

Ferromagnetism of SmCd

A. M. Stewart,^{A,B} G. Costa^B and G. Olcese^C

^A School of Physics, University of New South Wales, P.O. Box 1, Kensington, N.S.W. 2033 (present address).

^B Istituto di Scienze Fisiche (Research Unit of G.N.S.M.) dell'Università di Genova, Genova 16132, Italy.

^C Istituto di Chimica Fisiche, Università di Genova, Genova 16132, Italy.

Abstract

Measurements have been made of the magnetizations and resistivities of polycrystalline specimens of SmCd and LaCd. SmCd is found to be ferromagnetic with a Curie temperature of 194 K and a spontaneous moment of $0.05 \mu_B$ per samarium ion at 77 K. Above this temperature the magnetization increases, and no sign is found of the transition to diamagnetism reported in previous work. The susceptibility above the Curie point obeys a Curie–Weiss law, in agreement with a recent theory. LaCd is a Pauli paramagnet with a broad superconducting transition in the region of 3 K.

Introduction

There is currently much interest in the properties of metallic samarium compounds with regard to: (1) permanent magnet materials with very high anisotropy, e.g. SmCo₅ (Taylor 1971), (2) materials with anomalously large effects due to conduction electron polarization (Stewart 1972*a*, 1972*b*, 1972*c*) and (3) materials which show a valence change as a function of pressure or temperature, e.g. SmS or SmB₆ (Maple and Wohlleben 1971; Nickerson *et al.* 1971). Therefore, when Alfieri *et al.* (1967) reported that the intermetallic compound SmCd, which has the CsCl structure, became diamagnetic below 110 K and interpreted this as being due to a valence change, we thought that this material was worthy of further investigation. However, we have found no evidence that the samarium is in anything but its normal tripositive state below 800 K and we interpret our results as being characteristic of a ferromagnet with high crystal field anisotropy. Similar conclusions have recently been reported in conference abstracts by Sekizawa and Yasukōchi (1973) as well as by us (Stewart *et al.* 1973*a*).

Experimental Methods and Results

The samarium and lanthanum used were of 99.9% purity and the cadmium of 99.99% purity; they were obtained from Koch Light Laboratories Ltd, England. Stoichiometric portions of the metals were pressed into pellets and placed in a tantalum crucible which was sealed by welding under argon and heated at 1300°C for a few minutes. The compounds were examined metallographically and by X-ray powder diffraction. SmCd was found to be single phase and to possess the CsCl structure with a lattice constant of $3.789 \pm 0.002 \text{ \AA}$; previously reported values are 3.771 \AA (Iandelli 1960) and 3.765 \AA (Alfieri *et al.* 1967). The grain size was in the region of 50–100 μm . Very small quantities of the constituent metals (less than 1%) were found to have remained unreacted. Specimens of LaCd were prepared and examined with

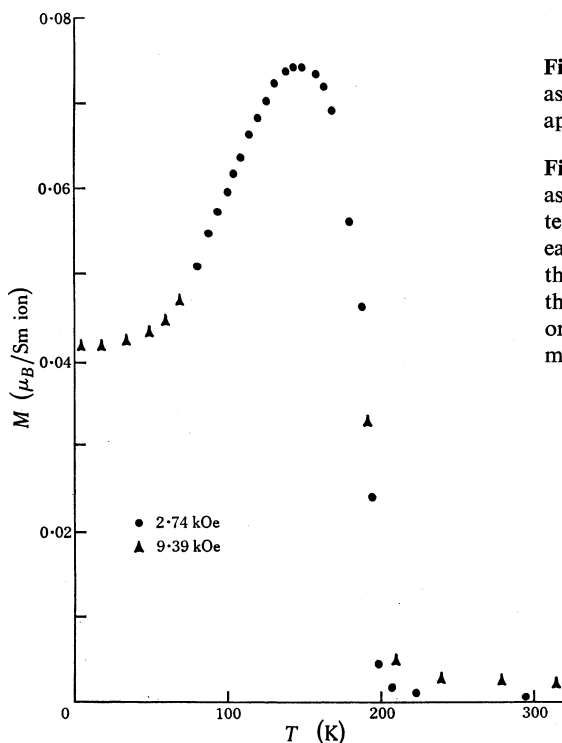


Fig. 1 (*left*). Magnetization M of SmCd as a function of temperature in two applied fields.

