calcium and magnesium in quantities less than one part per million each. The chemical analyses of the formed samples showed that they were within 5% of ideal. The standard deviation in the measured X-ray intensity was about ±5%. The procedure of taking the fractional intensities (Subramanyam, 1971) obviates the necessity for absorption and temperature factor corrections. The measured value of the canted-antiferromagnetic susceptibility of α-Fe_2O_3 is in excellent agreement with the reports of Bradley (1971) and others. The maximum error in the above measurement was ±5% with each of the input admittances contributing ±2·5% to the overall error.

The present results do not necessarily show that the removal of $(NiO)_x$ from the spinel structure of $NiFe_2O_4$ causes precipitation of α-Fe_2O_3. However, it may be reasonable to claim that for specimens having compositions $x \simeq 1{\cdot}0$ and $x \simeq 0{\cdot}0$, traces of α-Fe_2O_3 and Fe_3O_4 respectively could be present (Neel, 1949).

To conclude, the gradual degradation of the cubic spinel phase in polycrystalline $Ni_xFe_2O_4$ (x = 1·0 to 0·1) has been doubly confirmed by two independent methods of measurement and further, the sharp ferrimagnetic–antiferromagnetic transition occurring at x = 0·1 in the transformation indicates a change in crystal symmetry.

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Acta Cryst. (1979). A**35**, 503–505

Errors in diffuse scattering measurements associated with Bragg diffraction.*

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(*Received* 31 *July* 1978; *accepted* 11 *December* 1978)

Abstract

Multiple-scattering processes are identified as a source of error in diffuse-scattering measurements on solid solutions. Of the various methods used to account for such effects, a multiple-regression analysis using reduced weights for measurements having maximum interference appears to be the most satisfactory.

It is well known that when diffraction measurements are made on single crystals a second reciprocal-lattice point may simultaneously intersect the Ewald sphere. The first consequence of this is that the scattering from the second lattice point will attenuate the incoming beam, leading to a loss in intensity of the point under study. Secondly, the diffracted beam from this secondary point will also satisfy the Bragg condition for diffraction from a third reciprocal-lattice point, which will return intensity into the primary diffracted beam. These two effects are collectively known as the Renninger effect after their discoverer (Renninger, 1937).

Even before Renninger's work the importance of multiple scattering in studies of Compton scattering was pointed out by DuMond (1930). The methods for adequately accounting for this effect were developed more recently, and, following Halonen, Epstein, Tanner & Williams (1976), the problem appears to be reasonably well solved, although the methods are not particularly simple to apply. It has been recognized that multiple scattering is also important in the scattering from amorphous substances, where the effect is primarily limited to a 2θ dependence. Specifically, for silica the double scattering accounts for 8% of the intensity (Warren & Mozzi, 1966). The effect has also been observed (Sparks & Epperson, 1978) in the thermal diffuse scattering of graphite. In measurements of Compton scattering up to 15% of the photons have been doubly scattered (Halonen *et al.*, 1976).

To the author's knowledge, multiple-scattering processes in diffuse-scattering measurements from alloys have not been definitely identified. It was suggested (Williams, 1974) that part of the error in the intensity for a copper–aluminum alloy arose from this effect. Here I demonstrate that this suggestion is correct and give methods of eliminating or correcting for the effect.

Fig. 1 shows the geometry for measuring the diffuse scattering from point *hkl*, where S_0 and S are the primary and diffracted beam vectors. The circles represent the intersection of the two Ewald spheres with the S_0–S plane. If a reciprocal-lattice point, *HKL*, intersects the left sphere, then there will be an additional attenuation of the incoming beam due to Bragg diffraction. Similarly, the diffracted beam would be reduced in intensity if a reciprocal-lattice point intersected the right sphere. This loss of intensity is a form of extinction. As the sample is rotated around the *hkl* direction a whole set of reciprocal-lattice points would pass through these spheres.

A second part of the effect is that some intensity is returned to the diffracted beam by the diffuse scattering by the point $h-H$, $k-K$, $l-L$ of the intensity diffracted by point *HKL*. There is a second analogous contribution from the point $H-h$, $K-k$, $L-l$, where the Bragg scattering of the diffuse intensity occurs.

* Research sponsored by Materials Sciences, US Department of Energy, under contract W-7405-eng-26 with the Union Carbide Corporation.

