

contrast to the behaviour in Al-Si alloys where air-cooling drastically reduces the precipitation of Si [5].

**References**

1. M. HANSEN and K. ANDERKO, "Constitution of Binary Alloys" (McGraw-Hill, New York, 1958) p. 110.
2. S. P. BHAT, T. R. RAMACHANDRAN and A. K. JENA, *J. Mater. Sci.* **9** (1974) 1759.
3. D. P. LAHIRI, T. R. RAMACHANDRAN and A. K. JENA, *Trans. Ind. Inst. Metals*, **27** (1974) 360.
4. T. FEDERIGHI, in "Lattice Defects in Quenched

- Metals" (Academic Press, New York, 1965) p. 217.  
 5. H. S. ROSENBAUM and D. TURNBULL, *Acta Met.* **6** (1958) 653; **7** (1959) 664.

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*Temperature dependence of magnetic anisotropy*

The magnetic anisotropy of most ferromagnetics is a rapidly varying function of temperature. A number of workers [1, 2] have theoretically shown it to be related to the magnetization by

$$\frac{K_1(T)}{K_1(0)} = \left[ \frac{M(T)}{M(0)} \right]^n$$

where  $K_1(T)$ ,  $K_1(0)$ ,  $M(T)$  and  $M(0)$  are the anisotropy constants and magnetization at temperatures  $T$  and 0 K respectively, and  $n = 10$ .

Charap and Weiss [3] showed that this tenth power law should hold for all ferromagnetics with cubic lattices. However, these theories have not been substantiated by experiment. Iron gave a third or fourth power law at low temperature changing to a ninth at higher temperatures [4], while nickel followed a much modified tenth power type relation [5]. An alloy of 3% Si-Fe gave a third or fourth power changing to a ninth power at higher temperatures [6].

The different methods used in the theoretical calculations all involve basic assumptions of the coupling between neighbouring electron spins. In the limit of complete correlation between spins theory gives a tenth power law, while for the limit of no correlation a sixth power has been predicted [7, 8]. This spin correlation has been described as extending over a region containing an atom and several shells of nearest neighbours [9], and evidence of spin ordering in regions of this size has been obtained by neutron diffraction [10].

It is well known that Ni-Fe alloys of approximately 75 at.% Ni undergo an atomic order-disorder transformation when given an appro-

appropriate heat-treatment. This transformation has a marked effect on most magnetic properties. In particular, the development of atomic order increases the Curie temperature and the saturation magnetization [11]. Because of the dependence of these parameters on spin-order it has been proposed that atomic order and spin order are inter-related [12]. In particular, changes in short range atomic order should alter the amount of spin order in the regions described in [9]. In this investigation specimens were obtained in

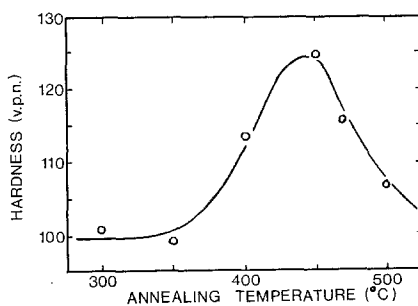


Figure 1 Relation between hardness and annealing temperature (5 h at each temperature).

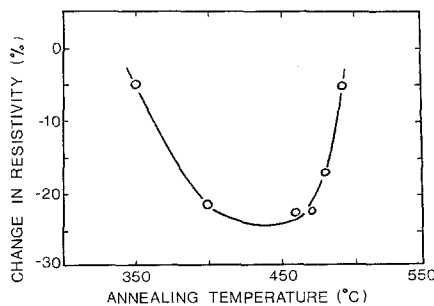


Figure 2 Relation between change in resistivity and annealing temperature (100 h at each temperature).

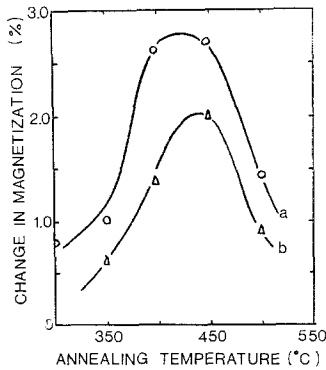


Figure 3 Relation between change in magnetization and annealing temperature (5 h at each temperature). (a) Measurements at 77 K; (b) measurements at 293 K.