Fig. 2 (*below*). Magnetization M of SmCd as a function of applied field at three temperatures. The specimen was cooled to each temperature in the remanent field of the magnet (~ 50 Oe), which was larger than the demagnetizing field. Above the ordering temperature of 194 K the magnetization is proportional to the field.

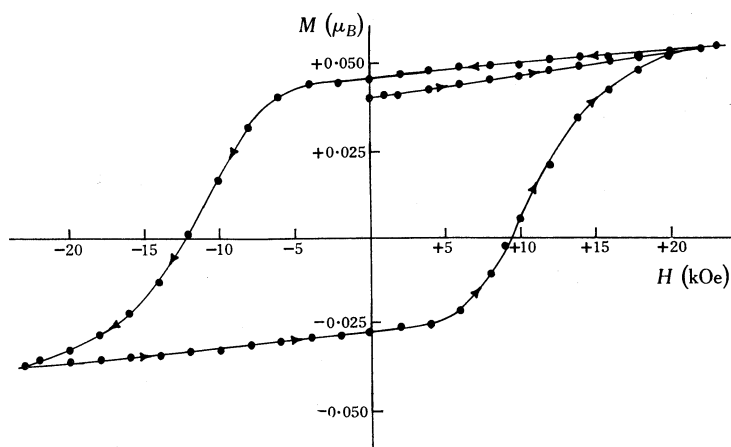
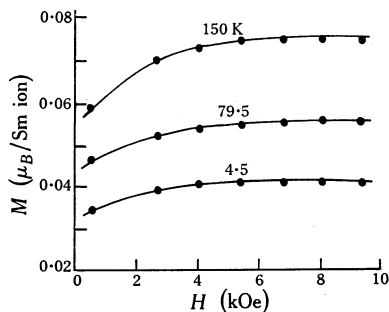


Fig. 3. Hysteresis loop of SmCd at 77 K. The specimen was cooled to this temperature in the remanent field of the magnet (~ 50 Oe). The demagnetizing field of a spherical specimen with a magnetization of $0.05 \mu_B$ per samarium ion would amount to 33 Oe.

similar results. We found no great difficulty in preparing these compounds, in contrast to Alfieri *et al.* (1967), who had to use large excesses of the rare earth in order to obtain the correct lattice structure. This may be due to the fact that we heated the metals well above their congruent melting points of 1010°C (SmCd) and 946°C (LaCd) (Bruzzone and Merlo 1973, personal communication), whereas the highest temperature which they used was 950°C .

