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Magnetization Measurements and Pressure Dependence of the Curie Point of the Phase Sc_3In†

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The approximate composition limits of the Sc_3In phase have been determined as 22 to 23 at.% In. Susceptibility measurements have been made on a number of alloys, containing various amounts of the Sc_3In phase, in the composition range 21–26 at.% In. Heat and mechanical treatments reveal a critical dependence of the magnetic properties on the degree of order of the Sc_3In phase. Although the susceptibility varies inversely with temperature, this behavior is not considered to be evidence for the presence of localized moments, since the magnetic moment per Sc atom is much smaller than that associated with $S=\frac{1}{2}$, and does not agree with the value obtained from the magnetization data as a function of magnetic field. Initial susceptibility measurements, below the Curie temperature, exhibit structure which suggests that a strong magnetocrystalline anistropy may exist at temperatures close to T_c. The pressure dependence of the Curie point has been determined as $\partial T_c/\partial P = 1.9_5 \times 10^{-4}$ °K bar^{-1}.

INTRODUCTION

THE theoretical understanding of magnetism in metals has, in the past,[1] been approached from the two extreme assumptions that the electrons responsible for the magnetic behavior are either situated in free- or nearly-free-electron energy bands (i.e., the itinerant model), or that they are located in discrete atomiclike orbital energy states (i.e., the localized model). The localized model has proved successful in accounting for the magnetic moments associated with the rare earths and their alloys (with the possible exception of cerium), but neither model, in its simplest form, has provided an adequate description of the magnetism of the transition metals and their compounds. This has led to a number of attempts to improve the agreement between experiment and theory by means of a suitable combination of appropriate features from both models. However, it is now[1] realized that the features which were considered to typify the localized, or Heisenberg model, can be reproduced in the itinerant model by the use of appropriate energy bands. Thus the important question which has to be answered in order to describe theoretically the magnetism of a particular system is to what degree does the spin-density distribution differ from that of a free-atom electron configuration. This question is of obvious interest when considering the reasons for the ferromagnetism of the compounds $ZrZn_2$,[2] Sc_3In,[3] and Au_4V,[4] all of which have non magnetic metallic constituents.

Considerable effort has been devoted to the investigation of the magnetic properties of $ZrZn_2$, both above and below its Curie point.[5–8] Pickart *et al.*[7] have interpreted their neutron diffraction data as showing that the spin density is predominantly associated with the zirconium atom, but more diffuse than that calculated from a $4d$ electron configuration. It was further observed that the spin density is anisotropically distributed and shows a marked pileup at the midpoint of the Zr–Zr bond. However, Foner[9] has questioned this interpretation and has suggested an alternative explanation associated with the presence of magnetic impurities, which polarize their environment in a manner similar to the behavior of Fe impurities in Pd.[10,11]

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[1] For general reviews see C. Herring, *Magnetism* (Academic Press Inc., New York, 1966), Vol. IV; and E. D. Thompson, Advan. Phys. **14,** 213 (1965).

[2] B. T. Matthias and R. M. Bozorth, Phys. Rev. **109,** 604 (1958).

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[5] S. C. Abrahams, Z. Krist. **112,** 427 (1959); S. Ogawa, J. Phys. Soc. Japan **20,** 2296 (1965); T. Yomadaya and M. Asanuma, Phys. Rev. Letters **15,** 695 (1965); C. E. Olsen, J. Phys. Chem. Solids **19,** 228 (1960); H. J. Blythe, Phys. Letters **21,** 144 (1966); F. E. Hoare and J. C. G. Wheeler, *ibid.* **23,** 402 (1966).

[6] S. Ogawa and N. Sakamoto, Phys. Letters **23,** 199 (1966); J. Phys. Soc. Japan **22,** 1214 (1967).

[7] S. J. Pickart, H. A. Alperin, G. Shirane, and R. Nathans, Phys. Rev. Letters **12,** 444 (1964); and in *Proceedings of the International Conference in Magnetism, Nottingham, 1964* (The Institute of Physics and The Physical Society, London, 1964), p. 223.

[8] R. L. Falge, Jr., and R. A. Hein, Phys. Rev. **148,** 940 (1966).

[9] S. Foner, Bull. Am. Phys. Soc. **12,** 311 (1967), and private communication.

[10] A. M. Clogston, B. T. Matthias, M. Peter, H. J. Williams, E. Corenzwit, and R. C. Sherwood, Phys. Rev. **125,** 541 (1962).

[11] G. G. Low and T. M. Holden, Proc. Phys. Soc. (London) **89,** 119 (1966).

TABLE I. Impurity content (ppm atomic) of starting materials and a Sc_3In phase alloy.

Impurity	ppm atomic Scandium[a]	Indium[a]		23.2 at.% In alloy[b]
Al	33	5		40
Ag	2	1		30
Ca	11	6		4
Cu	35	1	9	45
Cd			20	<1
F				700
Fe	250	8		55
Mg	2	2		4
Na	10			15
Ni			10	2
Pb			45	3
Si	8	3		130
Sn			50	15
Th			10	1
Rare earths	N.D.	N.D.		<100

[a] Typical analyses as supplied by Johnson Matthey. Two lots of scandium were used in the preparation of the alloys.

[b] Mass spectrographic analysis by Fulmer Research Institute.

Relatively little is, as yet, known about the magnetic properties of the other two compounds beyond the fact that they become ferromagnets at low temperatures. It is the main purpose of the present paper to report measurements of the magnetization of the Sc_3In phase as a function of magnetic field up to 40 kOe in the temperature range 1.25 to 32°K and measurements of the pressure dependence of the Curie point.

SAMPLE PREPARATION

Matthias *et al.*[3] originally reported that the ferromagnetism of the Sc–In system occurs over the very narrow composition range from 23.2 to 24.2 at. % In. Compton and Matthias[12] showed that a superlattice structure exists in this composition range and from NMR measurements Wyluda *et al.*[13] suggested that the ferromagnetism of the system was associated with this ordered phase. Accordingly alloys containing 21.1, 23.2, 24.2, and 26.2 at. % In were prepared by melting the constituents together in an argon arc furnace. These quoted compositions are those obtained after correcting for the weight loss which occurred during preparation, assuming that this was entirely due to the evaporation of In. The analysis of the starting materials, as given by the manufacturers is given in Table I.

Magnetic measurements and metallographic examinations were carried out on samples cut from these alloys in the "as cast" state, and following the heat treatment indicated in Table II. Metallographic examination of the "as cast" alloys revealed the presence of dendrites of a second phase which oxidized rapidly in air and this phase has been tentatively identified as Sc_2In. Only in the case of the 21.1% alloy were we able to remove this phase completely by the anneal for one week at 800°C, although the amount present in the other samples was reduced. However, a new second phase was present in the annealed 21.1% sample, which was shown by x-ray examination to have the Sc structure with a lattice spacing close to that of scandium and it was therefore assumed to be a Sc–In solid solution phase. The relative volumes of the Sc_3In and Sc_2In present in the samples were determined using a Quantitative Television Microscope. A summary of the sample phase composition is given in Table II. Crude determinations of the liquidus temperature were made at 23.2 and 33.3% In and from these and the metallographic examinations a schematic phase diagram has been constructed which is presented in Fig. 1. The Sc_3In phase field is estimated to extend from approximately 22 to 23 at. % In at 800°C with no observed change in these limits down to 400°C.

