

Broadening of resonance lines by charged dislocations

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Received 16 October 1973

Abstract. It is shown that the random electric fields of charged dislocations in insulators should cause appreciable broadening of sharp resonance lines such as spin-resonance signals. The degree of broadening is very sensitive to the screening of the dislocations by charged point defects. Since the shape of the inhomogeneously broadened resonance line monitors the distribution of the internal fields, the lineshape can be used to deduce properties of the charged dislocations, like their charge per unit length and the degree of screening. Quantitative calculations are presented which suggest that spectroscopic methods, notably spin resonance, should provide a convenient method of investigating charged dislocations.

1. Introduction

Dislocations in insulators or semiconductors may be electrically charged. In insulators the charge is associated with jogs and bound vacancies (for a recent survey see Whitworth 1973); in semiconductors, trapped carriers and impurities may play a rôle.

The measurement of the charge on the dislocation and of the effects of screening has always caused technical problems in the past. Here we discuss the application of methods used widely in related areas, namely the use of point defects with sharp resonance lines to monitor the random internal fields from the dislocation charges. The general area of inhomogeneous broadening of this sort has been reviewed recently (Stoneham 1969, 1971). Applications to the strain fields of dislocations (Stoneham 1966, 1970) and to the electric fields of charged point defects (Mims and Gillen 1966) are among those particularly closely related to the present work. Roitsin (1972) has recently reviewed much work on electric fields in solids. In the present paper we derive expressions for the effects of interest, and show that measurements of this sort are potentially of more than adequate sensitivity to give useful information, and should be easy to apply.

2. Theory of internal fields of charged dislocations

The basic ideas are very simple. An array of charged dislocations, plus their screening clouds, produce electric fields which vary from place to place in the crystal. Suppose there is a point defect present which has a sharp resonance line, such as an electron-spin resonance or an optical zero-phonon line, whose energy is changed by an electric field. Then the observed, inhomogeneously-broadened, line monitors the distribution of the internal electric fields. The lineshape and width then contain information about the sources of the electric field, their distribution and charges.

2.1. Basic theory

This approach can be made quantitative (see, for example, Stoneham 1969). Suppose the point defects whose resonance lines are observed have a transition energy $\hbar\omega$ which shifts linearly with applied field E :

$$\hbar\omega = \hbar\omega_0 + \hbar\omega_1\epsilon \quad (2.1)$$

$$\epsilon = \sum_{i=x,y,z} \alpha_i E_i / E_0. \quad (2.2)$$

Here E_0 is some arbitrary characteristic field, and the $\hbar\omega_1\alpha_i$ are coupling coefficients determined from separate experiments using a uniform external field. The lineshape observed measures the distribution of ϵ in the crystal. We shall assume that ϵ is the sum of contributions $\epsilon(z_i)$ from each dislocation. Here z_i denotes the relative position r , Burgers vector \mathbf{b} , charge per unit length Z , etc, of the i th charged dislocation.

The lineshape depends on $\epsilon(z)$ and on the distribution and density of the charged dislocations. The distribution is described by a function $p(z)$ related to the pair distribution function of the dislocation relative to the point defects. The charged-dislocation density, ρ , is conveniently defined as the limiting value of the total number of charged dislocations divided by $\int dzp(z)$. Apart from a numerical factor of order unity, ρ is just the dislocation length L per unit volume. Explicit expressions for $\epsilon(z)$, $p(z)$ and ρ are given in § 3.

In terms of $p(z)$, ρ and $\epsilon(z)$ the distribution of ϵ is given by:

$$I(\epsilon) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dx \exp(ix\epsilon) \exp[-\rho J(x)] \quad (2.3)$$

$$J(x) = \int dzp(z)\{1 - \exp[-ix\epsilon(z)]\}. \quad (2.4)$$

We shall consider explicit expressions later. For the present, we merely note that there are three essential assumptions. First, there is a linear Stark effect: $\hbar\omega$ is linear in ϵ . Secondly, the contributions $\epsilon(z)$ of different charged dislocations to ϵ are simply additive. And thirdly, the charged dislocations are assumed uncorrelated in position. This puts limits on the concentrations which can be used, normally at a few per cent for point defects, but this restriction is not serious in practice.