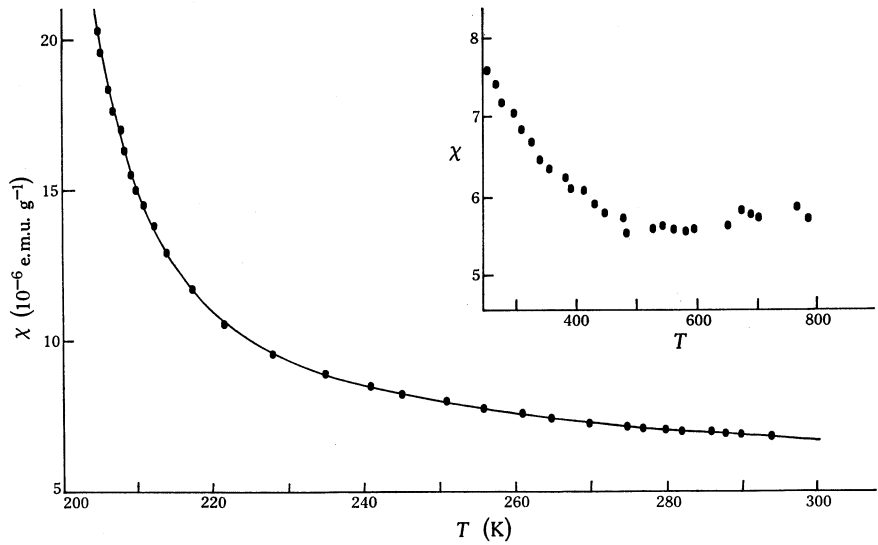


Fig. 4 (above). Plot of magnetic susceptibility χ of SmCd against temperature. The continuous curve is the best fit of equation (1) to the experimental points. The inset to the figure shows the susceptibility of SmCd above room temperature.

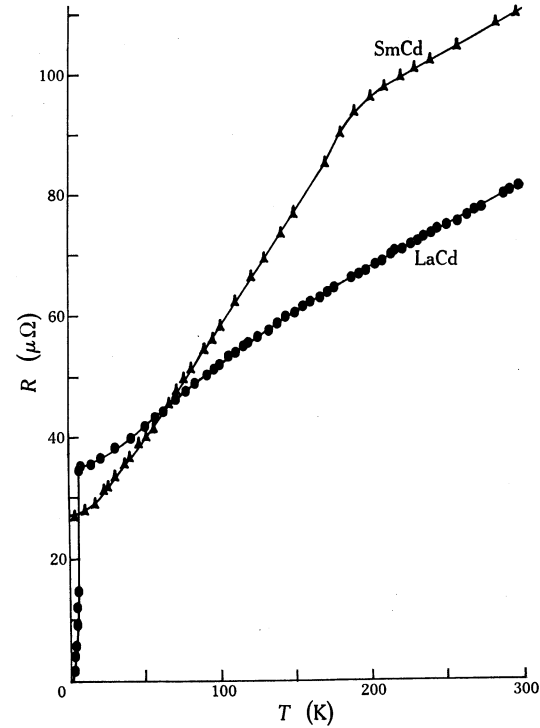


Fig. 5 (left). Resistances of SmCd and LaCd as a function of temperature. A resistance of $100 \mu\Omega$ is estimated to correspond to a resistivity of $\sim 25 \mu\Omega \text{ cm}$ for the SmCd specimen. The resistance of LaCd has been scaled so that the high temperature phonon slopes of the two materials are equal.

Most of the magnetic measurements were made with a Faraday magnetometer (Stewart and Rizzuto 1973) by methods described elsewhere (Stewart *et al.* 1973*b*). The susceptibility readings above room temperature were taken with a pendulum magnetometer of rather smaller sensitivity, and the hysteresis loop at 77 K, shown in Fig. 3, was determined using the vibrating sample magnetometer at the National

Standards Laboratory, CSIRO, Sydney. Measurements of the magnetization of SmCd against temperature, in two magnetic fields, are shown in Fig. 1. The magnetization is proportional to the field strength above 200 K but below this temperature it is nonlinear, as may be seen from Fig. 2. The points in this diagram were obtained by cycling the magnetic field between zero and the value at which the reading was taken until repeatability was obtained. The magnetization curve at 79.5 K was the same whether the specimen was cooled to that temperature in a field of 9.4 kOe or in the small remanent field of the magnet. The hysteresis loop of Fig. 3 shows that the coercive force of the material is of the order of 10 kOe and that the magnetization is still increasing at the highest field available (23 kOe). The loop is nonsymmetric, both because the specimen was cooled in the remanent field of the magnet (~ 50 Oe), which was larger than the estimated demagnetizing field of the specimen, and also because the applied field did not appear to be great enough to close the hysteresis loop completely. In other words, the loop shown in Fig. 3 is not the major hysteresis loop. The magnetization in low fields at 77 K is roughly $0.05 \mu_B$ per samarium ion; Sekizawa and Yasukōchi (1973) obtained a value of $0.032 \mu_B$. The magnetic ordering temperature was estimated to be 194 K by plotting the square of the magnetization against temperature just below the ordering point, and extrapolating it to zero magnetization.