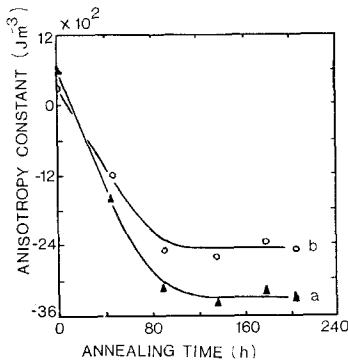


Figure 4 Relation between first anisotropy constant and time of anneal at 440°C. (a) Measurements at 77 K; (b) measurements at 293 K.

various states of atomic order, and hence spin order. The magnetic anisotropy and magnetization at 293 and 77 K were measured and a power law computed for each state.

The critical temperature for superlattice formation depends on composition and, firstly, the ordering range of the 75 at.% Ni alloy was investigated. The optimum heat-treatments were determined from measurements of hardness and resistivity on polycrystalline specimens using the conventional Vickers hardness machine and the four probe potentiometric method respectively. Specimens were disordered by annealing for 2 h in dry hydrogen at 1000°C, followed by a slow cool to 600°C and then a rapid quench to room temperature. Atomic order was developed by annealing for given periods in the temperature ranges shown in the diagrams. Figs. 1 and 2 are in reasonable agreement with published data [13, 14] and show that maximum changes

TABLE I

Specimen	Anisotropy ratio	Magnetization ratio	<i>n</i>
Quenched	0.504	0.934	10.0
20 h anneal	0.738	0.934	4.5
45 h anneal	0.750	0.934	4.2
90 h anneal	0.782	0.934	3.6

occurred at an annealing temperature of 440°C, somewhat below the temperature of 490°C usually used in experiments of this type.

The increase in magnetization, as measured by a modified ballistic technique [15], was completed in less than 5 h annealing. Because of the small change with atomic order (Fig. 3), specimens were measured in the disordered and equilibrium ordered state only. The ratio of the magnetization at 293 K to that at 77 K for these states gave a value of 0.934, constant to within the limits of experimental error. Anisotropy was measured on single crystal discs using a sensitive torque magnetometer [16]. From Fig. 4 the ratio of anisotropies at the two temperatures was calculated for different degrees of atomic order and varied quite markedly, as shown in Table I. Aoyagi [17] has investigated the relation between anisotropy and order for specimens of Ni-Fe-Mo at temperatures of 293 and 77 K. For an alloy of 78.8 at.% Ni and 1.35 at.% Mo he obtained curves similar to those of figure 4. Unfortunately, he did not compare the values of anisotropy at the two different temperatures, but inspection of his graphical data indicate this ratio is not the same for disordered and ordered specimens.

Using the relation

$$\frac{K_1(293 \text{ K})}{K_1(77 \text{ K})} = \left[ \frac{M(293 \text{ K})}{M(77 \text{ K})} \right]^n$$

and the experimental values obtained, the exponent *n* was calculated for various states of order. While this equation is not truly representative of the theoretical law, it does give an indication of the effect of atomic order on the power law.

Table I shows a value of approximately ten is obtained for a completely disordered specimen but this decreases with the formation of order until a value of about four is observed in the equilibrium state. Owing to the small difference between X-ray scattering factors of the disordered and ordered matrix of Ni-Fe, it is not possible to quote our results as a function of the

atomic order parameter. However, the ordering kinetics of Ni<sub>3</sub>Fe formed by annealing have been well established by Iida [18]. He has shown that short range order is completed after about 10 h annealing, while long range order requires about 60 h. Our results show that  $n$  changes markedly after short anneals, but annealing times of over about twenty hours have little or no effect. This indicates primarily a short range order dependence: as to be expected if the regions of spin correlation are as described earlier.

If the degree of spin order is assumed to increase with that of atomic order (as indicated by Curie temperature and magnetization results) then the present work appears to be in complete contrast with theoretical predictions. It is interesting to note, however, that the experimental results obtained by Graham [4, 6] using Fe and Fe-Si gave a fourth power law at low temperatures rising to a ninth power at higher temperatures. Spin order decreases with rise in temperature, thus Graham's results imply that  $n$  decreases with the formation of spin order, in agreement with our experiments.