2.2. Approximate results

In several cases, (2.3) and (2.4) are too complicated for analytic solution. It is then an advantage to have an approximate method of estimating the linewidth caused by the charged defects. A suitable method has been given by Schofield (1966) whose results have been expressed in a form appropriate to the present case in § 3.3.2 of Stoneham (1969). If the full width at half intensity of the line is Δ , and if u is $\epsilon(z)/\Delta$, then

$$1 = \rho \int dzp(z)u^2 F(u) \quad (2.5)$$

$$F(u) = 2(u^2 + 6)/[(u^4 + 4)(u^2 + 1)] \quad (2.6)$$

is an integral equation for Δ , and

$$I(O) = \frac{e}{\pi\Delta} \exp \left[-2\rho \int dz p(z) \left(\frac{u^2}{u^2 + 1} \right) \right] \quad (2.7)$$

gives the peak intensity. Equation (2.5) is readily solved numerically.

Other approaches give the asymptotic limits and moments of the distribution. The asymptotic form of $I(\epsilon)$ can also be found at large ϵ , when the centre contributing to the resonance line is strongly perturbed by a single nearby charged defect. For example, if r is the separation of the centre and the defect, and if $p(z) \sim r^n$ and $\epsilon(z) \sim r^{-m}$, then (Stoneham 1969, §4.5)

$$I(\epsilon \rightarrow \infty) \sim 1/\epsilon^{1+(n+1)/m}. \quad (2.8)$$

Moment methods (eg Stoneham 1969 §3.3.1) can give exact values for expressions such as

$$M_N = \int d\epsilon \epsilon^N I(\epsilon) / \int d\epsilon I(\epsilon). \quad (2.9)$$

A finite number of moments given only limited information about the lineshape. Further, there are technical difficulties for dislocations. The moments have a divergence because of the form of $\epsilon(z)$ at small separations. The special treatment needed causes problems because $\epsilon(z)$ is not known in detail in this range. The difficulties may be contrasted with the minor problems at large separations discussed in §4.1, where the finite crystal size is important.

The approximate results (2.5)–(2.8) and the moment methods will be necessary when we discuss screened charge dislocations, since $I(\epsilon)$ can be obtained analytically only in the unscreened case appropriate to freshly-produced dislocations.

3. Explicit forms for $\epsilon(z)$, $p(z)$ and ρ

We consider a cubic crystal containing only straight uniformly-charged dislocations. Non-cubic crystals can be treated similarly, with an increase in complexity because their dielectric tensors ϵ are not isotropic. The variables z which describe charged dislocations are r , Z , θ and ϕ . Here r is the distance from the origin (at which the electric field is being monitored), Z the charge per unit length in units $|e|$, and θ and ϕ define the dislocation axis. The Burgers vector needs additional variables to define it, but for present purposes these can be ignored provided we choose a suitable average value of Z .

3.1. Form of $p(z)$

If we assume a random distribution of dislocations, that is, one which is homogeneous throughout the crystal and where there are no preferred orientations for the dislocation axes, then (Stoneham 1969, §4.2):

$$p(z) dz = d\theta \sin \theta d\theta dr. \quad (3.1)$$

An additional weight factor $f(\theta, \phi, r)$ can be added to take account of obvious generalizations. Examples might be functions $f(\theta, \phi)$ which ensure only dislocations with axes along specific crystallographic directions occur, or functions $f(r)$ which take into account

correlations in position of the monitoring point defects with the charged dislocations.

With this definition of $p(z)$, ρ is related to the total dislocation density, L , by

$$\rho = L/2. \quad (3.2)$$

No account is taken here of the differences in screw and edge dislocations.

3.2. Form of $\epsilon(z)$

For a freshly-produced dislocation, the electric field at distance r is readily found from Gauss's theorem. With charge $Z|e|$ per unit length

$$\mathbf{E} = \left(2 \frac{Z|e|}{\epsilon r} \right) \left(\frac{\mathbf{r}}{r} \right). \quad (3.3)$$

This equation is modified by screening by charged defects present in the crystal. Normally there will be far more charges present as point defects than in the dislocations. Thus for 10^6 cm/cm³ of dislocations with $2|e|$ charges every 5 Å, there is a charge of $4 \times 10^{13}|e|/\text{cm}^3$, whereas there will be 10^{16} – $10^{17}|e|/\text{cm}^3$ of charged point defects even in the purest alkali halides. Thus, only a very small fraction of the charged point defects need actually be involved in screening. A satisfactory description of the effect of all the charged defects, including screened charged dislocations, can be obtained by assuming that there are two independent types of charged defect: point defects uncorrelated with the dislocations, and line defects with an electric field

$$\mathbf{E} = \frac{2Z|e|}{\epsilon r} \left(\frac{\mathbf{r}}{r} \right) \exp(-r/R_s). \quad (3.4)$$

Here R_s , the screening radius, will be adequately given by the Debye–Hückel form:

$$R_s^{-2} = \frac{4\pi e^2}{\epsilon kT} \sum_{\text{species}} Q_i^2 \rho_i \quad (3.5)$$

for point defects with charge $Q_i|e|$ and density ρ_i per unit volume. Whenever appropriate, we shall regard vacancy–impurity pairs as distinct species from vacancies and impurities in the sum in (3.5) and in the later discussion of broadening by point defects.