The susceptibility of SmCd above 200 K is shown in Fig. 4. The LaCd compound was found to have a temperature-independent susceptibility of 0.23×10^{-6} e.m.u. g $^{-1}$ between 77 and 300 K.

It proved impossible to solder or spot-weld electrical leads to the compounds, so a device was constructed in which the specimen was pressed against a Perspex plate by four spring-loaded pointed steel pins. Two were used as current leads and two as voltage probes. The resistances of the compounds are shown in Fig. 5. From the dimensions of the SmCd specimen a resistance of $100 \mu\Omega$ was estimated to correspond to a resistivity of $25 \mu\Omega\text{cm}$ to within a factor of three. The resistance of the LaCd specimen has been scaled so that the high temperature phonon slopes of the two materials are the same. LaCd showed a broad transition to superconductivity which started just above 4.2 K (suggesting the presence of a small quantity of free lanthanum); the compound finally attained zero resistance at 2.64 K. The phonon part of the resistivity of this superconducting compound is convex upwards in accordance with the Fisk-Lawson (1973) rule.

Discussion

Above 150 K our magnetization data for SmCd are in qualitative agreement with those of Alfieri *et al.* (1967), but below this temperature these authors reported that the susceptibility, which they measured in a field of 4 kOe with a vibrating sample magnetometer, plunged downwards, becoming diamagnetic below 110 K. We are unable to suggest any explanation for the difference between their results and ours. From Fig. 5 it is seen that there is no sign of any anomaly in the resistivity in the region of 100 K that is indicative of a valence change or even of a transition to a state of different magnetic order. The resistivity is characteristic of a typical metallic ferromagnet. Above the ordering temperature of 194 K the resistivity varies linearly with temperature, due to the phonon contribution. At the ordering temperature a change of slope can be seen. It is a gradual change characteristic of a ferromagnet

(Colvin *et al.* 1960) and not the sharp discontinuity of slope characteristic of an antiferromagnet (Stewart 1973*a*). Below the ordering temperature the resistivity decreases uneventfully to its residual value with an almost linear slope above 30 K, not unlike that observed in the ferromagnet gadolinium (Colvin *et al.* 1960).

The resistivity, then, is consistent with SmCd being ferromagnetic, but the ordered moment of $0.05 \mu_B$ is much smaller than that associated with either the doublet or quartet levels of the samarium ion in a cubic crystal field. In fact, a conventional crystal field calculation carried out within the $J = 5/2$ manifold of states (Freeman and Watson 1962; Lea *et al.* 1962) made by placing two positive electronic charges at the eight cadmium sites which surround a samarium ion ($A_4 \langle r^4 \rangle = 52$ K, $A_6 \langle r^6 \rangle = -2$ K) shows that the crystal field ground state is the isotropic doublet with the quartet lying 47 K above it. If this is so, the exchange field, of strength 200 K, should strongly mix the two crystal field states to give a magnetic moment which is greater than that given by either of them alone.

One possible explanation is that the small bulk magnetization is due to the magnetic order being of a non-collinear type, e.g. a conical spiral, that does not allow the samarium moments to become parallel until a very large external magnetic field is applied. In this way the hysteresis loop of Fig. 3 can be understood in terms of normal domain growth, and the feature that the magnetization is still increasing above 20 kOe when the loop is nearly closed can be understood as being due to the samarium moments being forced into the direction of the magnetic field. The magnetization is expected to increase with the applied field due to the mixing of the $J = 7/2$ level into the $J = 5/2$ ground state (Stewart 1972*c*), but this effect is estimated to be about five times smaller than the one observed. At higher temperatures, the single-ion anisotropy will decrease rapidly (Callen and Callen 1966) and allow a more easy alignment of the moments by a field, so giving rise to the increase of magnetization just below the Curie point that is seen in Fig. 1. Conduction electron polarization is not capable of accounting for the large decrease in moment because, as we shall see below, it is of a sign which should give rise to a moment increase.