Following the 800°C anneal the polished surface of the 24.2 at. % sample was examined by the glancing angle x-ray technique and superlattice lines were clearly resolved, the intensities of which were consistent with 100% order in the DO_{19} hexagonal structure. Lattice parameters were obtained from filings (300 mesh), which had been given a further 4-day anneal at 400°C, using Cu $K\alpha$ radiation in an x-ray powder camera. The values were $a=6.56\pm0.01$ Å; $c=5.12\pm0.01$ Å, which may be compared with $a=6.421\pm0.005$ Å; and $c=5.183\pm0.005$ Å obtained by Compton and Matthias.[12]

Magnetic measurements were also made on a sample of the 23.2% In alloy, which had been annealed at

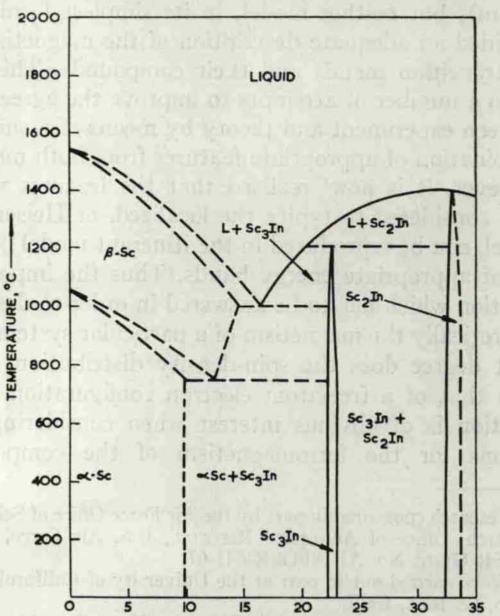

FIG. 1. Schematic phase diagram for the Sc–In system.

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[12] V. B. Compton and B. T. Matthias, Acta Cryst. 15, 94 (1962)

[13] B. J. Wyluda, R. G. Shulman, B. T. Matthias, and E. Corenzwit, Phys. Rev. 137, A1856 (1965).

TABLE II. Summary of the heat treatment and the phase composition of the Sc–In alloys studied.

Alloy (at.% In)	As cast	Phase composition[a] 800°C anneal one week	400°C anneal 4 days	Anneal 1000°C 15 h, quenched
21.1	8% Sc_2In^b	10% Sc–In^c (~30%)[d]	no change	no data
23.2	no data	1% Sc_2In^b	no change	9% Sc_2In^b
24.2	no data	5% Sc_2In^b	no change	no data
26.2	46% Sc_2In^b	30% Sc_2In^b	no change	no data

[a] Volume percent, remainder Sc_3In phase.
[b] Volume percentages determined by quantitative television microscope.
[c] Volume percentage determined by x rays.
[d] Volume percentage determined by visual estimate.

800°C and then heavily deformed (~10:1 reduction) by rolling between brass plates.

MAGNETIZATION MEASUREMENTS

The magnetization measurements were made by the Faraday method, the force on the sample being determined with a Sartorius balance with a resolution of 1 μg. The susceptibility results were obtained using an electromagnet[14] capable of producing 13 kOe, whereas magnetization measurements in fields up to 40 kOe were made in a superconducting solenoid. A uniform field gradient of 100 Oe/cm over a region ~1 cm in length was superimposed on the main solenoid field at the sample by means of two opposed coils situated at the ends of the main superconducting coil.

The superconducting magnet was maintained at 4.2°K in a liquid-helium bath. The sample was suspended at the center of the main coil in a copper tube surrounded by a separate helium bath, which on pumping could reduce the temperature at the sample to 1.2°K. Thermal contact between the sample and this variable bath was maintained by means of helium exchange gas. Temperatures between 4.2°K and room temperature could be established and maintained to ±0.1°K by passing a current through a Pt–Rh heater wound around the bottom of the sample tube. Temperatures were determined by one of three thermometers, depending upon the temperature range. From 1.2 to 4.2°K the vapor pressure over the helium refrigerant bath served as its own thermometer; between 4.2 and 30°K a calibrated Honeywell-Brown germanium resistance thermometer, mounted inside the sample tube close to the sample, was used; and temperatures above 30°K were determined by a copper-constantan thermocouple attached to the sample tube. A full description of the design and operation of this apparatus will be published elsewhere.[15]

Using the above arrangement magnetic isotherms were determined between 1.2 and 35°K in magnetic fields up to 40 kOe.

ZERO-FIELD CURIE-POINT DETERMINATION

The zero-field Curie point was determined from measurements of the initial susceptibility which were made in a separate apparatus capable of containing pressures up to 20 kbar. The pressure, generated in a hardened Be–Cu alloy cylinder at room temperature and transmitted to the sample through powdered Teflon, was retained by means of the "clamp" technique[16] prior to cooling to the low temperature. The pressure at the low temperature was determined from the superconducting transition temperature of a lead manometer[17] which was included in the sample assembly.

The initial susceptibility of the sample was followed as a function of temperature below 15°K by means of a standard inductance-measurement technique using a frequency of 100 cps and a signal strength equivalent to a peak-to-peak field of ~0.25 G at the sample. The temperature was determined from a Honeywell-Brown germanium resistance thermometer which had been calibrated against the zero-pressure superconducting transition temperature of lead, taken as 7.193°K,[18] and the vapor pressure of liquid helium at a number of temperatures between 4.2 and 2.5°K.

RESULTS

Magnetic Susceptibility

The magnetic susceptibility data below 250°K obtained on the 21.1, 23.2, 24.2, and 26.2 at. % In samples, following the 800°C anneal, are presented in Fig. 2. The 21.1 and the 26.2 at. % samples were also measured immediately after arc casting. Above 50°K the susceptibility values which were obtained for the arc-cast samples did not differ significantly from the values obtained for the annealed samples, but at lower temperatures they were some 5–10% higher than those shown in Fig. 2. It was also observed that the susceptibility decreased a further 10–15% from that shown in Fig. 2 below 25°K for the 21.1 and 24.2 at. % In samples after the 400°C anneal. It is clear therefore from the variation of the magnetic susceptibility observed for these four alloys that the magnetization of the Sc_3In phase critically depends upon the heat treatment that a sample has received.

In order to correct for the presence of Sc_2In in these samples the susceptibility of a sample of this composi-

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[14] W. E. Gardner and A. Davies, Atomic Energy Research Establishment Report M 1352 (unpublished).

[15] W. E. Gardner (to be published).

[16] P. F. Chester and G. O. Jones, Phil. Mag. **44**, 1281 (1953).

[17] T. F. Smith and C. W. Chu, Phys. Rev. **159**, 353 (1967).

[18] J. P. Franck and D. L. Martin, Can. J. Phys. **39**, 1320 (1961).