As a rule the screening lengths, R_s , are much smaller than the typical separations $1/\sqrt{L}$ of the dislocations. For a few parts per million of isolated charged defects in an alkali halide, R_s is of order 100 Å, whereas $1/\sqrt{L}$ is usually in the 10^4 – 10^5 Å range. Thus the screened dislocations can be considered distinct line defects and their mutual overlap ignored.

The contributions to ϵ of the electric fields \mathbf{E} still involve additional coupling coefficients ($\alpha_i \hbar \omega_1 / E_0$) which depend on the details of the point defects monitoring the internal fields. As well as giving a proportionality constant, the α_i ensure that we consider the projection of \mathbf{E} onto a specific direction, rather than $|\mathbf{E}|$ itself. If this direction is given by the unit vector \mathbf{a} , and if \mathbf{d} is the unit vector along \mathbf{r} , then

$$\epsilon = \frac{\Lambda(r)}{r} \mathbf{a} \cdot \mathbf{d} \equiv \frac{\Lambda(r)}{r} \psi(\theta, \phi) \quad (3.6)$$

where $\Lambda(r)$ is given by

$$\Lambda(r) = \frac{2Z|e|}{\epsilon E_0} \hbar \omega_1 (\alpha_x^2 + \alpha_y^2 + \alpha_z^2)^{1/2} \exp(-r/R_s); \quad (3.7)$$

R_s is infinite for unscreened dislocations.

4. The distribution of internal fields

We now calculate the distribution of the dimensionless parameter, ϵ , which is related to the observed lineshape by a simple scaling.

4.1. Lineshape for unscreened dislocations

The theory in this case is almost identical with that for dislocation strain fields given by Stoneham (1966, 1969 §4.2 and Appendix I). In consequence, we leave out most of the algebraic details. There are, however, simplifications over the earlier case. The expressions for $\epsilon(z)$ are much simpler, and the integrals over functions of $\psi(\theta, \phi)$ can be performed analytically. Collecting terms,

$$\rho J(x) = \Lambda^2 L x^2 (A - B \ln |x|) \quad (4.1)$$

where

$$A = \frac{1}{4} \{ [0.9228 + \ln(R_c/\Lambda)] I_1 + I_2 \} \quad (4.2)$$

$$B = \frac{1}{4} I_1 \quad (4.3)$$

R_c is the radius of the crystal, assumed spherical, and is introduced to avoid the usual logarithmic divergence frequently found in dislocation problems. I_1 and I_2 are the integrals over θ and ϕ of $|\psi|^2$ and of $-|\psi|^2 \ln |\psi|$ respectively. If we ignore any differences in Z between edge and screw dislocations, appropriate values are $4\pi/3$ for I_1 and $4\pi/9$ for I_2 . A and B become

$$A = 1.316 + 1.048 \ln(R_c/\Lambda), \quad B = 1.048 \quad (4.4)$$

The main effect of the B term is to give a slight deviation from a gaussian shape. The effect on the linewidth can be obtained by direct Fourier transformation, using (2.3) and (4.1). Alternatively, one can exploit the slow variation of $\ln|x|$ over the important part of the integrand in (2.3). We merely note here that, when B is zero, the full width at half intensity of the line, Δ , has the value

$$\Delta_0 = \Lambda \sqrt{L} 4 \sqrt{\ln 2} \sqrt{A}. \quad (4.5)$$

Expressed as an electric field by omitting the coupling coefficient ($\hbar\omega_1 |\alpha|/E_0$) in Λ , Δ_0 corresponds to a field of half width $0.96 (A)^{1/2} 10^4 \text{ V cm}^{-1}$ for the values:

$$Z = 0.4 \text{ electrons/\AA}, \quad \epsilon = 4 \quad \text{and} \quad L = 10^6 \text{ cm/cm}^3. \quad (4.6)$$

Since L can be raised to 10^8 cm/cm^3 and \sqrt{A} proves to be about 3, very substantial internal fields are expected.