Alternatively, if the crystal field parameters are in fact much greater than those calculated on the basis of a point charge model (and there is at present no experimental evidence available concerning their magnitude), then it is possible that the anomalous magnetization curve might be explained on the basis of the effects of strong crystal fields on the Sm^{3+} ion, such as those that have recently been discussed by de Wijn *et al.* (1973). Although one expects $\langle S^z \rangle$ to increase monotonically with decreasing temperature in the magnetically ordered regime because the exchange field acts on the spin, it does not follow that the ionic magnetization $\langle L^z + 2S^z \rangle$ increases monotonically also.

Buschow (1973) has observed, in DyCd, a magnetization-temperature characteristic which is rather similar to that of SmCd. He also found that DyCd had an unusual irreversible hysteresis curve which he attributed to small antiferromagnetic regions where dysprosium atoms were substituting on cadmium sites and vice versa. However, the hysteresis curve of SmCd appears to be comparatively normal, at least up to 23 kOe, and it does not seem necessary to invoke Buschow's hypothesis to explain the results reported here.

It has been shown elsewhere (Stewart 1972*a*) that if crystal field splittings can be neglected then, in the mean field approximation, the paramagnetic susceptibility $\chi(T)$

of a metallic samarium compound should be of the following form below room temperature:

$$\chi(T) = \chi_0 + D/(T-\theta). \quad (1)$$

The susceptibility of SmCd shown in Fig. 4 is seen to be in good agreement with the best fit of this expression to the experimental points. The fit is given by the continuous curve which is equation (1) with the parameters $\chi_0 = 5.44 \times 10^{-6}$ e.m.u. g^{-1} , $\theta = 195.7$ K and $D = 139 \times 10^{-6}$ e.m.u. g^{-1} . This value of D corresponds to an effective paramagnetic moment of $0.54 \mu_B$, which is close to the value of $0.53 \mu_B$ obtained by Sekizawa and Yasukōchi (1973).

Since an analysis of the parameters of equation (1) has been given twice before (Stewart 1972*a*, 1973*b*), in this paper we shall only quote the results of the analysis. Starting from the expression for the susceptibility χ_b of bare SmCd (i.e. with no interactions and no matrix susceptibility),

$$\chi_b = (2.63 + 340/T) \times 10^{-6} \text{ e.m.u. } g^{-1}, \quad (2)$$

we obtain $J(0)\rho = -0.04$, $T_\theta = 157$ K, and that the temperature-independent component of the susceptibility due to the samarium ions is 2.77×10^{-6} e.m.u. g^{-1} . Here $J(0)$ is the strength of the resultant exchange interaction between the 4f spin S and a conduction electron spin s , which may be written schematically as $-2J(q)S.s$; T_θ is the paramagnetic Curie temperature which the material would have if there were no admixture of the $J = 7/2$ level into the $J = 5/2$ ground state; and ρ is the conduction electron density of states for one spin direction.

If $|J(0)\rho|$ is calculated from a spin disorder resistivity of $10 \mu\Omega \text{ cm}$ according to the theory of Kasuya (1956), assuming free conduction electrons and making the assumption that $J(q) = J(0)$, a value close to 0.03 is found, but this good agreement is probably a coincidence.