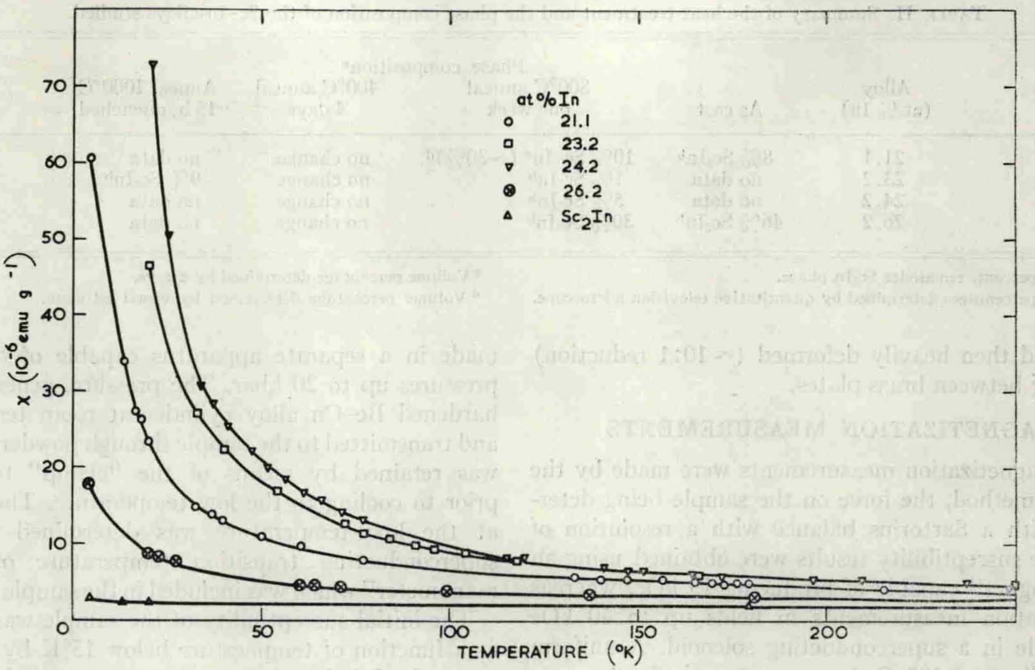

FIG. 2. Variation of the magnetic susceptibility with temperature for a number of Sc–In alloys annealed at 800°C.

tion was also determined and the data are also given in Fig. 2. Sc_2In is very nearly a temperature-independent paramagnet with χ_g varying from 1.90×10^{-6} emu/g at room temperature to 2.68×10^{-6} emu/g at 4.2°K.

The metallographic and x-ray examinations indicate that the 23.2, 24.2, and 26.2 at. % In samples are in the Sc_3In+Sc_2In phase field. The Sc_3In phase present in all three samples should, thermodynamically, have

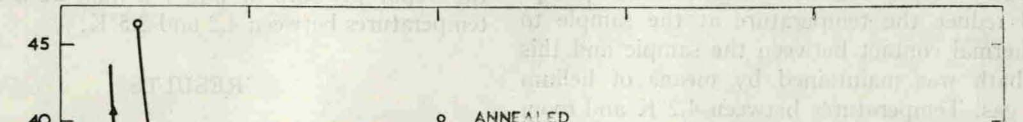

FIG. 3. Variation of the magnetic susceptibility with temperature for samples of a 23.2 at. % In alloy following various heat treatments and mechanical cold work.

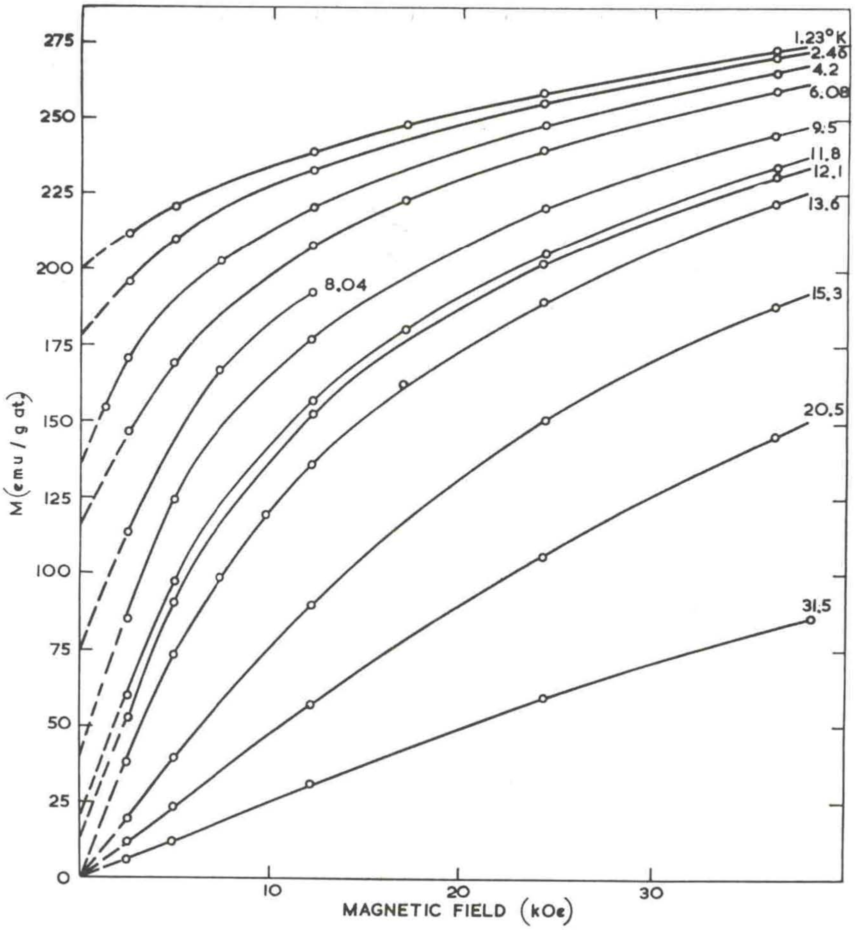

FIG. 4. Magnetization curves (corrected for the presence of 5% Sc_2In) for a sample of a 24.2 at. % In alloy.

the indium-rich terminal composition and therefore should have a fixed susceptibility. In fact, this was not found after correcting the observed susceptibilities for the appropriate amounts of Sc_2In present in the samples.

The 21.1 at. % In sample lies in the Sc_3In+Sc–In solid solution phase field and the Sc_3In phase in this sample should have the scandium-rich terminal composition. The susceptibility of this composition was determined by again correcting the observed results for the presence of the Sc–In solid solution.[19] The susceptibility so obtained falls between the extreme values obtained for the indium-rich terminal composition.

In order to study the possible dependence of the magnetic behavior on the degree of order of the Sc_3In phase measurements were made on a sample of the 23.2 at. % In alloy which had been water quenched from 1000°C, after a 15-h anneal, and a further sample which had been subjected to a large reduction (~10:1) by rolling. It is evident from the data presented in Fig. 3 that both of these treatments appreciably decreased the susceptibility for this nominal composition. Unfortunately, the quenched sample also underwent a phase composition change with ~9% of Sc_2In being precipitated as a consequence of the heat treatment (Table II). However, the decrease in the susceptibility is greater than can be accounted for simply by the formation of the Sc_2In, but as this increase in the amount of the Sc_2In phase in the sample must result in a change in composition of the Sc_3In phase we are unable to state specifically that the decrease in the susceptibility for this sample is solely associated with a change in the degree of order of the Sc_3In phase.

The sample subjected to heavy cold work, on the other hand, showed no change in composition and therefore this complication does not arise and we are able to conclude that the susceptibility of the Sc_3In phase is dictated by its degree of order.

Magnetization Behavior

The magnetization measurements were mainly confined to the 24.2 at. % In sample because it had the strongest magnetic behavior. Magnetization curves in fields up to 40 kOe at temperatures from 31.5 to 1.23°K were made and the results, corrected for the presence of 5 volume % Sc_2In, are shown in Fig. 4. Above 35°K the magnetization curves up to 40 kOe are linear with field within the limits of experimental accuracy. Below 35°K there is an increasing departure from linear behavior suggesting that the alloy becomes ferro-

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[19] In the absence of any susceptibility measurements for Sc–In solid solutions a value of $\chi=6\times10^{-6}$ emu/g, based upon measurements on Sc [W. E. Gardner and J. Penfold, Phil. Mag. 11, 549 (1965)], has been assumed.