Under common experimental conditions for the alkali halides, the majority of the charged dislocations have axes parallel to a single cube axis. If this is $[0, 0, 1]$, then A and B can be obtained in terms of the unit vector (a_x, a_y, a_z) describing the response of the monitoring centres. Specifically we have for the coefficients in (4.1):

$$A = [1.753 + 1.571 \ln(R_c/\Lambda)] [a_x^2 + a_y^2]^{1/2}$$

$$B = 1.571 [a_x^2 + a_y^2]^{1/2}. \quad (4.7)$$

The most important change in the A and B values is the $[a_x^2 + a_y^2]^{1/2}$ factor. This enters because there are no field components parallel to the dislocation axes.

4.2. Approximate methods

We shall use almost exclusively the solutions of the integral equation (2.5) in discussing

the linewidth. Solution is straightforward by a combination of analytic and numerical integration using standard methods.

Three cases are usefully distinguished, depending on the relative values of the crystal size R_c , mean dislocation separation $1/\sqrt{L}$, and screening length R_s .

4.2.1. No screening. In this limit the charged point defects are completely uncorrelated with the dislocations, although the crystal will be electrically neutral overall. A value of $R_c\sqrt{L}$ is needed, and we assume the value 10^4 typical of many of the systems studied. The linewidth is then:

$$\Delta \approx 11.4 \frac{Z|e|\sqrt{L}\hbar\omega_1|\alpha|}{\epsilon E_0} \quad (4.8)$$

With the parameters (4.6) the internal field distribution has a width $1.7 \times 10^4 \text{ V cm}^{-1}$. The results are only weakly dependent on $R_c\sqrt{L}$. If this parameter is reduced by an order of magnitude, the linewidth is reduced by just over 10%. Indeed, to halve the linewidth, $R_c\sqrt{L}$ must be reduced to less than 10, and this would correspond to a crystal which is almost dislocation-free.

The value of Δ should be compared with the broadening produced by the random point defects present. For one charged defect per 10^6 sites this other contribution is about $3.2 \times 10^4 \text{ V cm}^{-1}$, increasing as $(\sum_i \rho_i Q_i^{3/2})^{2/3}$ (Mims and Gillen 1966). Thus the point-defect and charged dislocation contributions are comparable.

4.2.2. Weak screening. This artificial limit corresponds to a screening radius larger than $1/\sqrt{L}$, yet smaller than the crystal dimensions. Both the moment methods and the asymptotic expressions agree in predicting that the main effect of weak screening is to narrow the centre of the line, with a smaller immediate effect on its wings. Thus the line moves towards lorentzian from gaussian. Quantitatively, the line is reduced from the value for no screening. The reduction is negligible for $R_s\sqrt{L} \sim 10^4$, about 23% for $R_s\sqrt{L} \sim 10^3$ and about 40% for $R_s\sqrt{L} \sim 100$. Even modest screening substantially reduces the width.

4.2.3. Strong screening. In this case the integral equation (2.5) has no solutions. This happens for two reasons: the lineshape is of such a nature that the approximations used in deriving the integral equation are invalid, and the assumptions which lead to (2.3) and (2.4) fail because most of the monitoring centres lie outside the screening clouds and are negligibly perturbed by the screened, charged, dislocations. Fortunately, the physics is reasonably clear: when the dislocations are fully screened, they do not have any significant effect on the observed lineshape. For this to be true, the centres monitored must not be trapped close to the dislocations, nor must the dislocations enhance significantly the intensity contribution of nearby monitoring centres. These criteria hold for most systems discussed in the next section. In such cases, with strong screening, the observed shape will be determined by the charged point defects and by a variety of residual mechanisms.

5. Discussion

The use of spectroscopic methods to probe the properties of charged dislocations has several clear advantages. The distribution of internal fields can be found, rather than

some mean square value, and the details involve both the dislocation charges and screening charges. The method should be sensitive too, so that the dynamics of screening should be observable as a reduction in linewidth as charged ions move to screen freshly-produced dislocations. Further, one can do equilibrium experiments as well as ones in which the equilibrium has been perturbed.

The practical success of the method does depend, however, on the choice of system used. One has a good deal of freedom in selecting the defect whose transition is to be monitored, and it would be disappointing if some suitable example could be found in any given host.

There are several important criteria to be used, namely:

(i) The transition must show a linear Stark effect. The larger the effect, the more suitable is the system chosen. This criterion eliminates defects with inversion symmetry. Useful information may be obtained when nonlinear corrections are important, but data will be harder to analyse quantitatively.