If ρ is taken to have the value corresponding to the Pauli susceptibility of LaCd ($\sim 0.47 \text{ eV}^{-1}$), $J(0)$ comes to -0.09 eV , larger in magnitude than the $+0.04 \text{ eV}$ of the free ion s-f interaction and, furthermore, negative. This is surprising in view of the fact that negative values are usually only obtained from rare earth ions situated in transition metal-like matrices in which the transition metal ions come from the second half of the transition series (Taylor 1971). A qualitative explanation for this systematic behaviour has been proposed by Campbell (1972). Cadmium is a simple metal and one would expect the resulting $J(0)$ to be small and positive. Alfieri *et al.* (1967) indeed found that the saturation magnetization of GdCd was less than the free ion value (which would be consistent with a negative $J(0)\rho$) but, as they pointed out, this could be merely a consequence of their magnetic field not being strong enough to achieve saturation. Little information can be gained from the nominal paramagnetic moment of the non S-state RCd compounds; some are greater than the free ion value, others are less. This is probably associated with the difficulty of obtaining the correct stoichiometry which Alfieri *et al.* discussed.

It was found in the above analysis that the samarium contribution to the temperature-independent part of the susceptibility was 2.77×10^{-6} e.m.u. g^{-1} . If this is subtracted from the value obtained from the Curie-Weiss fit of 5.44×10^{-6} e.m.u. g^{-1} , the susceptibility attributable to the matrix material is then 2.67×10^{-6} e.m.u. g^{-1} , which is much larger than the susceptibility of LaCd (0.23×10^{-6} e.m.u. g^{-1}). A

possible explanation for the discrepancy may be the neglect of the effects of the crystal field on the samarium ion.

The susceptibility of SmCd above room temperature is shown in the inset to Fig. 4. The susceptibility minimum that is characteristic of tripositive samarium (Van Vleck 1932) can be seen to be present.

If T_θ or the magnetic ordering temperature T_c is divided by $(g-1)^2J(J+1)$, the quantities obtained should be characteristic of the interionic exchange interactions which exist in each compound. It can be seen in Fig. 6 that these are not constant throughout the series of the RCd compounds but decrease continuously with atomic number. This leads us to speculate that in the RCd compounds the exchange interaction might be due to something other than the RKKY indirect exchange via the conduction electrons, which might not be expected to vary so greatly with atomic number. A possible mechanism might be direct exchange by means of 4f-4f overlap or overlap through the rare earth 5s and 5p shells.

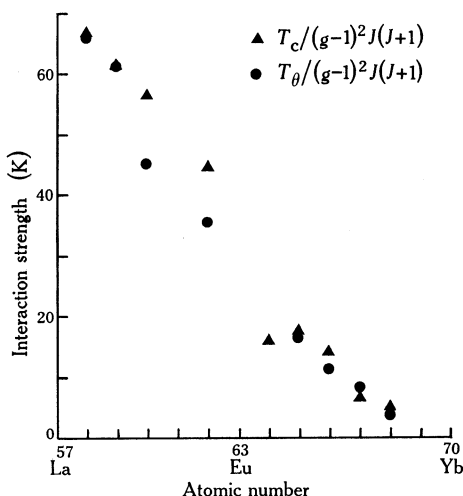


Fig. 6. Interionic exchange interaction strength for the RCd compounds, as measured by the quotients of the magnetic ordering temperature T_c or the paramagnetic Curie temperature T_θ and $(g-1)^2J(J+1)$, plotted against atomic number. The data for the compounds, apart from SmCd, were obtained from Alfieri *et al.* (1967). TmCd has a cooperative Jahn-Teller transition at 3.2 K (Luthi *et al.* 1973).

As the rare earth ionic radius decreases with atomic number (the lanthanide contraction), the distance between the rare earth atoms tends to change less than it would if the cadmium atoms were absent, because the cadmium atoms, of course, do not alter their ionic radii. The effect of decreasing the radii of the rare earths, while not decreasing the lattice constant to a comparable extent, would tend to reduce the overlap between the rare earths and so reduce the strength of the exchange interaction as the atomic number increased.