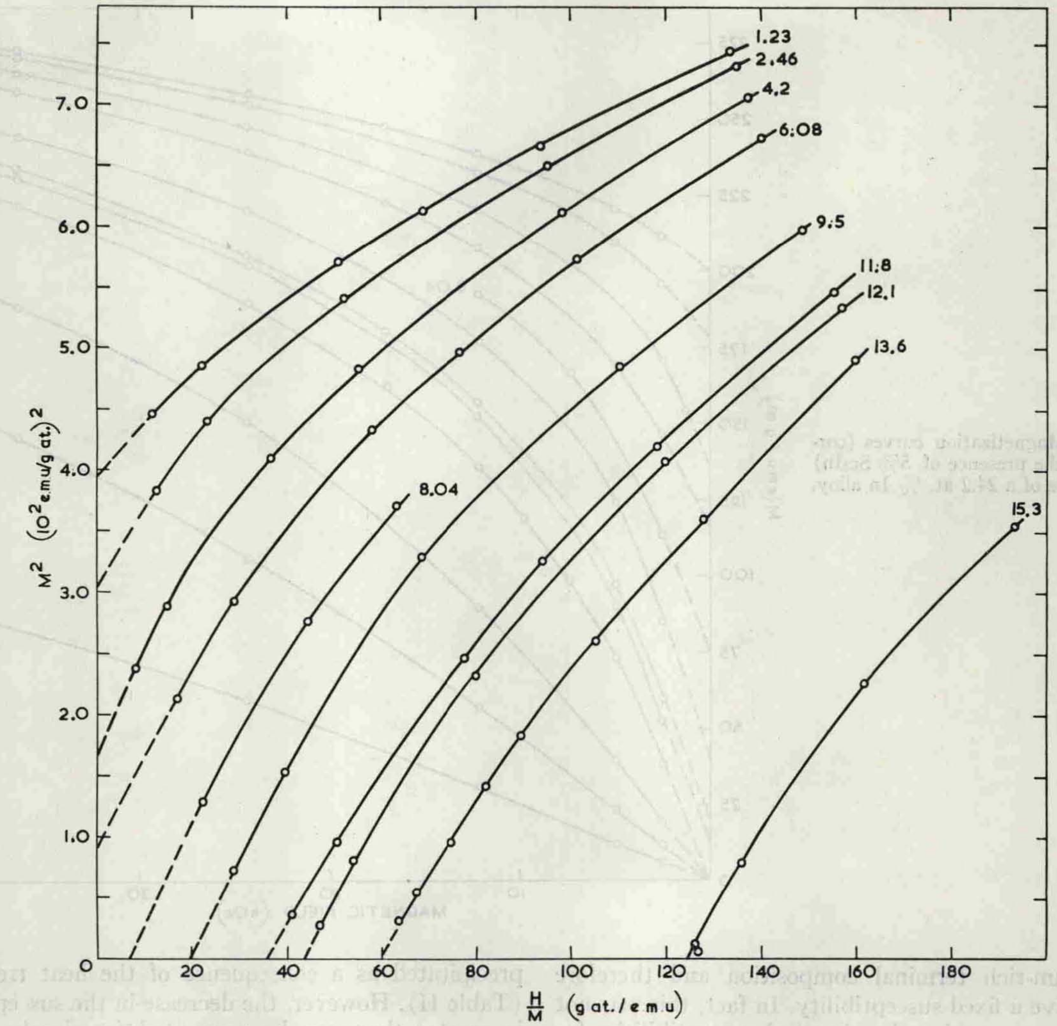

FIG. 5. Plots of M^2 versus H/M for a sample of a 24.2 at. % In alloy.

magnetic. It is clear, however, from the curve obtained at 1.23°K that it is not possible to magnetically saturate the sample in fields up to 40 kOe. Thus, the incremental susceptibility at 40 kOe and 1.23°K (1250×10^{-6} emu/g atom or 190×10^{-6} emu/g) is far higher than normal paramagnetism would produce.

The magnetization curves of the 21.1 at. % In sample also exhibited departures from linear behavior at liquid-helium temperatures. At 1.3°K the magnetization in 10 kOe was about 25% of that for the 24.2 at. % alloy at this field and temperature. However, the 26.2 at. % alloy showed only slight deviations from linearity in fields up to 13 kOe at 1.3°K with $\chi_g\sim40\times10^{-6}$ emu/g. Thus, although ferromagnetism persists in the Sc_3In phase present in the 21.1 and 26.2 at. % In samples, it is considerably weaker than that in the 24.2 at. % sample.

Determination of T_c

By definition, a ferromagnetic state commences with the appearance of spontaneous magnetization at a temperature known as the Curie point. It is, however, impossible to determine unambiguously the Curie point of a real ferromagnet. The following approaches are amongst those which are usually employed[20] to determine T_c:

(i) One is the appearance of remanence, i.e., the existence of a hysteresis loop, which is determined by magnetostatic forces.

(ii) A second is a direct application of the definition, namely attempting to determine the temperature at which the spontaneous magnetization goes to zero by means of an extrapolation to zero magnetic field of the high-field magnetization data, in order to avoid magnetocrystalline effects. Such an extrapolation is usually undertaken[21] by plotting M^2 versus H/M at a number of temperatures above and below the Curie point and associating T_c with the curve which passes through the

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[20] K. P. Belov, *Magnetic Transitions* (Consultants Bureau Enterprises, Inc., New York, 1961), Chap. II.

[21] K. P. Belov and A. N. Goryaga, Fiz. Metal i Metalloved. **2**, 441 (1956); A. Arrott, Phys. Rev. **108**, 1394 (1957).

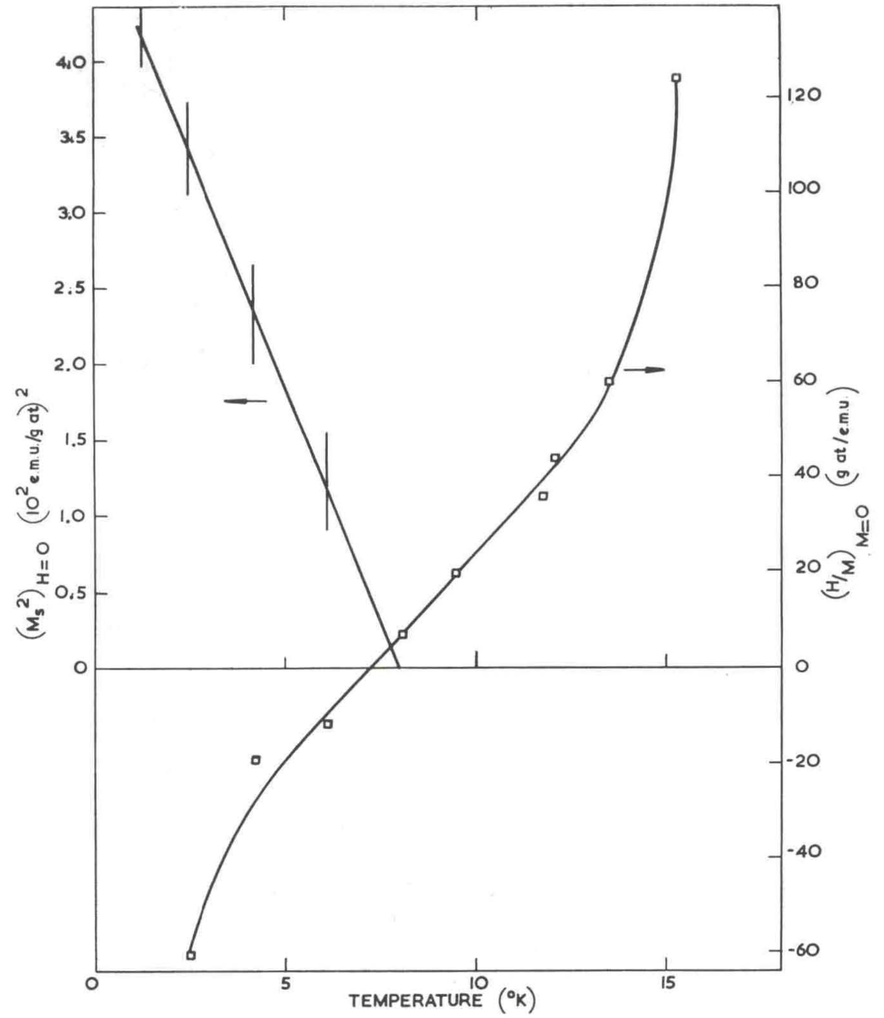

FIG. 6. Determination of the Curie temperature from magnetization data for a sample of a 24.2 at. % In alloy.

origin. Theoretically, such curves should be linear close to T_c, but, unfortunately, in many instances the curves obtained are nonlinear and the extrapolation can become very dubious.