## References

1. L. PAL, *Acta Phys. Acad. Sci. Hung.* **3** (1954) 294.
2. E. A. TUROV and A. I. MITSEK, *Sov. Phys. J.E.T.P.* **10** (1960) 801.

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3. S. H. CHARAP and P. R. WEISS, *Phys. Rev.* **116** (1959) 1372.
4. C. D. GRAHAM, *ibid* **112** (1958) 1117.
5. W. J. CARR, *ibid* **109** (1958) 1971.
6. C. D. GRAHAM, *J. Appl. Phys.* **31** (1960) 1505.
7. F. KEFFER, *Phys. Rev.* **100** (1955) 1692.
8. J. H. VAN VLECK, *ibid* **52** (1937) 1178.
9. C. ZENER, *ibid* **96** (1954) 1335.
10. C. G. SHULL and M. K. WILKINSON, *ibid* **96** (1954) 1439.
11. M. V. DEKHTYAR, *Fiz. Met. i Metall.* **3** (1956) 55.
12. T. TAOKA and T. OHTSUKA, *J. Phys. Soc. Japan* **9** (1954) 712.
13. R. G. DAVIES and N. S. STOLOFF, *Acta Met.* **11** (1963) 1347.
14. E. JOSSO, *Rev. de Met.* **69** (1952) 727.
15. T. F. FOLEY, D. A. LEAK, R. A. NEWBURY, A. R. POMEROY, A. R. MATTHEWS and M. V. TOMKEIEFF, *J. Iron Steel Inst.* **208** (1970) 147.
16. R. J. WILLEY, A. R. LANFEAR and D. A. LEAK, *J. Phys. E.* **5** (1972) 305.
17. K. AOYAGI, *Jap. J. Appl. Phys.* **4** (1965) 551.
18. S. IIDA, *J. Phys. Soc. Japan* **10** (1955) 769.

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## Thermal expansion anisotropy of a $\text{LiY}_{0.5}\text{Er}_{0.5}\text{F}_4$ single crystal

Interest has recently been renewed in the use of certain mixed fluoride single crystals as laser host lattices by the recognition that, when doped with holmium ( $\text{Ho}^{3+}$ ), stimulated emission can be obtained at a wavelength of 2.06  $\mu\text{m}$ . This radiation is somewhat safer to the eye than that emitted at 1.06  $\mu\text{m}$  in corresponding neodymium ( $\text{Nd}^{3+}$ ) based systems.

Compounds on the pseudo-binary section  $\text{LiY}_{1-x}\text{Er}_x\text{F}_4$  ( $0 \leq x \leq 1$ ) of the ternary system  $\text{LiF}-\text{YF}_3-\text{ErF}_3$ , have proved to be particularly efficient hosts for the  $\text{Ho}^{3+}$  ion, especially when sensitized with  $\text{Tm}^{3+}$  [1]. The end component,  $\text{LiYF}_4$ , of the series possesses the body-centred tetragonal structure ( $a = 5.175 \text{ \AA}$ ,  $c = 10.74 \text{ \AA}$ ) of the Scheelite group [2], and recent work in the authors' laboratories has shown that the tetragonal symmetry is retained across the entire section [3]. Crystals with a low symmetry such

as this often exhibit defects such as dislocation low-angle boundaries, twins and/or cracks, when produced as single crystals by melt growth processes such as the Czochralski or Stockbarger techniques [4, 5]; defects of this type are obviously detrimental in optical applications.

One of the major causes of these particular defects in low symmetry crystals is the stress arising from anisotropic thermal contraction in the crystal while cooling to room temperature subsequent to growth. For some of these materials, a knowledge of the thermal expansion characteristics is known to be very important in determining the optimum crystal growth direction for minimizing the stresses arising from thermal anisotropy [6, 7]. The present note reports the thermal expansion data obtained for a typical tetragonal fluoride which is of interest as a laser material.

Dilatometric measurements have been performed on a cubic specimen (cube edge  $\sim 4 \text{ mm}$ ) cut from a crystal grown by the Stockbarger