0567-7394/79/030503-03$01.00

In Fig. 2 I have plotted the positions where the various low-order Bragg diffractions take place for the $l = 0$ plane. Because these observations are taken in a mirror plane both the incident beam and the diffusely scattered beam are simultaneously attenuated by the same Bragg diffraction to double the effect. The strength of the Bragg diffraction decreases strongly with higher-index reflections, and I have indicated this by the line widths.

Three factors must be considered in comparing this figure with Fig. 3, which gives the observed intensity less the calculated intensity for a Cu–Al alloy (Williams, 1974). Intensity will be reduced along the lines in Fig. 2 by the competitive Bragg diffraction. Secondly, multiple scattering will return intensity of a distinctly different character to these regions. Thirdly, the calculated intensity will fit the observed intensity within the limitations imposed by the symmetry of the mathematical formulation. Thus, one can only expect that the intensity differences will tend to be larger along these lines but will not show a net positive or negative tendency. Qualitatively, the differences do appear to be larger in the vicinity of these lines in support of my earlier conclusion. As an example, the largest differences between 220 and 400 coincide almost exactly with positions where 220 diffraction occurs. The differences near the reciprocal-lattice points are also associated with the problem of resolution and need not be the sole result of multiple scattering.

While the correction for multiple scattering in these data is desirable, it would not be expected to result in substantially different parameters because the original error estimates are rather small. However, any correction that reduces the differences in intensity would reduce the error estimates by a similar amount. It is clear from Fig. 2 that such errors will affect the higher-order α's more than the lower ones. This would account for the residual error of 0·005, which appears to be present in α's for the higher-order shells (Williams, 1978).

To a first approximation the fractional loss in the diffuse intensity for a given Bragg reflection would be independent of θ but the amount of intensity returned to the diffracted beam should increase with θ. The increase results because as *hkl* becomes longer the vector $H-h$, $K-k$, $L-l$ becomes shorter and thus represents regions of stronger diffuse scattering. The observed intensity for the copper–aluminum data showed a definite tendency to be more positive than the calculated intensity for the highest values of θ which may have been a result of this effect.

If one is using the Borie & Sparks (1964) separation method for the data reduction, the only way in which this problem could be handled would appear to be the graphical examination of the data in the regions where the multiple scattering is strongest and making those adjustments that seem in order.

If one rotates a sample around its normal when this coincides with the *hkl* vector, then the presence of multiple scattering would be observed as intensity fluctuations. This is the method used (Cole, Chambers & Dunn, 1962) for studying the Renninger effect. Data obtained with the reciprocal-lattice points furthest from the spheres of reflection would be the most reliable. The attractiveness of this method is that one can get a direct measure of the magnitude of the effect. An adequate mapping of the diffuse intensity would require ten or so samples. Even if one were using only a single sample, an examination by this method is advisable, for this would indicate the importance of such corrections.

In using a multiple-regression analysis it is highly desirable to obtain data over a large volume in reciprocal space (Williams, 1972, 1974). By using lower weights for observations that are affected by multiple scattering one may proceed with the data analysis without any additional complications. Further, by examining how well the data are

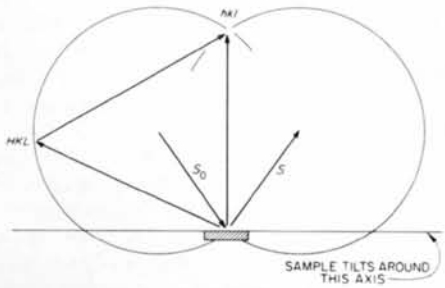

Fig. 1. Diffraction geometry. When a reciprocal-lattice point *HKL* intersects the Ewald sphere the intensity will be reduced by the Bragg diffraction. This diffracted beam may also scatter diffuse intensity back into the primary scattering direction.

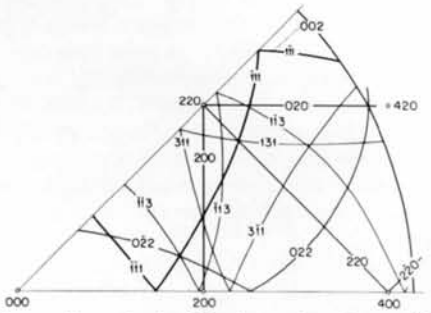

Fig. 2. The positions in the *hk*0 plane where Bragg diffraction by the indicated reflections takes place. This figure applies to the measurements for the Cu–Al alloy, but the frequency of such diffraction is characteristic of all such measurements.