(iii) The third is the behavior of the initial zero-field susceptibility.

We were unable to use the first method since remanence was not observed in measurements above 1000 Oe, the minimum field used with the superconducting magnet. Measurements in lower fields would require an actual determination of the field in the coil, whereas we obtained the field from a measurement of the current. This leads to errors in the field of less than 1% above 2 kOe, but would be unsuitable for lower fields because of the remanence of the coil.

We have however applied the second method to our data as illustrated in Fig. 5, where we have plotted M^2 versus H/M. It is evident that in the temperature range 1.23 to 15.3°K, M^2 is not linear in H/M and that this type of plot does not therefore lead to a precise extrapolation to zero field. Nevertheless, we have indicated reasonable extrapolations of $(H/M)_{M^2=0}$ and $(M_s^2)_{H/M=0}$ in Fig. 5, plotted these values against T in Fig. 6, and thus obtained a value of $T_c=(7.5\pm 0.5)$°K.

Although theoretically at T_c the initial susceptibility (χ_i) becomes infinite, in practice, since the measurements must always be made in finite field, the value of $\chi_i(T_c)$ remains finite. The expected form[20] of the initial susceptibility curve as a function of temperature is drawn schematically in Fig. 7(a), and curves of this shape have been reported for Ni and some ferromagnetic alloys by Belov.[20] However, more generally, the initial susceptibility curve exhibits a broad hump in the vicinity of T_c, and is represented schematically in Fig. 7(b). Such curves, as determined by the "transformer" technique[22] in studies of the pressure dependence of the Curie point, are unsuitable for an accurate determination of T_c. However, these curves do provide an adequate means of determining the change of T_c, with pressure, from their relative displacement. It is

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[22] L. Patrick, Phys. Rev. **93,** 384 (1954).

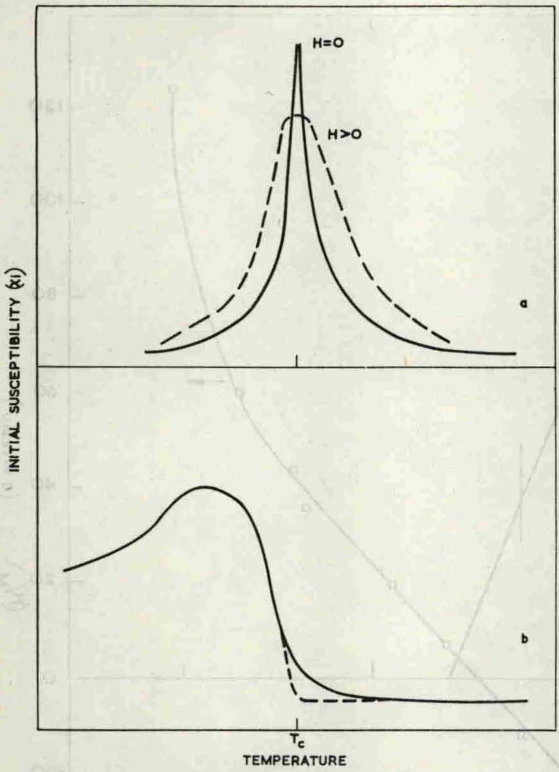

FIG. 7. Initial magnetic susceptibility as a function of temperature: (a) Theoretical curves for $H=0$ and $H>0$. (b) Typical curve obtained by means of the "transformer technique."

customary to extrapolate the sharply rising portion of the curve to intersect an extrapolation of the background reading and to define this point as an arbitrary Curie point $T_c(P)$ for the purpose of determining the pressure dependence.

In Fig. 8 we present the initial susceptibility curves observed for the 24.2 at. % In sample at 1 bar, 6.1 and 13.6 kbar between 12.5 and 1.2°K. Although only a limited number of initial susceptibility curves of ferromagnetic materials are available for comparison, it is evident that the present curves have a more complex structure than is usually observed. They do, however, have a remarkable similarity to those observed[23] for the ferromagnetic transition in Gd. It has now been established[24] that the magnetic properties of Gd in weak fields result from a strong magnetocrystalline anisotropy close to T_c, and are not, as originally proposed by Belov,[25] due to the formation of a helical antiferromagnetic state.[26] In view of the hexagonal structure of the Sc_3In phase, anisotropy may also be responsible for the observed behavior in the present case. In this respect we note that $ZrZn_2$, which has a cubic structure, does not exhibit any unusual features in its initial susceptibility curve.[8]

Because of broadening, the structure observed in the curves taken at 1 bar and 6.1 kbar cannot be resolved in the curve taken at 13.6 kbar, but it reappeared in the curve obtained when the pressure was removed. We obtained a mean value of T_c $(P=1\text{ bar})=6.1\pm 0.1$°K from the curves taken before and after the application of pressure. This value corresponds more closely to that obtained from the high-field measurements than in the case of $ZrZn_2$ where there is a marked difference in the values obtained by the two methods.[6]

It is clear that $T_c(P)$ increases with pressure and extrapolations similar to the one used at atmospheric pressure yield values of $T_c(P)$ at 6.1 and 13.6 kbar. A plot of these values, as a function of pressure, is given in Fig. 9, from which we obtain $\partial T_c/\partial P=1.9_5\times 10^{-4}$ °K bar^{-1}. The pressure dependence of the low-temperature peak in the susceptibility curve is also shown in Fig. 9. Following an initial increase of 1.1×10^{-4} °K bar^{-1} the pressure dependence falls off rapidly at high pressure, in contrast to the pressure dependence for T_c. However, in view of the broadening associated with the 13.6-kbar transition the relative value of $T_c(P)$ obtained at this pressure is questionable, and thus it is not impossible that $\partial T_c/\partial P$ may also be pressure-dependent.

DISCUSSION

Magnetic Susceptibility above T_c

The interpretation of strongly temperature-dependent magnetic-susceptibility data is "traditionally" carried out by plotting $1/\chi$ versus T and, if the variation is linear, the Curie-Weiss relationship

$$\chi=C/(T-\theta)=p_{\text{eff}}^2/8(T-\theta) \qquad (1)$$

may be applied to determine the parameter p_{eff}. Since the Curie-Weiss relationship is derived, theoretically, from the energy states of a system of atomiclike magnetic moments, the applicability of this equation to a given material is often cited as evidence for the existence of such moments. The nature of the interaction between these moments (i.e., ferromagnetic or antiferromagnetic) is then deduced from the sign of θ. As such moments are localized and do not contribute to the band-dependent properties of the solid a correction for the magnetic contribution from the conduction

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[23] L. B. Robinson, F. Milstein, and A. Jayaraman, Phys. Rev. **134**, A187 (1964); D. B. McWhan and A. L. Stevens, *ibid.* **139**, A682 (1965).