(ii) The transition must be more strongly affected by the dislocation charge than by the dislocation strain field. In practice this means that, for the transition energy:

$$\frac{(\text{Shift in eV per unit strain})}{(\text{Shift in eV per } 10^4 \text{ V cm}^{-1})} \leq 2 \cdot 10^4 \text{ V cm}^{-1}.$$

(iii) The monitoring defect must not be attracted or repelled by the dislocations to such an extent that $\rho(z)$ differs significantly from a random distribution. Thus the defect should not have a net charge, nor a large elastic misfit.

(iv) The resonance observed should be narrow in the absence of electric-field broadening. Thus emission lines with large spontaneous probabilities and spin-resonance centres with fast spin-lattice relaxation are eliminated.

(v) Since the screening cloud can be established in a matter of minutes at room temperature, it is an advantage to use a rapid method, so avoiding low-temperature work.

Examples of possible systems in alkali halides are these:

(i) Spin resonance of transition metal ions, charge-compensated by adjacent vacancies. Mn^{2+} is a good candidate, since it is readily observed, is relatively insensitive to strain, has slow spin-lattice relaxation, and its hyperfine structure allows easy identification of the inhomogeneous part of the line broadening. Indeed, Kawamura and Okubo (1962) have already reported the influence of dislocations on Mn^{2+} vacancy systems in NaCl, and show clearly measurable effects can be obtained. Their analysis assumed that rotation of the defect axes was the main source of inhomogeneous broadening, and their conclusion was that quantitative agreement was only possible if the Mn^{2+} ions were trapped close to the dislocations. In fact, rotation effects are probably negligible. Unfortunately, there are insufficient data to re-analyse the results in terms of electric field or strain effects. In order of magnitude, spin-resonance methods should be able to detect fields of order 10^4 V cm^{-1} (see Ludwig and Ham 1963, Royce and Bloembergen 1963, Mims and Gillen 1966).

(ii) ENDOR measurements on nuclei adjacent to F centres (eg Reichert 1967) are possible, although harder technically and less sensitive; fields of order 10^5 V cm^{-1} are needed in KCl.

(iii) Optical measurements on F aggregate colour centres, like the R centres. Again, the method seems less sensitive than spin resonance; the results of Davis (1970) show that fields of order 10^5 V cm^{-1} are needed.

(iv) Centres which can re-orient but which respond more to electric fields than strains. Unfortunately the obvious choices—OH⁻ and CN⁻, or the off-centre Li⁺ ion in alkali halides—seem to respond comparably to the electric and strain fields of charged dislocations (see eg the review of Narayanamurti and Pohl 1970).

Clearly, the most favourable systems in this list are the Mn²⁺-vacancy complexes, although there may be other better cases. The natural experiments to begin with are, first, a measurement of the effect of an external electric field on the spin resonance lines to determine the coupling coefficients. Then, should the results prove satisfactory, the natural next stage would be to observe the changes in lineshape both immediately after the creation of fresh (unscreened) dislocations, and again after allowing a screening charge to develop.

Acknowledgments

I am indebted to Dr R W Whitworth for stimulating comments on an earlier version of this report.

References

- Davis J A 1960 *PhD. Thesis* Cornell University, New York
 Kawamura H and Okubo Y 1962 *J. appl. Phys.* **33** 367
 Ludwig G and Ham F S 1963 *Paramagnetic Resonance* ed W Low (New York: Academic Press) pp 620–7
 Mims W B and Gillen R 1966 *Phys. Rev.* **148** 438–43
 ——— 1967 *J. chem. Phys.* **47** 3518–32
 Narayanamurti V and Pohl R O 1970 *Rev. mod. Phys.* **42** 201–36
 Reichert J F 1967 *Hyperfine Interactions* ed A J Freeman and R B Frankel (New York: Academic Press) pp 745–51
 Roitsin A B 1972 *Sov. Phys.—Usp.* **14** 766
 Royce E B and Bloembergen N 1963 *Phys. Rev.* **131** 1912–23
 Schofield P 1966 *AERE Report TP 217*
 Stoneham A M 1966 *Proc. Phys. Soc.* **89** 909–22
 ——— 1969 *Rev. mod. Phys.* **41** 82–108
 ——— 1970 *Fundamental Aspects of Dislocation Theory* ed J A Simmons, R de Wit and R Bullough *NBS, US Spec. Publ.* **317** pp 1169–77
 ——— 1971 *Proc. XVI Colloque Ampère* ed I Ursu (Bucharest: Romanian Academy Press) pp 219–27
 Whitworth R W 1973 *J. Phys., Paris* to be published