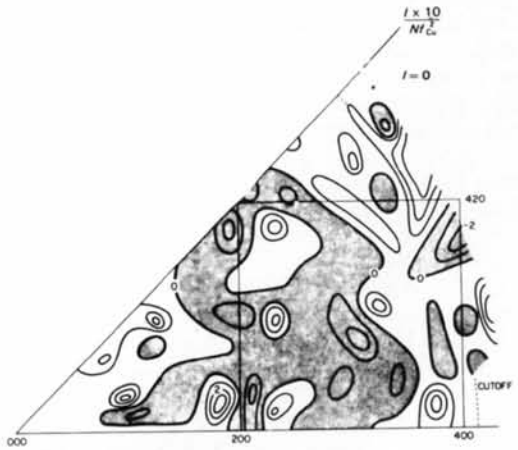

Fig. 3. The difference between the observed and the calculated intensity for a Cu–Al alloy. The data-reduction method is such that the positions of maximum Bragg scattering should correspond approximately to differences of larger magnitude, regardless of sign.

fitted *versus* the degree of weighting one can evaluate the importance of multiple scattering and its effect on the calculated parameters. Also, one can determine the relative reliability of data from different positions in reciprocal space. Because this method is so simple and powerful it is unquestionably the preferred approach.

It is presumably possible to treat the problem analogously to its treatment for Compton scattering although it is much more complex. A considerable computational effort would also be required (Halonen *et al.*, 1976). Our conclusion is that this approach is so difficult and subject to such uncertainties that it surely should be avoided. It should be pointed out that in certain cases, as for Compton scattering, multiple scattering cannot be eliminated so corrections are necessary; whereas, for diffuse scattering from crystalline solids, the data that are used need not be degraded by this effect.

In summary, I have shown that multiple-scattering processes are important in diffuse-scattering measurements. Data reduction by a multiple-regression analysis can handle the problem most satisfactorily.

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Specific heat and compression curves of erbium.

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(*Received* 3 *April* 1978; *accepted* 21 *December* 1978)

Abstract

Simple models for the thermal expansion of erbium, and for deducing the magnetic energy from the specific heat, are shown to give an approximate account of the facts. Values are given for the energy of magnetic ordering and the magnetic entropy.

1. Introduction

The heavy rare-earth metal erbium exhibits a rather complex magnetic ordering at low temperatures, which has a pronounced effect on the specific heat. Below a Néel point at 85 K the moments vary sinusoidally along the c axis, and below about 53 K the moments in the basal plane develop a helicoidal ordering. Er is ferromagnetic below 20 K, the helical arrangement of the spins in the basal plane being retained.

We present here calculations for erbium using the nearest-neighbour central-force model proposed by Srinivasan & Ramji Rao (1965), which has earlier been employed to study the lattice dynamics and thermal expansion of erbium (Ramji Rao & Ramanand, 1977). We compute the variation of the lattice parameters with pressure and find good agreement with experiment. We then determine the lattice heat capacity using the central-force model. Subtracting this, and an estimate of the electronic heat capacity, from the specific heat as determined experimentally we obtain a magnetic contribution. This in turn has been used to calculate the total energy of magnetic ordering, the magnetic contribution to the change in entropy due to ordering and an effective exchange parameter of Er.

2. Effect of hydrostatic pressure on the lattice parameters and volume of erbium

We have followed the method suggested by Thurston (1967) who has derived an expression for the change in the lattice parameter with application of pressure. The usual expression obtained by truncating the power series after the quadratic term is not suitable for extrapolation beyond a few tens of kilobars.

Thurston's extrapolation formula for the principal stretches λ_i ($i = 1, 2, 3$), which is consistent with a linear pressure dependence of the bulk modulus, is

$$\lambda_i = (B/B_0)^{-B_0^2 y_{i0}/(B_0')^2} \exp[(a_i + B_0 y_{i0}/B_0')P]. \quad (2.1)$$

For a uniaxial crystal $\lambda_1 = \lambda_2 = \lambda_\perp$ and $\lambda_3 = \lambda_\parallel$, and equation (2.1) can be written for the two cases:

$$\begin{aligned} a/a_0 = \lambda_\perp &= (B/B_0)^{-B_0^2 y_{\perp 0}/(B_0')^2} \exp[(a_\perp + B_0 y_{\perp 0}/B_0')P], \\ c/c_0 = \lambda_\parallel &= (B/B_0)^{-B_0^2 y_{\parallel 0}/(B_0')^2} \exp[(a_\parallel + B_0 y_{\parallel 0}/B_0')P]. \end{aligned} \quad (2.2)$$

a/a_0 and c/c_0 are the compression ratios of the lattice parameters, B is the bulk modulus at pressure P, B_0 and

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