Conclusions

Metallurgically satisfactory specimens of SmCd and LaCd have been prepared and measurements have been made of their magnetizations and resistivities. No evidence has been found of the valence change at 110 K in SmCd which was suggested in previous work by Alfieri *et al.* (1967), although a decrease in the bulk magnetization has been observed at this temperature. Possible explanations for this effect were suggested which involved a non-collinear spin structure and a strongly temperature-dependent magnetocrystalline anisotropy or strong crystal field effects. The spontaneous

magnetization at 77 K corresponded to about $0.05\mu_B$ per samarium ion. Above the Curie point of 194 K the susceptibility of SmCd obeyed a Curie-Weiss law, in accordance with a recent theory (Stewart 1972a). LaCd has been found to be a Pauli paramagnet with a broad superconducting transition in the region of 3 K.

Acknowledgments

We should like to thank L. G. Parry, C. Rizzuto and K. N. R. Taylor for valuable discussions and suggestions. We are particularly grateful to R. K. Day for his help with the use of the vibrating sample magnetometer at the National Standards Laboratory, CSIRO.

References

- Alfieri, G. T., Banks, E., Kanematsu, K., and Ohoyama, T. (1967). *J. phys. Soc. Japan* **23**, 507.
 Bruzzone, G., and Merlo, F. (1973). *J. less-common Metals* **30**, 303.
 Buschow, K. H. J. (1973). *J. appl. Phys.* **44**, 1817.
 Callen, H. B., and Callen, E. (1966). *J. Phys. Chem. Solids* **27**, 1271.
 Campbell, I. A. (1972). *J. Phys. F* **2**, L47.
 Colvin, R. V., Legvold, S., and Spedding, F. H. (1960). *Phys. Rev.* **120**, 741.
 Fisk, Z., and Lawson, A. C. (1973). *Solid State Commun.* **13**, 277.
 Freeman, A. J., and Watson, R. E. (1962). *Phys. Rev.* **127**, 2058.
 Iandelli, A. (1960). *Atti. Accad. naz. Lincei Rc.* **29**, 62.
 Kasuya, T. (1956). *Prog. theor. Phys., Kyoto* **16**, 58.
 Lea, K. R., Leask, M. J. M., and Wolf, W. P. (1962). *J. Phys. Chem. Solids* **23**, 1381.
 Luthi, B., Mullen, M. E., Andres, K., Bucher, E., and Maita, J. P. (1973). *Phys. Rev. B* **8**, 2639.
 Maple, M. B., and Wohlleben, D. (1971). *Phys. Rev. Lett.* **27**, 511.
 Nickerson, J. C., White, R. M., Lee, K. N., Bachmann, R., Geballe, T. H., and Hull, G. W. (1971). *Phys. Rev. B* **3**, 2030.
 Sekizawa, K., and Yasukōchi, K. (1973). Abstract from Conf. on Magnetism, Moscow, 1973.
 Stewart, A. M. (1972a). *Phys. Rev. B* **6**, 1985.
 Stewart, A. M. (1972b). *J. Phys. F* **2**, L44.
 Stewart, A. M. (1972c). *Phys. Status Solidi (b)* **52**, K1.
 Stewart, A. M. (1973a). *Solid State Commun.* **12**, 455.
 Stewart, A. M. (1973b). *J. Phys. F* **3**, 1024.
 Stewart, A. M., Costa, G., and Olcese, G. (1973a). Abstract from Conf. on Magnetism, Boston, 1973.
 Stewart, A. M., Dunlop, J. B., Andreone, D., and Costa, G. (1973b). *J. Phys. Chem. Solids* **34**, 1939.
 Stewart, A. M., and Rizzuto, C. (1973). *Cryogenics* **13**, 150.
 Taylor, K. N. R. (1971). *Adv. Phys.* **20**, 551.
 Van Vleck, J. H. (1932). 'The Theory of Electric and Magnetic Susceptibilities' (Oxford Univ. Press).
 de Wijn, H. W., Van Diepen, A. M., and Buschow, K. H. J. (1973). *Phys. Rev. B* **7**, 524.