[24] W. D. Corner, W. C. Roe, and K. N. R. Taylor, Proc. Phys. Soc. (London) **80**, 927 (1962); C. D. Graham Jr., J. Phys. Soc. Soc. Japan **17**, 1310 (1962); J. Appl. Phys. **34**, 1341 (1963); in *Proceedings of the International Conference in Magnetism, Nottingham 1964* (The Institute of Physics and The Physical Society, London, 1964), p. 740; M. I. Darby and K. N. R. Taylor, in *Proceedings of the International Conference in Magnetism, Nottingham, 1964* (The Institute of Physics and The Physical Society, London 1964), p. 742; K. P. Belov, in *Proceeding of the International Conference in Magnetism, Nottingham, 1964* (The Institute of Physics and The Physical Society, London, 1964), p. 266.

[25] K. P. Belov, D. F. Litvin, S. A. Nikitin, and A. V. Ped'ko, Zh. Eksperim. i Teor. Fiz. **40**, 1562 (1961) [English transl.: Soviet Phys.—JETP **13**, 1096 (1961)]; K. P. Belov and A. V. Ped'ko, Zh. Experim. i Teor. Fiz. **42**, 87 (1962) [English transl.: Soviet Phys.—JETP **15**, 62 (1962)].

[26] G. Will, R. Nathans, and H. A. Alperin, J. Appl. Phys. **35**, 1045 (1964).

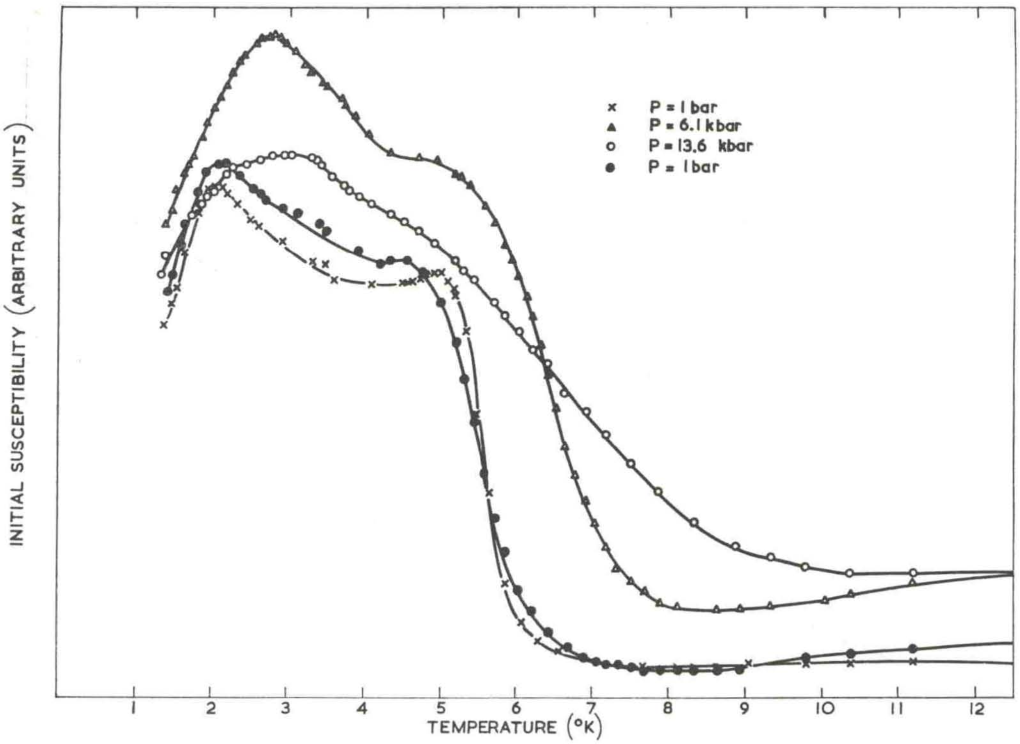

FIG. 8. Initial magnetic susceptibility as a function of temperature at a number of pressures for a sample of a 24.2 at. % In alloy.

electrons should be applied to the observed susceptibility of such a system before considering the temperature dependence of $1/\chi$.

The evidence for atomiclike moments is not established from such behavior if the value of p_{eff} is smaller than the value ($p_{\text{eff}}=1.73$) corresponding to a spin of $\frac{1}{2}$. In this case it is considered more appropriate to compare the susceptibility behavior with that expected from the itinerant model. In the absence of exchange interactions this model is usually considered to consist of two terms, a temperature-dependent (Pauli-Landau) term $\chi_c(T)$ associated with the electrons at the Fermi surface, together with a temperature-independent (Van Vleck) term χ_0 associated with all of the conduction electrons. If the electrons are free, or nearly free, then the variation of $\chi_c(T)$ with temperature is small ($\sim 5\%$ variation from 1 to 300°K) and is proportional to T^2. On the other hand, a strongly temperature-dependent χ indicates that the energy band or bands at the Fermi surface vary only slightly with k (i.e., tightly bound electrons), so that there is a sharp peak in the density of states. Such a peak may occur due to the presence of a Van Hove saddle point at an energy close to the Fermi energy.[27] However, such a peak will not produce divergence unless an exchange interaction is present, and then the susceptibility is given by

$$1/\chi(T)=1/\chi_c(T)-I/2\mu_B^2, \qquad (2)$$

where I is the exchange energy per electron which is assumed independent of the wave vector and the band, but is spin-dependent.[28] $\chi(T)$ is obtained from the observed susceptibility by correcting for χ_0 and the diamagnetism of the system. This equation has the same form as the Curie-Weiss equation,[29] but there are

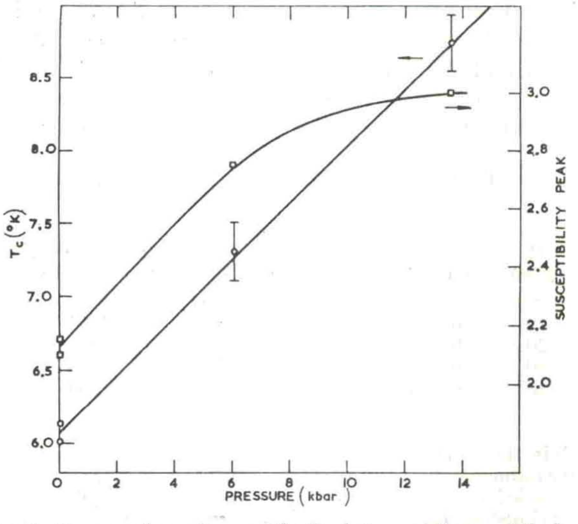

FIG. 9. Pressure dependence of the Curie temperature and the low-temperature peak in the initial susceptibility.

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[27] E. P. Wohlfarth and J. I. Cornwell, Phys. Rev. Letters **7**, 342 (1961); S. Alexander and G. Horwitz, Solid State Commun. **4**, 573 (1966); W. M. Lomer (private communication).

[28] W. M. Lomer, in *Proceedings of the International School of Physics, Varenna 1966*, (Academic Press Inc., "*Enrico Fermi*" London, 1967), p. 1.

