum holder.

reflections that appear at this angle in Fig. 1. The intensity of the (011, 101) magnetic reflection, $I(011, 101)$, was measured as a function of temperature and is shown in Fig. 2. A Néel temperature of 149°K was obtained from this measurement. A small sample from

[1] W. Rudorff, J. Kandler, and D. Babel, Z. Anorg. Allgem. Chem. **317**, 261 (1962).
[2] S. Ogawa, J. Phys. Soc. Japan **15**, 2361 (1960).
[3] V. M. Judin and A. B. Sherman, Phys. Status Solidi **20**, 759 (1967).
[4] E. F. Bertaut, Acta Cryst. **A24**, 217 (1968).
[5] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon Press, Inc., New York, 1958), Chap. 14.

the same material analyzed in a vibrating sample magnetometer yielded a Néel temperature of 138°K. Néel temperatures of 149°K,[2] 156°K,[3] and 142°K [6] were reported in the literature.

III. RESULTS AND DISCUSSION

The calculated intensities of the nonmagnetic G_x, A_z, and C_x modes are shown in Fig. 1. In these calculations, the atomic parameters of $GdFeO_3$ were used.[1] Preliminary calculations indicated that the calculated intensities of the four observed nuclear reflections (Fig. 1) are insensitive to small changes in these parameters. As for the magnetic reflections, a magnetic moment of $2.0\mu_B$ and the form factor

$$\exp\{-7.9[(\sin\theta)/\lambda]^2\}$$

were used. This yielded a ratio $I(011, 101)/I(002, 110)$ which was equal to the one measured at liquid-helium temperature. It is evident from Fig. 1 that G_x is the only magnetic mode compatible with the low-temperature diffraction results. It was estimated that the modes A_z and/or C_x should have been detected if 10% of the sample were in any one of these modes. This result contradicts the suggestion of Judin and Sherman[3] that A and C modes are admixed with the G mode in $NaNiF_3$. This compound in its magnetic state is a weak ferromagnet in the z direction,[3] a mode which belongs to the same irreducible representation as G_x. Thus the experimental results are in accord with what one expects and finds in this type of structure, as for example in the orthoferrites.[7]

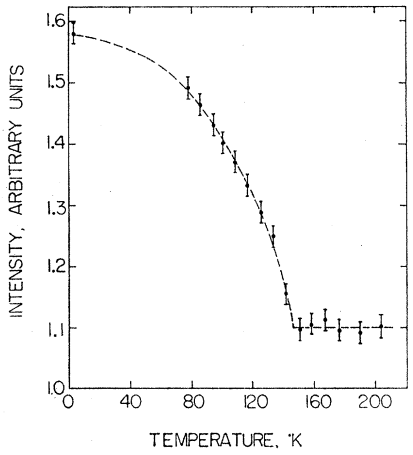

FIG. 2. Temperature dependence of the intensity of the (011, 101) magnetic reflection in $NaNiF_3$.

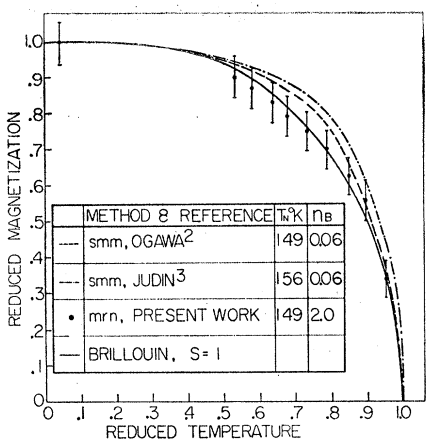

FIG. 3. Reduced temperature dependence of spontaneous magnetic moment (smm) and sublattice moment derived from the magnetic reflection (011, 101) of neutrons (mrn) in $NaNiF_3$. The magneton numbers n_B correspond to values extrapolated to 0°K.

The physical origin of the weak ferromagnetism may in general be found[8] in the antisymmetric exchange (AE) interaction or in the single-ion anisotropy (SIA) mechanism. The former requires that the canting angle[8] $\alpha(t)$, where t is reduced temperature, will be temperature-independent, whereas the latter requires a reduction in $\alpha(t)$ of about 30% as the Curie point is approached. It is estimated from Fig. 3 that $\alpha(t)$ ($\sim$smm/2mrn) is 15 mrad and is approximately constant with some tendency, if any, to increase with t. Hence, these data give support to the suggestion that the AE interaction is the dominant mechanism which is responsible for the weak ferromagnetism.

ACKNOWLEDGMENTS

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[6] M. P. Petrov, Fiz. Tverd. Tela **7**, 1663 (1965) [English transl.: Soviet Phys.—Solid State **7**, 1348 (1965)].

[7] R. M. Bozorth, Phys. Rev. Letters **1**, 362 (1958).

[8] D. Treves, J. Appl. Phys. **36**, 1033 (1965).