[29] This is seen by writing (1) in the following form:

$$1/\chi(T)=T/C-\theta/C.$$

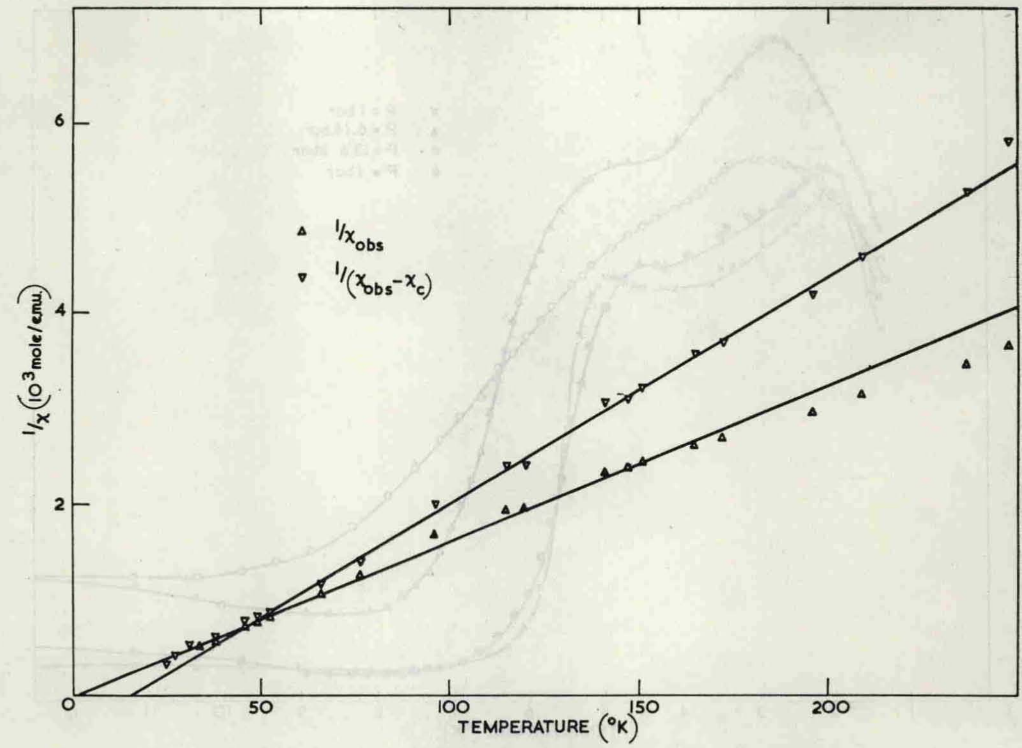

FIG. 10. Plots of $1/\chi_{obs}$ and $1/(\chi_{obs}-\chi_c)$ as a function of temperature.

no restrictions on the value or temperature dependence of $\chi_c(T)$, which is determined by the details of the shape of the density-of-states curve. Furthermore, the value of $T(\theta)$ which causes (2) to diverge,

$$1/\chi_c(\theta)=I/2\mu_B{}^2, \tag{3}$$

is not necessarily the same as the Curie temperature, since the latter is determined by the equation

$$1/N_+ + 1/N_- - 1/2I \gtrsim 0, \tag{4}$$

where N_+, N_- are the density of states of the up- and down-spin bands respectively at $T=T_c$.[28]

It is clear from Fig. 2 that the magnetic susceptibility of the Sc_3In phase is strongly temperature-dependent. We shall compare with theory only the data obtained for the 24.2 at. % In alloy since the sample taken from this alloy had the largest susceptibility at any given temperature. If we follow Matthias *et al.*[3] and simply plot $1/\chi_{obs}$ as a function of temperature we find the variation shown in Fig. 10. It can be seen that the points so obtained do not fall on a straight line over the full temperature range of the measurements. If, however, a straight line is drawn through the points between 50 and 150°K, values of p_{eff} and θ can be determined from it and these are presented in Table III, where they are compared with the values obtained by Matthias *et al.*[3]

TABLE III. Comparison of the values of θ and p_{eff} derived from plots of $1/\chi_{obs}$ and $1/(\chi_{obs}-\chi_c)$.

Plot	θ (°K)	p_{eff}/ g at.	p_{eff}/ (Sc atom)	Moment/ (Sc atom) (μ_B)
$1/\chi_{obs}$	3	0.70	0.81	0.29
$1/(\chi_{obs}-\chi_c)$	16	0.58	0.67	0.20
$1/\chi_{obs}$[a]	7	0.65		

[a] Reference 3.

A more satisfactory comparison with the Curie-Weiss relationship can be made by correcting the observed data for the Pauli term (assumed to be temperature-independent).[30] A plot of $1/(\chi_{obs}-\chi_c)$ as a function of temperature is also given in Fig. 10. A straight line can now be drawn through the points between 50 and 250°K and the values of θ and p_{eff} obtained from this line are also given in Table III. It can be seen that correcting the data causes the value of θ to increase

TABLE IV. Data from magnetization curves.

H (kOe)	Moment/Sc atom (μ_B) 6.08°K	4.2°K	1.23°K	$(\partial M/\partial H)$ at 1.2°K (10^{-6} emu/g at.)
10	0.048	0.051	0.056	2500
20	0.055	0.057	0.060	1450
30	0.059	0.061	0.063	1250
40	0.063	0.065	0.066	1200

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[30] In the absence of specific-heat data for the Sc_3In phase we have estimated this correction (100×10^{-6} emu/g at. from the data available for pure Sc [H. Montgomery and G. P. Pells, Proc. Phys. Soc. (London) **78**, 622 (1961)]. This correction may be contrasted with the somewhat smaller value (60×10^{-6} emu/g at.) which would be necessary to correct for the orbital and diamagnetic susceptibilities in order to compare the data with Eq. (2).

TABLE V. Comparison of the magnetic properties of Sc_3In and $ZrZn_2$.

	T_c(°K)				Moment/(TM atom) (μ_B)			($\partial M/\partial H$) at 2°K and 40 kOe
	Initial susceptibility	High field	θ (°K)	p_{eff}/(TM[a] atom)	c	10 kOe[b]	40 kOe[b]	(10^{-6} emu/g at.)
Sc_3In	6.1	7.5	16	0.67	0.2	0.055	0.066	1250
$ZrZn_2$	32[d]	17.5[e]	35[f]	0.75[f]	0.25	0.141[e]	0.191[e]	2830[e]

[a] Transition metal.
[b] Calculated from magnetization curves.
[c] Calculated from p_{eff}.
[d] Reference 8.
[e] Reference 6.
[f] Reference 5.

and the value of p_{eff} to decrease. If we assume that the moment is entirely associated with the scandium atom, the value of p_{eff} per scandium atom (Table III) is still much smaller than that corresponding to $S=\frac{1}{2}$. In fact the moment per scandium atom [obtained from the relationship $\mu=(1+p_{eff}^2)^{1/2}-1$] is only $0.20\mu_B$ (Table III), which suggests that the spin-density distribution differs considerably from a free-atom configuration and that the $1/T$ dependence is associated with the band structure. It follows, therefore, that the susceptibility data would be better interpreted with Eq. (2).

Since we have shown that the susceptibility depends critically on the heat and mechanical treatment that a sample has received, it is evident that the spin-density distribution at a scandium atom is sensitive to its location and may even possibly fall to zero when the scandium occupies an indium site.[31]

Now it might be considered extremely fortuitous that the band structure of Sc_3In is such that $\chi_c(T)$ is inversely proportional to T, and that a more reasonable possibility, retaining the localized model, would be that the low moment is due to an averaging process over scandium sites having an *integral* moment and zero moment. However, in view of the fact that the 24.2 at. % In showed full ordering, within the limits of the resolution associated with the x-ray determination, it would seem impossible that a sufficient number of inequivalent sites exist so as to account for so small a moment. We therefore reject the localized model and conclude that the band structure of ordered Sc_3In is indeed such as to produce the observed susceptibility behavior.

Magnetization below T_c

Plots of H/M versus M^2 are normally associated with ferromagnets exhibiting localized behavior, but they are equally appropriate for a band ferromagnet where the Fermi energy occurs in the middle of a parabolic peak in a $1/N(E)$-versus-n plot, where n is the total number of electrons and $N(E)$ is the density of states.[28] As discussed above in the determination of T_c from high-field magnetization measurements, plots of H/M versus M^2 do not yield straight lines for the Sc_3In phase. Moreover, we have not been able to find any simple function which will represent the magnetization data, and thus it has not been possible to obtain the spontaneous magnetization as a function of temperature. Furthermore, as the magnetization curves are strongly field-dependent up to 40 kOe at low temperatures, it has not been possible to obtain a saturation moment for the Sc_3In phase.[32] However, smoothed values of the magnetic moment, assumed to be entirely associated with the scandium atoms, are given in Table IV at 10-kOe intervals for three temperatures. These values may be compared with the 10% lower value of $0.051\mu_B$/(Sc atom) at 1.4°K in 14 kOe given by Matthias *et al.*[3] We attach no significance to this difference due to the sensitivity of the magnetization of the Sc_3In phase to heat treatment. It should be noted that the moment per Sc atom obtained from the high field measurements is only about $\frac{1}{3}$ of the value deduced from the susceptibility results (Table III), which adds further support to our contention that the magnetic behavior is best described in terms of the band model.

Values of instantaneous susceptibility at a number of fields at 1.2°K are also given in Table IV. The value of $\partial M/\partial H$ at 1.2°K and 40 kOe, 1200×10^{-6} emu/g at. is much larger than the susceptibility obtained for pure scandium at this temperature, namely 300×10^{-6} emu/g at.

A remarkable similarity exists between the magnetic properties of $ZrZn_2$ and those of the Sc_3In phase. This is illustrated in Table V where a direct comparison of the values of θ, p_{eff}, and the moment expressed per transition metal atom is given.

Variation of T_c with Pressure

The present theoretical understanding of exchange forces provides no *a priori* guidance as to the magnitude or even the sign of the expected pressure dependence

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[31] The same model may be equally appropriate for $ZrZn_2$ since the susceptibility of this compound has also been observed to vary from sample to sample (Ref. 6).

[32] The failure of magnetization curves to saturate at high fields and low temperatures has been interpreted as evidence for nonlocalized magnetic behavior (Ref. 6). However, very dilute alloys (~0.02 at.%) of Mn in Cu [J. A. Careaga, B. Dreyfus, R. Tournier, and L. Weil, in *Proceedings of the Tenth International Low-Temperature Conference, Moscow, 1966* (Proizvodstrenno-Izdatel'skii Kombinat, VINITI, Moscow, USSR, 1967)]; and dilute alloys (~1 at. %) of Gd in yttrium [W. E. Gardner and H. J. Williams, in *Proceedings of the Tenth International Low-Temperature Conference, Moscow, 1966* (Proizvodstrenno-Izdatel'skii Kombinat, VINITI, Moscow, USSR, 1967)], systems which closely adhere to the concept of localized moments, also fail to saturate under similar conditions.

TABLE VI. Comparison of $\partial T_c/\partial P$ for the Sc_3In phase with values for other ferromagnets.

Element or alloy	$\partial T_c/\partial P$ (10^{-3} °K bar^{-1})	T_c (°K)	$\frac{\partial \ln T_c}{\partial \ln V}$	K[a] (10^{-7} bar^{-1})
Fe[b]	0 ± 0.1	1036	0	5.9_4
Co[b]	0 ± 0.1	1404	0	5.2_3
Ni[b]	0.35 ± 0.02	624	-1.0_5	5.3_5
Gd[c]	-1.63 ± 0.07	293	2.1_3	26.1
Tb[c]	-1.08 ± 0.03	228	1.8_9	25.1
Dy[d]	-1.24 ± 0.1	174	2.7_4	26.0
$Fe_{0.7}Ni_{0.3}$[b]	-5.8 ± 0.2	372	$26._3$	5.9_4[f]
$Ni_{0.68}Fe_{0.32}$[b]	-0.1 ± 0.1	885	0.2_1	5.3_5[g]
Au_4Mn[e]	2.7 ± 0.3	333	$-14._1$	5.7_7[h]
Sc_3In	$0.19_5\pm0.01$	6.1	$-13._9$	23.0[i]

[a] Values from K. A. Gschneidner Jr. Solid State Phys. **16**, 275 (1964).

[b] Reference 22.

[c] Reference 23.

[d] J. E. Milton and T. A. Scott, Phys. Rev. (to be published).

[e] T. Hirone, T. Kaneko, and K. Kondo, in *Physics of Solids at High Pressures*, edited by C. T. Tomizuka and R. M. Emrick (Academic Press Inc., New York, 1965), p. 298.

[f] Value for iron.

[g] Value for nickel.

[h] Value for gold.

[i] Value for scandium, C. E. Montfort and C. A. Swenson, J. Phys. Chem. Solids **26**, 623 (1965).

of magnetic transitions. The greater part of the effort expended[23,33] in the study of the pressure dependence of magnetic transitions has been directed towards the rare-earth materials and their alloys, in which the magnetic interaction is of an indirect nature. For these materials it has been observed that T_c decreases with pressure. No such single sign has been observed for the transition metals and their alloys.

In Table VI we compare the values of $\partial T_c/\partial P$ and the dimensionless quantity $\partial \ln T_c/\partial \ln V$ for the Sc_3In phase with values previously reported for some other ferromagnets. It would appear that the magnitude and sign of the observed pressure dependence for the Sc_3In phase cannot be considered to differ from those observed for other ferromagnetic materials.

CONCLUSION

(i) The Sc_3In phase field exists over a narrow range of composition (approximately 22–23 at. % In at 400°C).

(ii) The magnetic susceptibility of this phase depends critically on the degree of order and is considerably reduced by disordering.

(iii) The inverse of the corrected susceptibility is proportional to temperature between 50 and 250°K, but since the slope corresponds to a moment of $\sim 0.2\mu_B$/(Sc atom), it is felt that this behavior is a consequence of a fortuitous energy band shape at the Fermi surface.

(iv) The magnetization of the Sc_3In phase shows no evidence of saturation in fields up to 40 kOe at 1.2°K. The maximum moment achieved per scandium atom was $0.066\mu_B$, which is considerably smaller than that deduced from the susceptibility by assuming it follows a Curie-Weiss relationship.

(v) The initial susceptibility curve contains structure at temperatures below 6.1°K (the low-field Curie temperature). It is suggested that this may be due to the presence at T_c of appreciable temperature-dependent magnetocrystalline anisotropy.

(vi) The structure in the initial susceptibility curve is unaffected by pressures up to 6 kbar, but cannot be resolved at 13.6 kbar. The Curie temperature increases with pressure with $\partial T_c/\partial P = (0.19_5\pm0.01)\times10^{-3}$ °K bar^{-1}.

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[33] D. Bloch and R. Pauthenet, in *Proceedings of the International Conference in Magnetism, Nottingham 1964* (The Institute of Physics and The Physical Society, London, 1964), p. 255; L. B. Robinson, S. I. Tan, and K. F. Sterrett, Phys. Rev. **141**, 548 (1966); K. P. Belov, S. A. Nikitin, and A. V. Ped'ko, Zh. Eksperim. i Teor. Fiz. **45**, 26 (1963) [English transl.: Soviet Phys.—JETP **18**, 20 (1964)]; I. G. Austin and P. K. Mishra, Phil. Mag. **15**, 529 (1967).